Advanced Optical Metrology

Additive Manufacturing | Thin Film Metrology | Roughness | Electronics | Composites







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Yours sincerely, Dr. Christina Poggel Editor-in-Chief of Wiley Analytical Science

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Part I

Additive Manufacturing

Introduction: Additive Manufacturing

It all started in the 1960s as science fiction in Star Trek. A person asked the computer to replicate a part or object, and the computer did—without the challenges that we're familiar with today, such as casting and milling. Today, additive manufacturing goes beyond simply replicating an existing object. It offers new functionality and efficiency during manufacturing. Nevertheless, these technological changes require that we relearn or even reinvent a lot of engineering common sense. The limits of what is possible change with every new iteration of additive manufacturing.

In recent years, there has been a new surge of interest in 3D printing, which is defined as building successive layers of materials to form a desired object [1,2]. The interest in 3D printing methods is twofold. First, the advent of 3D printing has triggered the creation of numerous intricate designs, whether in the micro or macro scale, that would otherwise be difficult to create using conventional fabrication methods. Second, 3D printing enables quick evaluation of ideated solutions, often within the same day. Feature-wise selection of printing parameters and multistep printing processes enable users to pay extra attention to the tiny details of their objects [3]. In addition, material specifications (e.g., Young's modulus or transparency) can be adjusted based on the printing method. It is estimated that the market size of 3D printing will triple in the next half-decade, growing from 7.3 billion dollars in 2017 to 23 billion dollars by 2022 [4]. As structures manufactured by 3D printing methods can be in the range of micrometers to centimeters, a new challenge emerges for microfabrication [5].

1 STEREOLITHOGRAPHY AND SOFTLITHOGRAPHY

Stereolithography (SLA) is a light-based 3D printing technique in which layers of a liquid resin are sequentially photo-cross-linked into a solid 3D structure [6]. 4 Of all 3D printing techniques, SLA is the most versatile, accurate, and precise additive manufacturing technique [6,7]. In SLA resins are photo-cross-linked (cured) in two different manners [8]: by use of a laser beam or by use of digital light projection (DLP).

Stereolithography-based additive manufacturing is rapidly gaining interest for manufacturing ceramics due to its ability to form complex-shaped architectures without molds [9-11]. Stereolithography is an effective UV light-cured technology based on the photopolymerization of a photosensitive ceramic slurry, exhibiting a great potential in the fabrication of complex-shaped ceramic parts with high accuracy. During the process, the x-y resolution, layer thickness, and exposure parameters of a 3D model are imported into a printer. Next, each individual layer is cured by a UV light. After the first layer is cured, the supporting platform is moved up, and the ceramic slurry is recoated with a blade. Then, the second layer is cured analogously. These steps are repeated until the whole part is eventually produced. In the past, many kinds of oxide ceramics, including Al₂O₃[12-14], ZrO₂ [15-17], ZTA [18], and other oxide ceramics [19-21] have been widely reported using this method.

Among all 3D printing methods, stereolithography apparatus (SLA) and digital light processing (DLP) offer many advantages, making them ideal candidates for microfluidics and biomedical applications [22]. However, one of the limitations of 3D printed SLA/DLP master molds for softlithography is the requirement for tedious pretreatments prior to poly dimethyl siloxane (PDMS) casting. The pretreatment of the resin is necessary to ensure the complete curing of the PDMS in contact with the resin. Otherwise, the surface of the PDMS replica in contact with the resin cannot be polymerized due to the presence of residual catalysts and monomers, and its transparency would be also compromised [23].

As further elaborated in the herein presented digest article "Rapid Softlithography Using 3D-Printed Molds", the effects of pretreating the master mold are more significant in channels with smaller feature sizes [24], and, in the case of relatively large 3D printed parts, this challenge is not significant [25]. To address this issue, many researchers have proposed various pretreatment protocols to treat the 3D printed master mold before PDMS casting [23,24,26-29].

Four procedures are commonly used among other proposed postprinted protocols: 1) UV curing; 2) surface cleaning (e.g., ethanol sonification and soaking); 3) preheating; and 4) surface silanization. Waheed et al. introduced an efficient but time-consuming pretreatment protocol for PDMS softlithography [29].

Further Reading: https://onlinelibrary.wiley.com/ doi/10.1002/jbm.b.34354

https://onlinelibrary.wiley.com/ doi/10.1002/adma.201904209

Appl. Note: https://www.olympus-ims. com/en/applications/quantitative_ investigations_of_the_interconnect/

2 ELECTRON BEAM MELTING

Electron beam melting (EBM) is an additive powder-bed fusion process, which builds up bulk metallic components by a defined sequence of process steps. First, a thin layer of powder is applied using a recoater system within a vacuum chamber. This layer is rapidly heated by a defocused electron beam, inducing slight sintering of the particles. The weak connectivity between the particles is necessary to provide a minimum of mechanical strength and electrical conductivity. These properties are necessary for the following step when a focused electron beam with high power density is used for selective melting of the current layer cross-section. After lowering the build platform and applying the next powder layer, the cycle is repeated until the desired geometry is reached.

The EBM process requires a vacuum environment and is performed at a base temperature slightly below the melting point of the processed material. Therefore, the evaporation of volatile alloy elements during melting causes severe metallization on all surfaces, which are not shielded from melt pool exposure. In addition, the interaction between the electron beam and material produces damaging X-ray radiation. In summary, the environment is extremely challenging for most process monitoring devices. Further Reading: https://onlinelibrary.wiley.com/ doi/10.1002/adem.201901524

3 3D PRINTING AND LASER-ASSISTED CRYSTALLIZATION OF TIO₂

Titanium dioxide (TiO₂) powders possess advantageous properties, including chemical stability, nontoxicity, and low manufacturing costs that are exploited in a wide variety of industrial applications [30,31]. These applications include water treatment [32], water splitting for hydrogen production [33-35], surface modification [36-39], photocatalysis [40,41], microelectronic circuits [42,43], sensors [44-46], and solar cells [47,48]. Most properties of TiO₂ stem from its crystallization into two polymorphs, namely, anatase and rutile. Depending on the desired application, the anatase structure will appear when annealing the amorphous TiO₂, around 450 °C (840 °F), whereas the rutile structure will appear between 800 and 1100 °C (1472 °F and 2012 °F) [49]. However, all these applications would greatly benefit from the ability to fully convert precursor solutions into anatase or rutile TiO₂ in an ambient environment and at much lower temperatures. This is especially true in applications that involve multiple materials and fabrication steps. This would significantly reduce the energy consumption during manufacturing and could expand the use of TiO_2 to the additive manufacturing of energy conversion, wearable and flexible hybrid electronic devices, and systems. In recent years, careful control of the phase transition and phase stability of TiO₂ polymorphs induced by low-power visible light gained attention in the scientific community [50-58]. Indeed, it is possible to promote or inhibit the laser-induced phase transition from anatase to rutile TiO₂ by the addition and careful control of the concentration of metallic ions in the TiO₂ matrix [59]. Such is the case in doping with iron (Fe) or aluminum (Al). Induced by laser radiation, iron promotes the phase transition from anatase to rutile, whereas aluminum inhibits it [50]. However, this process still involves temperatures over 350 °C (662 °F) to achieve only partial crystallization of the TiO₂ nanoparticles. Meanwhile, scandium (Sc) and vanadium (V) can also be used as dopants in TiO₂ nanoparticles to shift the transition temperature from anatase to rutile [60]. Others achieved phase transition at a lower temperature, but under partial oxygen pressure [51] or

in vacuum chambers [25], to enable the photoactivation of the TiO₂ precursor. However, this dramatically increases the manufacturing costs and limits its use for modern low-cost additive manufacturing applications. Finally, other approaches achieved complete control of the synthesis of only one specific crystalline phase of TiO₂ nanoparticles [53,54] with considerably lower temperatures compared with traditional crystallization techniques. In the digest article "Laser-Assisted, Large-Area Selective Crystallization and Patterning of Titanium Dioxide Polymorphs", a large-scale laser-assisted conversion of amorphous TiO₂ films under ambient conditions with an inexpensive approach using a low-cost, commercially available 3D printer platform with a 405 nm laser engraving attachment module to spatially control the TiO₂ crystallization is presented.

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01

In Operando Monitoring by Analysis of Backscattered Electrons during Electron Beam Melting

C. Arnold, J. Böhm and C. Körner

ADDITIVE MANUFACTURING by electron beam melting (EBM) is a complex process that currently lacks reliable tools for process monitoring. However, the detection of back-scattered electrons (BSEs) is a promising process monitoring solution. In this chapter, we detail the results of a series of experiments to evaluate the efficacy of this system. In the experiment, we used a detection system for BSEs to record the in operando signal during melting inside an EBM system. The data were then postprocessed by mapping the data points to spatial coordinates. We compared the result-ing density map to the as-built surface and analyzed the topography using a confocal laser scanning microscope. The results demonstrate that this system is a promising solution for process monitoring and quality control.

INTRODUCTION

Electron beam melting (EBM) is an additive powder-bed fusion process, which builds up bulk metallic components by a defined sequence of process steps. Like other additive processes, EBM enables the cost-effective fabrication of complex components in small batches. Nevertheless, to compete with conventional manufacturing methods, high quality standards must be met, which is currently a barrier for breakthrough additive manufacturing technologies. [1] Better insight by process monitoring is necessary, but, so far, there is still a lack of reliable tools.

Most of the work done on process monitoring during EBM focuses on the use of infrared (IR) thermography. Drawbacks of this approach are the high amount of data to be processed [2] and the susceptibility to errors. The detection of backscattered electrons (BSEs) has been suggested as an alternative for EBM process monitoring.

Electron optical (ELO) images can be obtained using the electron beam in a way that is comparable with scanning electron microscopy [3,4]. The beam is used to record the topography of the molten surface, enabling quality control engineers to compare the features and defects in the ELO image to the final sample's surface. [3] This has the potential to be used to deduce processing windows in a fast and reliable manner [5]. Despite the benefits of this approach, it requires an additional process step for image acquisition and is only capable of imaging the final molten surface, increasing the build time. In addition, the nature of the test means that it's not suitable for a real-time correction of the process parameters by a closed-loop control.

This chapter discusses how these limitations can be overcome by recording the BSEs directly during the melting of the layers in an in operando approach. This approach would not increase the build time and can deliver information about the process quality in real time.

METHODS

The experiments were conducted using the Athene system and its integrated BSE detection hardware. A more detailed description of this in-house developed EBM system can be found in Arnold et al. [6]. In the first experiment, single-square-shaped areas were made molten on a base plate made of X15CrNiSi20-12 stainless steel at room temperature. The experiment was designed to deliver basic information about electron backscattering during melting without considering the complex conditions of an EBM process, such as the interaction between the beam and powder bed. In the second experiment, three cuboid samples with a constant layer thickness of 50 µm were produced by EBM. A Rigol MSO1104Z oscilloscope was used for recording the BSE and deflection signal during melting and saving the data. A detailed description of the experimental setup and methods can be found in the full article of this digest version.

The as-built samples were further investigated using an Olympus[®] LEXT[™] OLS4000 laser scanning microscope. Standard laser scanning microscopy (LSM) was used to acquire optical images of the molten surfaces, whereas confocal laser scanning microscopy (CLSM) enabled 3D measurements of the surface topography. The microscope's stitching feature was used to acquire images of the whole sample surface with a spatial resolution of approximately 3 µmpx⁻¹ for both LSM and CLSM.

RESULTS

Figures 1 and 2 show the molten surfaces of the base plate and the powder bed experiment, respectively. In both figures, the comparisons show the in operando ELO signal, optical images of the as-built surface by LSM, and the surface topography obtained by CLSM. The scaling of the linear color map was adjusted for each image to obtain maximum contrast (Table 1).

Despite keeping the area's energy density constant, the analysis by LSM/CLSM shows a different surface topography for each hatch line

Sample	Height [µm]		BSE signal [V kW ⁻¹]		D D D	N I 1 I 11
	Min	Мах	Min	Max	Power [W]	Velocity [ms ⁻¹]
Base-plate, 50 µm	68	493	2.05	2.76	600	1.00
Base-plate, 100 µm	104	1122	1.98	2.66	600	0.50
Base-plate, 200µm	268	565	1.76	2.48	600	0.25
Powder-bed, porous	230	577	1.52	1.93	150	1.00
Powder-bed, dense	161	450	1.36	1.75	1000	5.00
Powder-bed, bulging	490	1425	1.26	1.67	1000	3.33

Table 1: Color map scales and process parameters of images in Figures 1 and 2. The measured BSE signal is normalized to the beam power to achieve comparable values between different samples.



Figure 1: Base plate experiment; Molten surfaces on steel base-plate (X15CrNi-Si20-12). The comparison shows the in operando ELO signal, an optical image of the as-built surface by laser scanning microscopy (LSM), and the surface topography obtained by confocal laser scanning microscopy (CLSM). The hatch line spacing was varied between (50, 100, and 200)µm to investigate different levels of spatial resolution. The details on the color-map scale for each image are shown in Table 1.

spacing. The 50 µm sample has a range (i.e., distance between the lowest and highest points) of around 450 µm. There are two big, distinct elevations with a rather smooth profile, which are extended in y-direction. The middle part of the surface is flat but shows a slight, periodic texture. The 100 µm sample shows a very high range of around 1000 µm. Again, there are two big elevations extending in the y-direction whose profiles are rough and jagged. The 200 µm sample is fairly flat with a range of around 300 μ m. On the left and the right sides, there is a slight elevation of the surface. The visibility of the single melt track increases with bigger hatch line spacing.

The lower part of Figure 1 shows the images obtained after processing the in operando ELO signal. For all three samples, the normalized signal lies in a similar range of $1.7-2.8 \text{ V kW}^{-1}$ (Table 1), and the line-by-line reconstruction

of the image is clearly visible. On the left and the right sides, the 50 µm sample shows two large, distinct regions of low signal intensity. In the middle part, the intensity is higher but shows a weak periodic pattern. The 100 µm sample shows a complex distribution of signal intensity. The upper part of the image has a low but, toward the center, gradually increasing intensity. The main part with a medium intensity can be distinguished from the left and right sides by a clear boundary. These outer regions show several local intensity maxima, which seem to have a line-like shape. In addition, the left one of these regions encloses a medium-sized area with low signal intensity. The 200 µm sample is poor in details. The upper part of the image shows a lower intensity than the other parts that are dominated by a line-wise alternating intensity pattern. The LSM/CLSM analysis of surface topography shows that the porous sample has a flat surface with several scattered voids (Figure 2). The range of this sample is about 350 μ m. The dense specimen is almost perfectly flat with only small elevations toward the boundaries of the sample. This is also reflected by the small range of around 300 µm. In contrast, the bulging sample has a very uneven surface with a smooth cross-shaped elevation in an x/y-orientation, a distinct local maximum in the center of the sample, and strongly elevated edges. The range has a high 950 µm value. On the surfaces of all three EBM samples, single melt tracks are slightly visible.

The lower part of Figure 2 shows the images obtained by processing the in operando ELO signal. After normalizing the images to the respective beam power, the signal lies in a similar range of 1.2–2.0 V kW 1 (Table 1). Compared with the base plate experiment, the line-by-line reconstruction of the images is hardly visible. The porous sample shows a smoothly varying intensity distribution with single spots of very low signal. In contrast, the dense sample has a very homogeneous but noisy intensity distribution. The bulging sample has a similar signal structure but, in addition, distinct regions with lower intensity are visible.

DISCUSSION

Comparing the surface data acquired by CLSM and the images obtained by processing the in operando ELO signal indicates good correlation in both experiments. For the 50 µm base plate sample, the shape of the low-inten-



Figure 2: Powder-bed experiment; Molten surfaces of powder-bed samples (Ti–6Al–4V). The comparison shows the in operando ELO signal, an optical image of the as-built surface by laser scanning microscopy (LSM), and the surface topography obtained by confocal laser scanning microscopy (CLSM). The energy input was varied to investigate the capability of detecting different surface conditions (porous, dense, and bulging). The details on the color-map scale for each image are shown in Table 1.

sity regions correlates with the shape of the corresponding elevations. Even details such as the protrusion in the right region or the slight texture in the brighter middle part are depicted correctly. In the 100 μ m base plate sample, the elevated structures are also clearly visible in the in operando ELO image, and details such as the shape and size of the topographical features are depicted accurately.

Similarly, the porous powder bed sample shows an excellent correlation between actual pores on the surface, and the intensity decreases in the in operando ELO signal. This is valid for both the position as well as the size of the pores. As expected, the dense powder bed sample with its flat surface shows no remarkable details in the in operando ELO image. In contrast, the correlation between the two imaging methods is more complex for the bulging powder bed sample. Using the in operando ELO approach, the elevated structures are not clearly visible like those in the base plate experiment.

The topography contrast can be seen at the edges of the bulging areas in Figures 1 and 2 where a change of the local incident angle results in a variation of the measured BSE signal. The effect is even more pronounced at the steep edges of pores. Inside these cavities, electron scattering decreases the signal intensity even more, facilitating the detection of pores. In contrast, an even surface reflects the major part of the BSEs in the direction of the incident beam, which coincides with the position of the BSE detector in the experiment. Therefore, while comparing CLSM and in operando ELO images in terms of topography, the imaging principles are very different. While the first is designed to return absolute elevation data, the second delivers information about the interaction between the electron beam and material, which is independent of the absolute height. This causes the images of the porous surface to be similar for both methods, while the images of the bulging samples are more difficult to compare.

An better understanding of the correlation between the in operando BSE signal and beam-material interaction is necessary to apply this approach to a real-time feedback control system. This concept of mapping the recorded in operando signal to a 2D intensity map is considered a tool to identify quantitative process quality metrics in future experiments. To eventually apply these findings to a system that is capable of automatically optimizing process parameters in real time, a direct analysis of these metrics in the continuous in operando signal is preferred to achieve the best performance.

CONCLUSION

For the first time, we acquired ELO images during the melting step of the EBM process. The resulting signal intensity maps show a remarkable correlation to the final topography of the molten samples. The approach is capable of detecting pores and bulging areas, whereas the image quality differs between the base plate and powder bed experiments. It is assumed that the image contrast is dominated by the effect of surface topography on the emission of BSEs, but subsequent experiments are required to develop a better understanding of signal formation. As soon as the reliable interpretation of the in operando ELO signal is accomplished, it might be the essential part of a powerful feedback control system. By gathering information about the molten surface quality in real time, the system could be capable of optimizing process parameters during melting. An advanced control system like this would make a significant contribution to the reliability of the additive manufacturing process and the quality of the produced components.

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02 Rapid Soft Lithography Using 3D-Printed Molds

S. R. Bazaz, N. Kashaninejad, S. Azadi et al.

POLYDIMETHYLSILOXANE (PDMS) is widely used in microfluidics due to its unique features such as good oxidative and thermal stability, high hydrophobicity and high gas permeability. Consequently, rapid prototyping of PDMS-based microchannels is of great interest. The most common and conventional method for the fabrication of PDMS-based microchips relies on soft lithography. Yet, the soft lithography method requires the preparation of a master mold, which is a costly and time-consuming task. Another challenge is that silanization is required to prevent PDMS from attaching to the master mold, which can be detrimental for cellular studies. While recent advances in 3D printing can potentially speed up the microfabrication process, current 3D printing techniques are inadequate for PDMS soft lithography. This study explores the feasibility of producing master molds suitable for rapid soft lithography by investigating a newly developed 3D-printing resin. The utility of this technique for cell culture is also highlighted to show the biocompatibility of the process.

INTRODUCTION

Many publications today recognize the importance of lithography for the fabrication of PDMS-based microchannels. However, lithography is limited in its ability to fabricate non-straight microchannels. As a result, research groups have provided alternative methods for the fabrication of molds used in soft lithography processes [1]. One alternative is the use of 3D printing technology. Among the 3D printing methods, stereolithography apparatus (SLA) and digital light processing (DLP) offer significant advantages that make them ideal options for microfluidics and biomedical applications [2]. However, these methods require tedious pretreatments prior to PDMS casting. Several pretreatment protocols have been proposed to treat the 3D printed master mold before PDMS casting [3-8].

Four procedures are commonly used among other proposed post-printed protocols: UV curing, surface cleaning, preheating, and surface silanization. Yet, there is no consensus about the optimal protocol to treat 3D printed templates for PDMS casting. These protocols are also time-consuming, labor-intensive, and lack reproducibility. Further, the treatment parameters, such as UV curing time, preheating temperature, and duration, seem to be a function of the feature size and, consequently, differ from one experiment to another [8]. In particular, preheating is a common step in many procedures and often induces high levels of material strain, which can cause cracks to form in microstructures [3,9]. Most importantly, surface silanization of the 3D-printed templates is essential to help ensure the PDMS peels off correctly. Yet, some silanizing agents, such as perfluorooctyl triethoxysilane, are cytotoxic and not suitable for biological applications.

Using a new resin developed by Creative CADworks (CCW Master Mold for PDMS devices) for the direct fabrication of master molds using the DLP 3D printing method can help address these issues and save time. For instance, the 3D printed templates obtained using this resin can be immediately casted with PDMS without pretreatment or surface modification. As a result, the process of master mold design for microchip fabrication is reduced from a timeframe of several days (for a conventional soft lithography process) to fewer than five hours. To demonstrate this resin's functionality, four microfluidic devices were developed. In this chapter, we will focus on the application in cell culturing, as well as evaluate the surface of the PDMS replica obtained from the 3D printed mold to investigate the bonding quality of PDMS.

METHODS

Figure 1 below shows the workflow to prepare the master mold using the DLP/SLA 3D printing method and microfluidic resin. (A) First, draw the desired master mold. Since microfluidic devices require neither intricate geometries nor a professional CAD drawer, the CAD drawing process is quick. (B) Next, print the design using a DLP/SLA 3D printer, and remove the residuals from the mold's surface. (C) Then, pour PDMS into the master mold. (D) In the final step, peel off the PDMS and bond it to a glass or PDMS layer, and then install the inlets and outlets.



Figure 1: The master mold preparation workflow using the DLP/SLA 3D printing method and microfluidic resin.



Figure 2: The PDMS casting process in (A) conventional DLP resin and (B) microfluidic resin. The insets depict the contact angles on the mold surface. In conventional resin, PDMS in contact with the mold surface cannot provide a temporary bonding, and the PDMS surface cannot replicate the pattern used in the resin. In microfluidic resin, the PDMS starts to detach from the surface as soon as the blade reaches the mold surface, and it can easily peel off. The mold after PDMS casting in microfluidic resin shows no residual PDMS on its surface, while the conventional DLP resin has residuals on the surface. Figure 2C illustrates the experiment setup used in these series. (D) No leakage occurred during the experiments after the PDMS bonding with the plasma surface treatment method.

Surface characterizations of the 3D printed mold and PDMS were analyzed using the Olympus[®] LEXT[™] OLS5000 3D laser microscope and an Olympus LMPLFLN 20X LEXT objective lens. Arithmetic mean deviation (Ra) – the arithmetic mean of absolute ordinate Z (x,y) documented along a sampling length – and arithmetical mean height (Sa) – the arithmetic mean of the absolute ordinate Z (x,y) documented along an evaluation area – were chosen to evaluate the surface characterization.

RESULTS

PDMS Characterization

After fabricating the 3D printed molds and removing any residual resin, PDMS was casted on the master molds. For comparison, two molds were fabricated: one with a conventional DLP resin and the other with the new microfluidic resin. The main challenge with the conventional DLP resin is that complete polymerization of PDMS cannot occur due to the presence of unreacted monomers, resulting in residual material on both the PDMS and the mold. The comparison shows that both molds have identical surface roughness, and the smallest channel height for the fabrication of molds can be achieved with a thickness layer of 30 µm. The curing time of each thickness layer for the newly developed resin is 6.5 seconds, while the conventional one is 1.3-1.5 seconds. The curing time is longer for the new mold since more time must be devoted to the methacrylated resins to be completely polymerized and cured. All in all, the fabrication time for both molds took less than an hour - much faster than other methods. Another notable difference is the contact angle. While the contact angle measurement reveals that both surfaces are hydrophilic, the microfluidic resin is slightly more hydrophilic than the conventional one. The inset in Figure 2A below shows the contact angle of the 3D printed molds.

Figure 2A indicates that PDMS surfaces in contact with the resin surface were improperly cured in the conventional DLP resin, and uncured PDMS layers remain on both surfaces. Notice how the casted PDMS fails to adopt the mold pattern. In addition, PDMS tends to stick to the resin as the PDMS detaches from the mold, confirming that the conventional DLP resin surface is unsuitable for PDMS casting. After analyzing the materials constituting the conventional DLP resin, we believe this problem is related to the resin's chemical composition. We hypothesized that the remaining catalyst and monomers on the printed mold surface disrupt the complete polymerization of a thin layer of PDMS in contact with the mold. This can be clearly seen when the PDMS replica is removed from the mold (Figure 2A). Therefore, the "acrylate group" in the resin's chemistry is an unsuitable choice for PDMS casting. This discovery has prompted scientists to explore less time-consuming strategies for the surface treatment of DLP printed molds. Through extensive research conducted by Creative CADworks, scientists have developed a new resin that contains methacrylated monomers and oligomers. Casted PDMS does not react with the methacrylated monomers because the mold surface is free of residual monomer units that may impede PDMS polymerization. As Figure 2B illustrates, once a blade cuts through the PDMS layer down to the mold, the PDMS replica detaches easily. The operation of each device and the quality of bonding were also analyzed for a wide range of flow rates (to check the simulation results of surface roughness and bonding quality, see Section 2.2) with the experiment setup shown in Figure 2C. The results, as depicted in Figure 2D, confirm there was no leakage between flow rates ranging from 0.1–5 mL min⁻¹. This finding indicates that the proposed method for fabricating a PDMS-based microdevice is an ideal technique for a variety of applications.

BIOLOGICAL APPLICATIONS

To fabricate the microchamber arrays, Liu et al. used standard dry etching on a silicon substrate followed by PDMS soft lithography. Figure 3A shows the dimensions and characteristics of the 3D printed microchamber. The total printing time from the initial design to the final product took only 45 minutes. MCF-7 cells with a concentration of 10⁶ cells mL⁻¹ in culture media (Roswell Park Memorial Institute (RPMI) 1640 with 10% fetal bovine serum (FBS) and 1% streptomycin-penicillin) were introduced into the PDMS microchamber. The device was incubated for 24 hours at 37 °C (98.6 °F) with 5% CO₂. To evaluate the cell viability in the PDMS microchamber, live/ dead cell double staining was performed. As shown in Figure 3B and C, more than 98% of the cells remained viable in the microchamber 24 hours after the initial cell seeding. This confirms that no cytotoxic residual material had been left on the PDMS from casting on the 3D



Figure 3: (A) Whole-chip image of the cell culture device with its related Sa, Ra, and height profile. (B) Live and (C) dead images of the cells after a 24-hour incubation, which show that cell viability in these devices are noticeable and the total numbers of dead cells are rare. (D) Concentration gradient profile of two food colors of red and green. The results show that the newly developed microfluidic resin is suitable for cell culture applications.

printed resin. Additionally, in cell culture platforms, flow rates exist in the order of μ L min⁻¹ [10], and the values of Ra and Sa (as shown in Figure 3A), indicate that the device is functional within its flow regime. This demonstrates that the newly developed resin for 3D printing master molds is suitable for cell culture applications and does not compromise cellular viability. Currently, our group is investigating lungon-a-chip studies using 3D printed microfluidic resin molds. These studies demonstrate long-term cell viability (more than a week).

DISCUSSION

The gradient of biomolecules plays a crucial role in controlling various biological activities, including cell proliferation, wound healing, and immune response. One of the most popular types of concentration gradient generators (CGGs)that produces discontinuous concentrations is the tree-like CGG. This type of CGG is based on the fact that one can divide and mix the flow through bifurcations and pressure differences downstream. This type of CGG is usually used for cancer cell cultures, as these CGGs transfer more oxygen and nutrients to cells as they develop a convective mass flux. Among various tree-like CGGs proposed in the literature, we chose the S-shaped CGG design developed by Hu et al. [11] The authors used micromilling to fabricate the CGG on a polymethylmethacrylate substrate. Here, we developed the same structure in PDMS using a soft lithography-based master mold fabrication from our new microfluidic resin. The device has two inlets and six outlets to produce six different concentration ranges. To examine the device performance, we used two colors of food dyes (please refer to the supporting information for the dye preparation protocol). Figure 5D illustrates the concentration profile of the fabricated CGG, which is similar to those reported in the literature [11]. Since the velocity in CGG devices is small [12], surface roughness cannot impose problems on the binding of PDMS. For the printing of planar structures, 3D printing can be performed with a higher slice thickness, resulting in reduced printing time.

In summary, using the microfluidic resin for 3D printing is an ideal method for fabricating different bio-microfluidic devices and can replace cost-intensive and time-consuming fabrication methods.

CONCLUSION

This study shows that using microfluidic resin for direct fabrication of master molds for PDMS soft lithography can replace time-consuming master mold fabrication methods. In master mold microfluidic resin, methacrylated monomers and oligomers have been used to facilitate PDMS casting, as illustrated by the fabrication of a cell culture device (and three other benchmark microfluidic devices, as described in the full article). It was shown that the surface roughness must be small enough to avoid creating extra shear stress that endangers PDMS bonding. In the conventional soft lithography process, silanization is needed to prevent PDMS from attaching to the master mold, which can be detrimental for cellular studies. In contrast, the 3D printed mold obtained from the microfluidic resin requires no silanization, and the cellular studies in the PDMS-based cell culture device confirmed the biocompatibility of the resin. As PDMS-based microchannels are common in microfluidic devices, this study can be considered a milestone in the microfluidic field. This new process can reduce the brainstorming-to-production timeframe from several days (including the time required for conventional master mold fabrication and post-treatment) to less thwan five hours (with the new microfluidic resin method).

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O3 Stereolithography of Silicon Oxycarbide (SiOC) Polymer-Derived Ceramics Filled with Silicon Carbide (SiC) Micronwhiskers

S. A. Brinckmann, N. Patra, J. Yao et al.

DUE TO complicated manufacturing methods and lack of machinability, the use of engineering ceramics is limited by the manufacturing processes used to fabricate parts with intricate geometries. The 3D printing of polymers that can be pyrolyzed into functional ceramics has recently been used to significantly expand the range of geometries that can be manufactured, but large shrinkage during pyrolysis has the potential to lead to cracking. In this chapter, we describe a method to additively manufacture particle-reinforced ceramic matrix composites. Specifically, stereolithography is used to crosslink a resin comprised of acrylate and vinyl-functionalized siloxane oligomers with dispersed SiC whiskers. Printed ceramic porous structures, gears, and components for turbine blades are demonstrated.

INTRODUCTION

While additive manufacturing, or 3D printing, is readily used to fabricate various metallic and polymeric materials, fabrication with ceramics is inherently difficult. Methods currently used to 3D print ceramics most often rely on a sacrificial polymer resin with suspended ceramic particulates; printed parts are subsequently sintered at high temperatures where the ceramic particles permanently sinter together [1-3] or are laser sintered [4,5] These structures are plagued by porosity, which is often not uniform or well-controlled [6]. Consequently, the mechanical properties for structural uses are lacking, which severely limits potential applications.

Recently, a handful of emerging studies have explored the use of polymer-derived ceramics (PDCs) in conjunction with stereolithography [7-11]. Using 3D printing, PDCs can be printed into complex forms where their functional properties may be used for a wide range of applications. One benefit of using 3D printing PDCs is that the resulting ceramics have been described as "fully dense" or lacking any porosity [7]. In contrast, the structures of more standard sintered 3D printed ceramics without any additional processing can possess porosities near 65% [12-15]. However, PDCs still undergo a large amount of shrinkage during pyrolysis, which can lead to cracking. Particle-reinforced PDCs undergo reduced shrinkage and cracking of the final ceramic material during pyrolysis, as compared to unreinforced PDCs [16,17]. Furthermore, particle-reinforced PDCs can be formulated to tailor creep resistance, corrosion resistance, and mechanical



Figure 1: (a) XRD of the SiC whiskers used as reinforcement and (b) a laser scanning confocal microscopy intensity image of the SiC whiskers where the dimensions of the SiC whiskers can be measured.

properties [18,19]. Since the addition of reinforcement hinders the initial polymerization process [20], care must be taken to ensure that any additive to the resin will still be able to be 3D printed and will not cause underpolymerization and loss of printing resolution.

The purpose of this study was to derive a preceramic polymer system for use as a 3D printing resin that would result in a highquality polymer-derived ceramic reinforced with SiC micronwhiskers. Using a siloxane precursor and the addition of reinforced 3D printing resin, we fabricated and characterized a 3D-printable SiOC–SiC whisker ceramic. The resulting 3D printed samples were formed into ceramics via pyrolysis.

METHODS

The resin formulation consisted of an initial mixture of the poly(vinylmethoxysiloxan (VMS) and poly-(ethyleneglycol)-diacrylat (PEGDA) in a 1:1 ratio by mass. Following initial mixing, a photoinitiator and free radical scavenger were added at 0.3 and 0.7 wt%, respectively, and mixed for another 30 minutes at 1000 rpm. For resins containing SiC whiskers, the particles were added at 0.5 wt% corresponding to 1.45% volume fraction as determined by the densities and weight fractions of the materials. The mixture was again mixed at 1000 rpm for 30 minutes, resulting in a well-dispersed mixture, as observed visually.

The SiC whisker reinforcement size and geometry was investigated by laser scanning confocal microscopy (LSCM). Images were captured with an Olympus[®] LEXT[™] OLS4000 LSCM (Olympus Corporation, Tokyo, Japan) capable of 3D measurements with 10 nm height resolution and 25 nm x-y resolution. Quantitative analyses of SiC diameter and length-to-diameter ratios were measured using the Olympus software. The as-received SiC whiskers were also characterized by X-ray diffraction (XRD).

Preceramic polymer resins were 3D printed using a FormLabs Form 1+ stereolithographic (SLA) printer, where polymers are photo-cured using a 405 nm wavelength laser. After printing, parts were cleaned using isopropanol to remove the residual uncured resin on the surface and subsequently post-cured under a 20W UV lamp (Quans High Power UV LED light) with a wavelength of 405 nm for 20 min.

RESULTS

Through a systematic study varying both the free-radical scavenger and photoinitiator, the final resin formulation utilized a ratio of free-radical scavenger to photoinitiator ratio of 3:7 by weight. This ratio resulted in the most distinct features for the 3D printed structures.

SiC whiskers were selected as a filler as they would have no complex interaction with the PDC matrix and have been previously investigated in traditional composite PDCs [21].



Figure 2: Comparison of the x-y resolution of the base resin and the resin reinforced with 0.5 wt% SiC whiskers printed using identical initial designs and printer settings. The filled resin results in a sample with significantly less over-polymerized and is more defined in the x-y plane.



Figure 3: Image of a 3D-printed pre-ceramic polymer and subsequent pyrolyzed material at 1000 °C (1832 °F) ceramic using the base resin.

XRD (Figure 1a) and laser scanning confocal microscopy (LSCM) measurement of SiC whiskers confirmed material and manufacturer dimension specifications, with whiskers approximately 2 µm in diameter and having a length-to-diameter aspect ratio of roughly 20 (Figure 1b). Most of the whiskers were relatively straight. However, several were had curling or spiraled geometries while remaining intact. With the addition of 0.5 wt% SiC whiskers into the base resin, no apparent changes in the viscosity or strength of the polymerized part were identified. The SiC whiskers maintained suspension in the mixture for up to 12 hours before naturally settling. For all results shown here, printing was performed within 1 hour of mixing.

A key parameter in stereolithography is the selection of the energy used to cure the resin. Through Fourier-transform infrared (FTIR) spectroscopy, the chemical functional groups' reactions and structural changes of the polymer system were observed for two different ultraviolet (UV) exposure times during the base resin's polymerization process. Comparing FTIR results of VMS-PEGDA with and without SiC whiskers, C=C bonds from both the vinyl group and acrylate functional groups exhibited a smaller normalized peak intensity in the base resin than those with SiC whisker reinforcement, indicating the presence of SiC whiskers inhibited crosslinking during the polymerization process.

The 3D printing of both materials was successful; however, when printing the base resin, there were some areas of over-polymerization, especially on the edges of the print with some areas containing what looked like cured droplets jutting off the features. When comparing the printing processes, we noted that the resin with the inclusion of SiC whiskers tended to result in more defined structures with few areas of over-polymerization (Figure 2). As such, the SiC-reinforced resin was preferred for most 3D printed parts.

To understand the pre-ceramic polymer's polymer-to-ceramic conversion process, a sample of 10 mg of material was pyrolyzed in a TGA in an argon atmosphere where the change in mass and heat flow were analyzed over the course of the pyrolysis process. When initially heated from room temperature, there is a steady mass loss beginning at 350 °C (662 °F) and terminating at about 500 °C (932 °F). Within this temperature range, the pre-ceramic polymer fabricated with the base resin loses 63.1% of its initial mass, whereas



Figure 4: Examples of polymer-derived ceramic parts fabricated via 3D printing and a finer image of the inverse FCC structure, highlighting the resolution capable with this method.

the resin reinforced with SiC whiskers only loses 61.6% of the initial mass. During preliminary investigations, there was a heat flow dip at both 500 °C (932 °F) and 725 °C (1337 °F). This is represented by the severe drops in Figure 3 where the TGA temperature was held isothermally. In the case of the heat flow change at 500 °C (932 °F), this corresponded to the material's transformation to an inorganic material. At 725 °C (1337 °F), there is again a change in heat flow associated with the formation of amorphous SiOC. Not only does the mass loss change with the addition of SiC whiskers, but the heat flow at higher temperatures is slightly reduced as the changing matrix is mixed with stable SiC whiskers.

After the pyrolysis process, the polymer-derived ceramic sample is measured to calculate shrinkage and ceramic yield. The base resin resulted in an average isotropic shrinkage and ceramic yield of $43.1 \pm 0.38\%$ and $36.9 \pm 0.31\%$, respectively, over a study of 10 samples and in all three directions for shrinkage measurements. With SiC reinforcement, the shrinkage and ceramic yield are both impacted with a decrease in shrinkage to $37.2 \pm 0.38\%$ and an increase in ceramic yield to $38.4 \pm 0.26\%$, similar to the increase in retained mass noted in the TGA results. With or without further processing, the 3D-printed PDC may be used for small scale turbine blades or applications that require high surface area to volume ratios. Several scale models of ceramic 3D printed geometries made from this process can be seen in Figure 4. The three larger turbine blades are manufactured from pyrolysis of the base resin, where surface cracking of the polymer during post-curing was a minor problem. The remainder of these samples are manufactured from the SiC-reinforced resins with 10 µm resolution. Of particular interest is the wheel hub (far left), which has 3D-printed threads such that the appropriate axel can be attached, demonstrating the ability to create machinery elements, and the inverse FCC structure, which demonstrates the scales of accomplishable porosity using this 3D printing methodology. However, note that this is not the finest resolution possible.

DISCUSSION

The addition of SiC particles into polymerderived ceramics has been shown to mitigate both mass and shrinkage in addition to helping reduce cracking [11]. Therefore, 3D printing a polymer-derived ceramic reinforced with SiC whiskers was investigated. SiC was chosen as the reinforcement due to its high-temperature stability [22-24].Through this process, we achieved our research goals of reducing shrinkage and mass loss. By varying the ratios of free-radical scavengers and photoinitiators, we achieved an optimal ratio through a systematic study that reduced overpolymerization by increasing the free-radical scavenger, which aided in localizing the reaction. However, a balance of photoinitiator was required to ensure that polymerization occurred and that sufficient polymerization depths during 3D printing could be achieved.

The XRD of the ceramics agrees with existing literature that the resulting SiOC is amorphous. Comparing fabrication of typical SiOC at temperatures around 1000 °C (1832 °F), it is well established that this material should be amorphous [25]. XRD plots of the base and SiC-reinforced resins look nearly identical. Some trace of SiC peaks might be expected within the ceramics that are reinforced with the whiskers. However, at 1.45% volume fraction of the whiskers to the matrix of the ceramics, it is likely that the SiC peaks are on the same order as the noise in the data and, therefore, cannot be detected.

The reduction in shrinkage is as expected with the SiC reinforcement hindering shrinkage during pyrolysis. With the notable exception of shrinkage in the material, ceramics made from the base resin or those with SiC whiskers appear nearly identical. As the shrinkage was uniform in all three dimensions, these ceramics look like scaled models of their preceramic stage with no discernible difference in shape retention and no cracking from internal stresses of dimension mismatch during pyrolysis.

CONCLUSION

Throughout the study, a siloxane-based preceramic polymer and the resulting pyrolyzed SiOC fabricated via stereolithography 3D printing created both a SiOC polymer-derived ceramic and SiOC–SiC ceramic matrix composite, which was characterized. The photopolymerizable resin was comprised of a vinylmethoxysiloxane homopolymer and poly(ethyleneglycol)-diacrylate and was studied with and without the addition of SiC whiskers as a reinforcement. Both the base polymer and polymer matrix composite's pyrolysis behavior were analyzed via TGA and subsequently shown to be an amorphous SiOC ceramic using XRD. Not only did the SiC whiskers act as a de facto UV absorber during photopolymerization, they also hindered shrinkage to an average of 37.2% from the base resin's 43.1% shrinkage after pyrolysis. The final ceramic yields were measured to be, on average, 36.9% and 38.4% for the base resin and those that used SiC reinforcement, respectively.

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04 Laser-Assisted, Large-Area Selective Crystallization and Patterning of Titanium Dioxide Polymorphs

L. F. Gerlein, J. A. Benavides-Guerrero and S. G. Cloutier

ALTHOUGH UBIQUITOUS in multiple industrial applications, the widespread use of solution-based precursors for crystalline titanium dioxide (TiO₂) for optoelectronic device integration remains limited due to its high processing temperature. It is currently possible to crystallize TiO_2 at lower processing temperatures, but it requires a carefully controlled atmosphere or metallic doping of the amorphous precursor and can only achieve a low-yield conversion of the precursor. Herein, a qualitative method is presented for the processing of an amorphous photosensitive precursor to achieve high-yield conversion to highly crystalline TiO₂ at room temperature and in an ambient environment using a low-energy laser. We demonstrate a real potential for the additive manufacturing of TiO_2 structures for photocatalysis, printable flexible hybrid electronics, and low-cost photovoltaics using low-energy laser processing that is compatible with heat-sensitive materials and flexible substrates.

INTRODUCTION

In recent years, careful control of the phase transition and phase stability of TiO_2 polymorphs induced by low-power visible light gained attention in the scientific community [1-9]. These previous efforts all arise from the need for high-quality crystalline TiO_2 converted at room temperature in an ambient environment. Yet, hurdles prevent their scaling-up to modern industrial-like environments. In par-

ticular, the inclusion of TiO_2 precursors into laser-based 3D printers and digital inkjet printing systems, including electrohydrodynamic inkjet, has been limited by two defining factors: the high processing temperatures (beyond 400 °C, or 752 °F) still necessary to crystallize into different polymorphs [1,10], and/or the specific atmospheric conditions required to crystallize under visible light at room temperature [2,6,9]. Both factors are detrimental for the widespread integration of TiO_2 precursors into large-volume manufacturing of many photocatalysis, energy conversion, wearable, and flexible hybrid electronic solutions.

Previously, a novel TiO₂ precursor formulation was developed that relied on an incomplete nonhydrolytic sol–gel ester elimination to yield films of amorphous TiO₂ suitable for laser-induced conversion in ambient conditions [8]. This formulation allows lowenergy, laser-induced conversion of amorphous-to-anatase, amorphous-to-rutile, anatase-to-rutile, or amorphous-to-mixture of anatase/rutile in ambient environment and at room temperature, without metallic ions or specific atmospheric conditions.

In this article, large-scale, laser-assisted conversion of amorphous TiO₂ films under ambient conditions is presented with an inexpensive approach using a low-cost, commercially available 3D printer platform with a 405 nm laser engraving attachment module to spatially control the TiO₂ crystallization. To this end, we described in detail how this unique formulation can be used to achieve selective conversion of this amorphous TiO₂ into combined anatase and rutile patterns over a large surface area. The laser-induced conversion process is carefully optimized (laser velocity, laser power setting, and number of passes) to achieve selective conversion of the TiO₂ over a large surface area. The morphology and integrity of the converted areas are analyzed using laser-scanning microscopy.

METHODS

The TiO_2 precursor synthesis followed the procedures published in previous studies [8,11].

Optical imaging and laser 3D reconstruction were made using the Olympus[®] LEXT[™] OLS4100 laser confocal microscope.

The 3D printer of choice was the BIBO-2 Touch printer that possesses a positional accuracy in the Z-direction resolution of $20 \,\mu$ m. This accessible 3D printing system was purchased for less than 850 USD with a laser engraving module that replaced the extruder heads and was controlled by the fan TTL control circuit.

RESULTS

A dispersion of TiO_2 nanoparticles was prepared following a procedure fully described in previous studies [8,11]. Pieces of standard glass slide were placed inside a plastic container containing a solution of an as-synthesized amorphous TiO_2 nanoparticle suspension in hexane.



Figure 1: a) Evolution of the laser emission power of the 405 nm laser unit used to convert the TiO_2 as a function of the setting number. b) Micrograph of an amorphous film atop glass after complete drying. c) Photograph of the conversion process using the 405 nm laser source atop the amorphous TiO_2 film.

The container is then sealed within a box with breathing holes to avoid external contamination and provide a slow and uniform evaporation of the hexane, yielding smoother films. After 12 hours inside the fume hood, a densely packed film of amorphous TiO₂ nanoparticles remains atop the glass after all the solvent has evaporated. The resulting film displays a reddish coloration and covers the area of the glass as shown in Figure 1. The physical microscopic quality of the amorphous, as-deposited film is shown in Figure 1b, and the overall look of the film atop glass is shown in Figure 1c.

The laser head consists of a 405 nm continuous-wave blue-violet source with a maximum 500 mW power output. At maximum power, the laser emission reaches 465 mW from the 500 mW nominal specification for the module (Figure 1a). Under low-power operation, with the power control set under 50 (about 388 mW measured emission), the laser emission will not damage the unit, and the impact of the poor cooling is less dramatic, but this lack of stable emission reflects in the results.

Initial experiments demonstrate that square areas of the film fully converted to crystalline TiO_2 using the BIBO printer's laser module. Each area is filled with a simple square mesh pattern, which provides uniform converted areas by keeping the lines close enough to each other to trigger conversion along the area of interest. Microscopic analysis of the square patterns shows a strong penetration of the laser throughout the film to the point of complete ablation of the material, exposing the substrate, as shown in Figure 2a,b.

The main goal is to minimize this material ablation while promoting exclusively the crystallization of the amorphous TiO_2 layer under environmental conditions, delivering a uniform film in which the presence of both, anatase and rutile crystalline phases is possible. Because of this unwanted material etching, lower laser power settings were explored going from 1 to 16, corresponding to power emission between 4 and 230 mW (13.7–732 W mm⁻²). With a new film deposited atop glass using the same described procedure, the patterns of choice are lines 100 µm thick created by doing five contiguous traces of 20 µm each (Figure 3).

For each pattern, the power setting of the laser is fixed and ranges from 16 down to 1, in single steps. To further reduce the material displacement, the laser speed parameter was increased from 50 to 100 mm min⁻¹. Of course, this also reduces the total dosage received by the film. The travel speed, number of passes, and pass depth remain unchanged from the previous run. From laser power setting 16 down to 6, the resulting line patterns exhibit complete crystallization to rutile. These results are like those previously obtained in the square patterns realized



Figure 2: Microscopic analysis of the morphology of the square features created using the power setting 25. a) Low-resolution image of the whole square. b) Magnified portion of the red square in (a). c) 3D reconstruction of the topology of the magnified portion of the square.

with higher power settings, with important material displacement and/or ablation, leaving bare areas of exposed glass where the amorphous TiO_2 was previously present.

At power setting 5, the equivalent laser power density is $216 \pm 10 \text{ W} \text{ mm}^{-2}$ (Figure 1a). At this emission power, one can already observe a smoother and more uniform, fully crystallized film (Figure 3b). The presence of cracks in the film after crystallization is largely attributed to the natural densification of the material and subsequent volume loss due to the atomic reorganization. Reported values in density for both anatase and rutile phases are 3830 and 4240 kg m⁻³, respectively,2 highlighting the structural differences of both phases. Indeed, the unit-cell volume of anatase is 130.36 Å³, whereas for rutile it is 62.45 Å³. This factor explains the stronger fracturing present in the rutile conversion [8] when coming from an amorphous state. This fracture effect also depends on the film thickness, being more prominent in thicker films. Here, the thickness of the film used to pattern these lines is estimated to be 24 μ m, as shown in Figure 3c.

To showcase the possibilities of this TiO₂ solution and low-energy conversion process for additive manufacturing, a geometric pattern has been chosen for printing that has both rutile and anatase areas coexisting along with amorphous unconverted sections, as shown in Figure 4. In the initial pat-



Figure 3: Line patterns produced with a laser speed of 100 mm min^{-1} and varying the power setting from 25 to 1 on a 24 µm-thick film of amorphous TiO₂. a) Line patterns from 16 to 3. Lines produced with power settings 2 and 1 do not affect the area and are not visible in the micrograph. b) Micrograph from the line pattern produced with power setting 5. c) 3D laser micrograph reconstruction from the image on (b).

tern design, as shown in the inset in Figure 4a, there are three distinctive colors: dark brown is the amorphous film, dark gray is the anatase section, and light gray is the rutile section.

Optical characterization of the sample, shown in Figure 4b, clearly shows each section labeled (Am) amorphous, (A) anatase-rich, and (R) rutile-rich. These regions are easily recognizable in this intimately dense mixed film.

The advantageous and synergistic effects associated with having both phases in the same environment for photocatalytic applications are well established. This setting reduces charge recombination, boosting the degradation of organic contaminants [8,12,13]. However, previous results require the use of two types of independent nanoparticles working together, without the level of spatial control offered here. As demonstrated by the results herein, this is the first time that a TiO_2 large-area film can be produced on-demand where the ratio anatase:rutile is controlled directly by the geometry of each.

DISCUSSION

Just recently, approaches that involve the use of TiO_2 as part of the active material in photovoltaic applications [14] and the potential of the heterojunction composed of both phases in light harvesting have just being explored [15]. This is done using a Degussa P25 (biphasic TiO₂ nanoparticles) with a fixed ratio of anatase to rutile presence in the mix. The results included in this article describe the possibility of having spatially selective biphasic TiO_2 layers compatible with conventional laboratory fabrication techniques for optoelectronic devices in addition to the possibility of largescale production lines.

However, integration in large production lines requires more adept control of the crystallization conditions, specifically the quality and stability of the source of illumination, whether it is a low-power laser source or a high-power photonic curing flash lamp [16] using a mask for faster, large-area conversion. In this case, the laser's unstable emission tends to variate the power delivered and creating partially converted spots in the wings. This configuration does not guarantee a uniform conversion over the area of interest. A square profile emission



Figure 4: a) Micrograph of the patterned film with the presence of both phases next to each other and an amorphous part left unconverted in between. Each section corresponds to either amorphous, anatase, or rutile. Inset: photograph of the patterned sample. b) Magnified 3D reconstruction of a section of the sample. The unconverted amorphous (Am) area is represented in blue color. The rutile area (R) is the more red-yellow section and the anatase area (A) is the green-blue area. These colors are automatically assigned by the 3D reconstruction software.

present in much more expensive and reliable sources [17] will increase the yield of a single crystalline phase per unit area.

Despite the low cost of the approach presented here, good spatial resolution, control, and reproducibility as well as the lack of proper thermal and emission stability in the laser unit makes it inappropriate to meet high-precision industrial standards. We, however, believe this proof-of-concept is concrete evidence that it is possible to crystallize TiO₂ under ambient environmental conditions, using a low-cost approach, with the possibility of obtaining spatial control of the phases by only adjusting the emission parameters of a laser source.

CONCLUSIONS

As a wide bandgap semiconductor, TiO₂ is an attractive candidate, especially for application into dye-sensitized solar cells (DSSCs) [18,19], where the light absorption role and the charge transport role are separated. The integration of TiO₂ in novel organic and inorganic photovoltaic devices is limited to a charge transporting role due to the incompatibility of the crystallization process of TiO₂ that damages the other materials involved in the fabrication of the device. Crystallized TiO₂, whether as anatase (3.2 eV bandgap) or rutile (3.0 eV bandgap), exhibits optical absorption at the violet portion of the optical spectrum, and with this technique, it is possible to fabricate and integrate devices that take full advantage of this asset.

By utilizing a defect-rich synthesis of nonhydrolytic TiO_2 that shows enhanced sensibility to photoconversion while avoiding costly and lengthy thermal crystallization procedure, we demonstrate that it is possible to have largearea deposition and conversion of biphasic thin layers of TiO_2 . Complete area-selective conversion to either anatase or rutile is possible, while preserving the state of the other one.

In addition to creating fully crystallized largearea patterns with an "a la carte" ratio of each phase, it is now possible to experiment with unconventional patterns between these two phases. In addition, this improvement brings new possibilities for low-cost printed flexible electronics, wearable devices, and novel additive manufacturing schemes. Most importantly, with the presented approach, this procedure could be automated and repeated by a machine learning platform for large-scale production of devices.

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Advanced Optical Metrology

Part II

Thin Film Metrology

Introduction: Thin Film Metrology

Thin film technology is ubiquitous across materials science for applications such as semiconductors,^[1,2] electronics (*e.g.*, light-emitting diodes, soft electronics),^[2,3] microelectromechanical systems (MEMS),^[4] memory devices,^[2,5] energy storage (batteries, capacitors),^[6,7] photovoltaics,^[8,9] fuel generation,^[10] catalysis,^[11] chemical sensors,^[12,13] environmental coatings (*e.g.*, thermal),^[14] chemical barriers (*e.g.*, diffusion, corrosion),^[15,16] radiation detection,^[2] photodetectors,^[17] microfluidics,^[18] piezoelectric devices,^[19] mechanical layers (*e.g.*, adhesion, lubrication, hardness),^[20–22] magnetic devices (*e.g.*, SQUID),^[23] optical coatings (*e.g.*, electrochromic, antireflection, interference, waveguides),^[24] biomaterials and biomedical applications,^[25] and many more. Furthermore, there are sufficient fabrication techniques that virtually any type of material can be prepared as a thin film, such as metals, alloys, oxides, ceramics, glasses, polymers, inorganic complexes, organic molecules, and biological molecules.

The ability to prepare a material into a thin film can enable specific material properties and unlock particular applications. Often, the nano-, micro-, and millimeter-scale morphologies of the thin film have important implications on its properties and eventual application. Therefore, the characterization of the morphology of thin films is an integral part of materials science research. There are a variety of different characterization techniques with different pros and cons in terms of resolution, the field of view, sample size, ease of use, speed, and information that can be obtained.

This brief introduction will discuss some of the techniques to characterize thin films. The methods are characterized by their distinct operating principles, namely mechanical characterization techniques, thermal analyses, scanning probe methods, and methods that involve the interaction of radiation (*e.g.*, electrons, ions, and photons) with matter. The introduction will highlight laser scanning confocal microscopy as a promising method to characterize the morphology of a wide variety of thin-film materials.
THIN FILM CHARACTERIZATION

Mechanical Characterization. The mechanical properties of a thin film can provide information on the underlying morphology of the material. The manner in which a thin film responds to a particular mechanical deformation is dependent on the assembly of its constituent components. Furthermore, the influence of volumetric and interfacial constraints can cause mechanical properties to differ from bulk values. Cantilever beam or plate type structures are commonly used to measure residual stress, from deflection and curvature measurements. The Young's modulus and plastic properties of thin films can be determined by analyzing the stress associated with thermal cycling using thin wafer or cantilever beam measurements. Elastic moduli and other mechanical properties of thin films can be measured by cantilever beam resonant frequency methods. Furthermore, measurement techniques such as microindentation and substrate curvature can be utilized to determine the plastic properties of submicron thin films and multilayers on substrates. Peel, pull, and scratch tests are used to characterize the adhesion properties of materials; however, they do not provide quantitative information regarding interfacial atomic bonding strength. Lastly, microindentation and micro-scratch characterization methods can provide a further understanding of the mechanical processes of thin films.^[26]

Thermal Characterization. The thermal properties of materials can also shed light on the underlying morphology of thin films. Thermal characterization can provide physical and chemical information of the thin film.^[27] Thermogravimetric analysis (TGA) is used to measure the mass change of a sample as a function of temperature. The off-gas from TGA experiments can be analyzed by mass spectrometry (MS) and Fourier transform infrared spectroscopy (FTIR) to understand the chemistry of the thermal decomposition products.^[28] Differential thermal analysis (DTA) measures the temperature differences between a sample and a reference as they are simultaneously heated or cooled, whereas differential scanning calorimetry (DSC) measures the difference in heat flow. Both DTA and DSC can be used to determine properties such as the crystallinity, glass transition, phase changes, chemical reactions, heat capacity, etc.^[27,29] Finally, dynamic infrared thermography can be used to determine the thermal conductivity, heat capacity, and thermal diffusivity of thin films.^[30]

Scanning Probe Characterization. Physical probes can be used to scan the surface of thin films to understand both their surface and, to some extent, their bulk morphologies. Surface profilometry is a useful tool for measuring the thickness, roughness, and texture of thin films. In profilometry, a stylus probe is brought into direct contact with the film, and a line scan is performed.^[31] In atomic force microscopy (AFM), a sharp probe is raster-scanned across a sample surface, in contact or non-contact modes. Interaction forces between the sample and the probe are measured by the deflection of the cantilever containing the probe and used to generate an image.^[32] Different force modes can be analyzed, such as attractive, repulsive, magnetic, electrostatic, and van der Waals. In certain thin conductive films, bulk morphologies can be constructed using conductive AFM (cAFM).^[33] Also, Kelvin probe force microscopy (KPFM) can be used to measure charge accumulation^[34] and the work function of thin films.^[35] Although AFM is capable of sub-nm resolution and is nondestructive, it is not rapid, it is susceptible to artifacts, and has difficulties capturing large variations in sample thickness.^[36] Scanning electrochemical microscopy (SECM) uses an ultramicroelectrode tip and can be used to map the electrochemical activity of a thin film.^[37] Finally, scanning tunneling microscopy (STM) utilizes a metallic probe which is scanned over a thin film, and a voltage is applied between the tip and the surface. In this way, the quantum tunneling current is used to image the sample. ^[38] STM can achieve angstrom-scale resolution but requires specialized vacuum equipment.

Electron Microscopy. Transmission electron microscopy (TEM) can be used to elucidate the structure, chemistry, and properties of thin films. In TEM, the transmission of an electron beam through a sample is used to generate an image. Since electrons interact strongly with matter, both structural and chemical information can come from TEM characterization. Additional techniques in TEM include selected area electron diffraction (SAED), electron energy loss spectroscopy (EELS), and energyfiltered TEM (EFTEM). In TEM, due to the small de Broglie wavelength of electrons, the lattice spacing of atoms can be imaged. The sample requires special preparation and must be very thin so that the electron beam is not attenuated by the sample, and special vacuum equipment is required.^[39] Meanwhile,

in scanning electron microscopy (SEM), an electron beam is raster-scanned over a sample, and either secondary electrons or backscattered electrons from the sample are detected to map the sample topology. SEM has a wider field of view than TEM, and it does not require ultrathin samples because it does not rely on electrons being transmitted through the sample; however, the resolution of SEM is less than TEM, around 1 nm. Further, energy-dispersive X-ray spectroscopy (EDS) can be used to spatially map the elemental content of thin films. Also, the orientation and phase of crystalline domains can be determined by the diffraction of backscattered electrons (EBSD).[40]

Ion Beam Techniques. Helium ion microscopy (HeIM) is an imaging technique similar to SEM, but instead of an electron beam, a helium ion beam is scanned over the sample. Secondary electrons ejected from the sample due to the impact of helium ions are detected. The HeIM beam can be less than 1 nm, enabling high resolution with a fairly wide field of view.^[41] In another method, elemental maps of thin films can be constructed by time-of-flight secondary ion mass spectrometry, where a pulsed ion beam is scanned over a sample, which removes particles from the surface that are detected by MS.^[42]

X-ray-based Techniques. The interaction of X-rays (and neutrons, which is not discussed here) with matter is a useful tool to determine thin film morphology. Small-angle X-ray scattering (SAXS) characterization of a thin film, either in transmission or grazing incidence (*i.e.*, GISAXS) configurations,^[43] can give information on the periodic structures in the film at the nanometer scale. Whereas, X-ray diffraction (XRD) and wide-angle X-ray scattering can provide structural information at the angstrom-scale [44] Soft/resonant X-rays can be used to probe particular chemical groups in the material.^[45] Furthermore, X-ray reflectivity (XRR) is a useful tool for determining the thickness of thin films. ^[46] Lastly, X-ray microtomography (µCT) uses X-rays to create cross-sections of samples, which can be constructed into 3D images.^[47]

Photon-based Methods. Optical microscopy (OM) is one of the oldest methods to determine a sample's morphology, dating back to the seventeenth century. OM is one of the most important techniques for identifying features > 500 nm in materials and thin films. Par-



Figure 1: Schematic of the laser scanning head of the LSCM. The incoming laser beam is reflected by the dichroic mirror and directed toward the sample by the two galvanometric mirrors. The reflected, transmitted, or fluoresced light from the sample is transmitted by the dichroic mirror and is spatially filtered by the pinhole before reaching the detector.

ticular techniques in OM include brightfield, darkfield, polarization, interference, and phase-contrast microscopies. Contrast in OM is created by various mechanisms, depending on the imaging mode, such as absorption of light, scattering, rotation of polarized light, and interference.^[48] Lastly, near-field scanning optical microscopy (NSOM) is a technique where nanoscale morphologies can be elucidated by scanning a small fiber-optic probe over thin films. When the distance between the probe and the sample is smaller than the wavelength of light, the resolution of the image is not limited by the optical wavelength.^[49] Finally, confocal microscopy has several advantages over conventional widefield OM, such as the ability to control depth of field, elimination or reduction of background information, and the capability to collect serial optical sections from specimens.[36,48,50] In particular, laser confocal scanning microscopy will be discussed in the next section.

LASER CONFOCAL SCANNING MICROSCOPY

In far-field optical techniques, imaging is accomplished by focusing elements. In a microscope, the objective lens forms a magnified image of the illuminated object that can then be examined with the eyepiece. If we consider the image of a single point, the light intensity is distributed around the focal point in a

focal volume described by a point spread function (PSF). The extent of the PSF determines the resolution. In the ideal case where no aberrations are present, the resolution is limited by diffraction and is determined by the wavelength of light in the medium (λn) and the aperture angle of the lens $NA=n \sin(v)$, where *n* is the refractive index of the medium and v is the half-angle of the lens aperture, and can be expressed by the Rayleigh theoretical resolution limit : $RL=0.61\lambda/NA$. Much research has been devoted to developing tools able to image objects with a resolution lower than the Rayleigh limit. By confocal microscopy, a resolution about 30% less than the Rayleigh limit is obtained. This considerable advantage of confocal microscopy follows by the use of a point detector, obtained in practice by placing a circular pinhole in front of the photodetector that cuts off the out-offocus light from surrounding planes.^[36]

Although the confocal microscope was invented in 1955 by Minsky,^[51] it was not widely adopted until the invention of lasers and the availability of high-performance computing. Laser scanning confocal microscopes (LSCMs) use collimated laser light as a 'point' illumination source, with point focus on the sample, and focus the reflected, transmitted, or fluoresced light through a pinhole to provide a 'point' detector. A schematic of the laser scanning head is shown in Figure 1. [50]

Multiple imaging detection modes can be used with LSCM, including but not limited to



Reflection LSCM image

Fluorescence LSCM image

Superposition of (a) and (b)

Figure 2: LSCM images of poly(styrene-ran-butadiene) and polybutadiene films, using (a) reflection and (b) fluorescence modes. (c) Superposition of reflection LSCM and fluorescence LSCM images.

reflected light, transmitted light, fluorescence, and Raman spectroscopy. The different imaging modes can provide different information about the thin film, and the different modes can be superimposed to create a composite image of the sample (Figure 2).^[48] As long as surface topology is the only characterization needed, reflection mode can be an ideal method to characterize thin films.^[52] One benefit of reflection mode for materials science is that the material does not need to be fluorescent to be imaged; this is ideal for many materials systems. Thus, as-prepared samples can easily be characterized. For reflected light imaging, the smallest available wavelength laser (e.g., 405 nm) is optimal, as the optical resolution is directly proportional to wavelength. ^[50] The high spatial resolution, wide field of view, minimal sample preparation, relative ease of measurement (i.e., no vacuum equipment required), the ability to characterize samples that have large height variation, the ability to construct 3D and pseudo-infinite depth of field imaging, and versatility (i.e., material selection and imaging modes) of LSCM make it an ideal tool of characterizing the morphology of thin films in materials science.

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01 The Use of Laser Scanning Confocal Microscopy (LSCM) in Materials Science

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ABSTRACT

Laser scanning confocal microscopes are essential and ubiquitous tools in the biological, biochemical, and biomedical sciences, and play a similar role to scanning electron microscopes in materials science. However, modern laser scanning confocal microscopes have several advantages for the characterization of materials, in addition to their obvious uses for high resolution reflected and transmitted light optical microscopy. Herein, we provide several examples that exploit the laser scanning confocal microscope's capabilities of pseudo-infinite depth of field imaging, topographic imaging, fluorescence imaging, and photo-stimulated luminescence imaging for the characterization of different materials.

INTRODUCTION

Confocal microscopy is a ubiguitous technique in the life sciences, as it provides precise optical sectioning of fluorescently labeled thick specimens. To date, however, it has been underutilized in materials science. Recent advances in both instrumentation and computing power now make confocal microscopy an attractive imaging and analytical tool for materials scientists. When properly configured, a confocal microscope can serve as a high-resolution optical microscope (in either transmission or reflection) with 'infinite' depth of field, while at the same time serving as a non-contact optical profilometer. Combined and synchronized with an external spectrometer, techniques such as photo-stimulated luminescence spectroscopy are enabled.

Though the confocal microscope was invented in 1955 by Minsky, ^[1] the widespread use of confocal imaging was not possible until the invention of lasers and the availability of significant computing power. [2-6] Laser scanning confocal microscopes (LSCMs) use collimated laser light as a 'point' illumination source, with point focus on the sample, and focus the reflected, transmitted, or fluoresced light through a pinhole to provide a 'point' detector. The pinhole defines a second crossover focal point and serves as a wide-angle filter to the detector. If scattered light does not pass through the pinhole, then it is not in focus. Once the light passes through the pinhole, it is typically split into different wavelengths using dichroic mirrors and filters, and then detected by photomultiplier tubes (PMTs). Imaging of large areas of the sample is achieved by raster scanning the beam across the sample using mirrors controlled by piezoelectric actuators (Figure 1).

This paper is arranged as follows. The equipment is briefly described, after which several examples using different imaging modalities that exploit the advantages of confocal microscopy are shown. The advantage of using a hot stage in a confocal microscope, and of adding a high-resolution spectrometer for photo-stimulated luminescence imaging is also addressed.



Figure 1:. The optical path of a confocal microscope. The use of point focus and a pinhole aperture located at a crossover focal point (i.e., the confocal point), before the detector provides superior rejection of out-of-focus light. The detector section can be one or more PMTs and/or a spectrometer.

METHODS

All of the data presented in this paper were obtained with an Olympus FV1000 filter-based confocal scan head coupled to an Olympus BX62 upright motorized microscope (Olympus Corp., Tokyo, Japan). Four lasers provide a total of six different wavelengths (405, 458, 488, 514.5, 543, and 633 nm), which can be combined into a single beam before imaging. For reflected light imaging, we prefer the 405 nm laser, as the optical resolution is directly proportional to wavelength. The FV1000 scan head is equipped with three PMTs for reflected/fluoresced light, one PMT for transmitted (non-confocal) light, an Acton 2300i 0.3 m spectrometer (Princeton Instruments, Acton, MA, U.S.A.) equipped with a Princeton Instruments PIXIS 100BR backilluminated, deep depletion, thermoelectrically cooled charge-coupled device detector (Princeton Instruments, Trenton, NJ, U.S.A.).

RESULTS AND DISCUSSION

Traditionally, to get the highest lateral resolution from a metallurgical microscope, samples had to be polished to a high degree of flatness and then lightly etched to provide optical contrast. If the sample was not perfectly flat or was over-etched, it became difficult or impossible to obtain high-quality optical images. With conventional brightfield optical microscopy, in-focus regions are crisp and clear, whereas out-of-focus regions are less distinct. ^[7] In con-



Figure 2: (a) Conventional brightfield optical micrograph of a polished and etched PH13–8Mo martensitic stainless steel. (b) An image of the same region taken using the 405 nm laser in the laser-scanning confocal imaging reflection mode.

focal microscopy, in-focus regions are similarly crisp and clear, but the intensity in out-of-focus regions drops rapidly. ^[2-4] As a result, little to no signal is obtained from out-of-focus regions. When combined with a motorized focusing mechanism, it is relatively simple to take a series of images at different focal planes and form a composite image to obtain an 'infinite depthof-field' image. For a well-prepared metallographic sample, such as the polished PH13– 8Mo martensitic stainless steel shown in Figure 2, the confocal image is noticeably sharper, but the actual increase in resolution is modest.

Confocal microscopy has much more significant advantages for samples that cannot be polished to a flat surface. For example, the surface of a sintered aluminum oxide (Al_2O_3) sample was imaged without further specimen separation using brightfield optical microscopy, and it is difficult to resolve the microstructure clearly because of the narrow depth of field of a high numerical aperture objective (Figure 3a). With laser scanning confocal imaging, however, the depth of field becomes slightly smaller, but the outof-focus regions are dark (Figure 3b). Multiple images can be obtained over a range of focal planes; collecting all the in-focus data and combining the maximum intensity pixels yields an essentially infinite depth-of-field image (Figure 3c). Further, in the process of obtaining adequate images to provide an infinite depth-of-field micrograph, sufficient information is also gathered to produce a topographic map of the sample surface (Figure 4).



Figure 3: (a) Conventional brightfield optical micrograph of a sintered Al_2O_3 sample. (b) Single confocal image (405 nm laser) of the same specimen. (c) An 'infinite depth-of-field' confocal image of the same region. This image was acquired by taking 441 images and changing the focal plane by 20 nm between each image and creating a maximum-intensity projection.



Figure 4: A 3D topographic model of the surface of the sintered Al_2O_3 sample in Figure 3. The infinite depth-of-field image has been projected onto the modeled surface. The z-axis has been exaggerated by a factor of 2 to highlight the topographic features.



Figure 5: A three-dimensional model of a piston ring used in an engine. The regions experiencing more wear had increased deposition of zinc oxide (ZnO), which can be recognized by the green fluorescence when stimulated with a 405 nm laser.

For materials scientists, many ceramics, semiconductors, and polymeric materials can provide strong fluorescence, although metals do not fluoresce. By using multiple PMTs, wavelength-specific dichroic mirrors, and bandpass wavelength filters in front of the PMTs, it is possible to image with reflected and fluoresced light simultaneously. An example of this is given in Figure 5, where a piston ring removed from an engine was imaged using both reflected and fluoresced light. The lubricant from the engine deposited ZnO on the piston ring, which is visible as a green fluorescent signal when imaged with the 405 nm laser. By simultaneously imaging with both the reflected laser and the fluoresced radiation, it is possible to obtain a topographic image (from reflected light) and two infinite depth-of-field images

(from reflected and fluoresced light, respectively). The infinite depth of field fluorescence image shows a bright band corresponding to increased ZnO deposits. By taking a 3D model of the surface and applying the fluorescence image as a texture, it is possible to see clearly where the greatest deposits of ZnO occurred.

 α -alumina (α -Al₂O₃) has strong fluorescence in response to visible laser illumination if trace quantities of chromium are present. In practice, this means that any α -alumina samples, short of a semiconductor-grade sapphire wafer, fluoresce under laser irradiation. This fluorescence is known as the 'ruby' fluorescence and occurs as a peak doublet around 693 nm, known as the R1/R2 doublet. The specific wavelengths of the two peaks are



Figure 6: (a) Stress map generated from the R2 fluorescence of the TGO formed on a nickel- platinum-aluminum (NiPtAl) bond coat after 24 one-hour cycles at 1100 °C (2012 °F). (b) The topographic map from the same region.



Figure 7: A 3D model of the surface from Figure 6b, with the stress map projected onto the surface. The regions with downward curvature have lower stress, whereas the regions with upward curvature have greater stress.

stress-sensitive, with the R2 peak being sensitive only to the trace of the stress tensor. The R2 peak shift of ruby has long been used to calibrate the pressure in diamond anvil cells, and the piezospectroscopic coefficients are well established. [8-10] Via spectroscopic analysis of photo-stimulated luminescence in LCSM measurements, stress maps of materials surfaces can be generated, which we call confocal photo-stimulated microscopy (CPSM). ^[10]

Platinum-modified nickel aluminide (β -phase NiPtAl alloys) bond coats on Ni-base single crystal superalloys have been the subject of extensive studies because of the propensity of these coatings to 'rumple' upon thermal cycling. ^{[11-} ^{16]} This rumpling can increase the heat transfer from the thermal barrier coating to the underlying metal substrate, accelerating the degradation of structural components. It has also been predicted that the rumpling may affect the stresses in the thermally grown oxide (TGO), leading to premature spallation of the thermal barrier coating. Previous modeling using finite element analysis had predicted that large stress variations would be present due to topography of the TGO, with 'peaks' being less compressive and 'valleys' being more compressive. [17,18] A NiPtAl bond coat on a René N5 superalloy was thermally cycled for 24 one-hour cycles at 1100 °C (2012 °F). A topographic map was obtained by operating the LSCM instrument in reflected-light mode. A series of images were taken at various focal planes to reconstruct the surface topography (Figure 6b). Without moving the sample, a CPSM stress



Figure 8: The progression of a transformation front within an oxide scale across a γ -phase NiCrAl alloy oxidized at 1000 °C (2012 °F) using a hot stage. A 405 nm laser was used for imaging in reflection mode. An oxidation front can be seen progressing across the sample. Transformed regions showing dark contrast are denoted with numbered white arrows.

map was obtained (Figure 6a). Comparing Figure 6a to 6b, a correlation is evident between the topography and the residual stress in the TGO. This can be confirmed by using the topographic data to create a 3D model of the surface. The stresses measured from the same region can then be projected onto this surface as a texture, and as shown in Figure 7, an apparent correlation between topography and residual stress is obtained. The stresses are less compressive in the areas with downward curvature and more compressive where the curvature is upward, providing agreement with previous finite element models. ^[17,18]

A hot stage attachment is a useful addition to LSCM. Generally, with high-temperature optical imaging, incandescence significantly degrades the image quality. With LSCM, a short wavelength of 405 nm laser can be used for imaging; combined with wavelength filters in the detector section, incandescence can be eliminated. The result is image quality at elevated temperatures that is equivalent to that at room temperature.

An example of hot stage imaging on our LSCM is shown in Figure 8. A γ -phase NiCrAl alloy was oxidized at 1000 °C (2012 °F) and held for 60 min. Upon reaching the oxidation temperature, a 'reaction front' was observed to progress across the surface. At the conclusion of the experiment, the hot stage was cooled at 100 °C min⁻¹ (212 °F min⁻¹) to freeze in the feature of interest. As can be seen in Figure 8, the reaction front progressed only modestly as the sample returned to room temperature.

CONCLUSIONS

In conclusion, the confocal microscope is a very useful tool for materials scientists. The microscope can provide the pseudo-infinite depthof-field imaging of a scanning electron microscope, without the need for a vacuum system or the coating of non-conductive samples. At the same time, topographic capabilities of a profiliometer or atomic force microscope are possible, along with fluorescence imaging, and photo-stimulated luminescence spectroscopy (the CPSM mode). These capabilities make the confocal microscope a versatile addition to the materials science characterization toolkit.

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02 A Novel Slicing Method for Thin Supercapacitors

Hao Sun, Xuemei Fu, Songlin Xie et al.

ABSTRACT

Thin and flexible supercapacitors with low cost and uniform thicknesses were fabricated by a new and efficient slicing method. The morphology of the thin supercapacitors was analyzed by scanning electron microscopy and laser scanning confocal microscopy, which revealed uniform thicknesses and well-formed interfaces between the electrode and the gel electrolyte. Tunable output voltages and energies were realized with a maximum specific capacitance of 248.8 F g⁻¹ or 150.8 F cm⁻³. The devices showed a maintained 96% of the maximum specific capacitance after 300 cycles, and 91% specific capacitance retention when bent to a maximum angle of 180°.

INTRODUCTION

In recent years flexible and miniature electronic devices have accelerated the development of new energy storage systems.^[1] Thin energy storage devices have shown promise in a variety of applications, including miniature robotics, implanted microelectronics, and wearable electronics.^[1-12] Several strategies, such as photolithography, sputtering, laser scribing, and chemical vapor deposition, have been investigated for the fabrication of miniature electronics.^[13–26] Despite the recent achievements, it remains challenging to realize uniform, neat, and low-cost fabrication of thin energy storage devices.

A slicing technique, which uses a sharp blade to cut bulk materials into thin slices, presents a general and efficient method that has been adopted in various fields. In biological and medical sciences, ultrathin slices of tissues and organs are obtained using a microtome. ^[27,28] Slicing offers low cost, controllable thickness, and small individual variation. However, it is rare to use slicing for microelectronic devices as there remain several challenges, including the difficulty in selecting suitable materials, instability for the interface between different components, and complexity in the design of device structure.

Herein, a new slicing method is developed for fabricating thin supercapacitors with low cost and individual variation. The fabrication of the thin supercapacitor is illustrated in Figure 1. Briefly, aligned multiwalled carbon nanotube (MWCNT) arrays with or without polyaniline (PANI) as electrodes and poly(vinyl alcohol) (PVA)/H₃PO₄ as the gel electrolyte. The aligned MWCNT electrodes allow electrons to hop from one MWCNT to the neighboring others based on a 3D hopping mechanism.^[29,30] The composites are embedded in epoxy resin, followed by cutting, using a microtome, into thin supercapacitors that are composed of many supercapacitor units. The thin supercapacitors are tunable in thickness,

demonstrate uniform surfaces, and have compact interfaces for excellent electrochemical properties, e.g., a high specific capacitance of 248.8 F g^{-1} (150.8 F cm⁻³). This slicing method can be generally applied to the fabrication of other thin energy and electronic devices.

METHODS

Aligned MWCNT arrays with an average height of 1 mm were vertically grown on silicon wafers via chemical vapor deposition. These arrays were uniaxially pressed with a precleaned glass slide and then removed from the substrate with a sharp blade.^[31,32] To prepare the aligned MWCNT/PANI composites, the MWCNT film was immersed in an aqueous electrolyte containing 0.1 M aniline and 1 M sulfuric acid and polymerized electrochemically at a potential of 0.75 V using platinum wire counter electrode (CHI115, a diameter of 0.5 mm (0.02 in.)) and a silver/silver chloride (Ag/AgCl)l reference electrode (CHI111, a diameter of 4 mm).^[33] The weight percentage of PANI was 70%, which was controlled by assuming an average of 2.5 electrons per aniline monomer. The resulting composite film was twice washed with deionized water and dried in the air before use. The supercapacitors were fabricated by coating the MWCNT electrodes with PVA/ phosphoric acid (H_3PO_4) and treating in vacuo for 10 min to enhance the infiltration of the electrolyte into the electrodes. The above process was repeated at least two times. Next, the two electrodes were stacked together along the MWCNT-aligned direction to form a thin film supercapacitor. Each electrode shared a width of approximately 110 μ m, and the distances between two electrodes ranged from 400 μ m – 600 μ m.

The stacked films were successively immersed in embedding solutions in acetone. The embedding solution was prepared by mixing an epoxy resin (SPI-PON 812) with T-168 (Shenyang Southeast Chemical Institute) as a plasticizer, dodecenyl succinic anhydride and methyl-5-norbornene-2,3-dicarboxylic anhydride (SPI Supplies Division of Structure Probe, Inc.) as curing agents, and 2,4,6-tris (dimethylaminomethyl phenol) (SPI Supplies Division of Structure Probe, Inc.) as a curing catalyst. Then the composite was put under vacuum to remove air bubbles.^[34] It was then placed in a ribbon-shaped mold containing an embedding solution and cured at 60 °C (140 °F) for 24 h. The resulting sample was removed from



Figure 1: Schematic illustration depicting the fabrication of thin supercapacitors via the slicing method. The left bottom image is the magnified area of the dashed rectangle, showing the alignment of the MWCNTs.

the mold and fixed on the microtome sample stage. A tungsten carbide disposable blade (Leica TC65, a length of 65 mm, or 2.56 in.) was used to cut the thin supercapacitors along the direction of the aligned MWCNTs.

The structures were characterized by an Olympus[®] LEXT[™] OLS4100 laser scanning confocal microscope and scanning electron microscopy (Hitachi FE-SEM S-4800 operated at 1 kV). The thicknesses were measured using a stylus profilometer (Veeco Dektak 150). The electrical resistances were measured using a Keithley 2400 Source Meter. Electrochemical measurements and depositions were performed using an electrochemical workstation (CHI 660E). The cyclic stability was characterized by Arbin electrochemical cycler (MSTAT-5 V/10 mA/16 Ch).

RESULTS

The slicing method enabled a controllable tuning of the device thickness from 10 μ m – 60 μ m. The gel electrolyte was in close contact with the aligned MWNCTs (Figure 2a). Close contact between the electrode and epoxy resin was also verified (Figure 2b), which is vital for the device to bend without breaking.

Furthermore, the 3D surface topography of the thin supercapacitor was characterized by laser scanning confocal microscopy. Figure 2c shows the reflection mode micrograph from laser scanning confocal microscopy. The green arrow indicates the interface between the MWCNT electrode and the gel electrolyte, and the red arrow indicates the interface



Figure 2: SEM micrographs of a) the interface between the MWCNT electrode and the gel electrolyte, and b) the interface between the MWCNT electrode and the epoxy resin. c) Reflection laser scanning confocal image of the interface in the thin supercapacitor. The green arrow indicates the electrode/electrolyte interface, and the red arrow indicates the electrode/epoxy resin interface. d) Height map of the thin supercapacitor obtained by laser scanning confocal microscopy.

between the electrode and the epoxy resin. Laser scanning confocal microscopy shows that the interfaces in the device are well-formed and relatively defect-free. Figure 2d shows the height map obtained from laser scanning confocal microscopy. The results show a uniform thickness without apparent defects at the interfaces, which is essential for highperformance electronic devices. The uniform surface and compact interfaces are attributed to the high compatibility of the constituent components.



Figure 3: a) Galvanostatic charge-discharge curves for bare MWCNT electrodes at increasing slicing speeds from 2 mm s⁻¹ – 75 mm s⁻¹ and a current density of 0.15 A g⁻¹. b) Specific capacitance vs slicing speed. c) Cyclic voltammograms for MWCNT/PANI electrodes at different scan rates. d) Galvanostatic charge-discharge curves for thin supercapacitors with aligned MWCNT/ PANI composite electrodes at thicknesses from 10 μ m – 60 μ m at a current density of 0.50 A g⁻¹. e) The specific capacitance of the thin supercapacitors vs thickness. f) Comparison of the energy and power densities with other energy-storage devices.

The dependence of the specific capacitance on slicing speed was investigated (Figure 3a). The specific capacitances of thin supercapacitors based on bare MWCNTs were increased from 10.3 F g⁻¹ to 12.8 F g⁻¹ with increasing slicing speed from 2 mm s⁻¹ – 20 mm s⁻¹ and remained almost unchanged from 20 mm s⁻¹ – 75 mm s⁻¹ (Figure 3b). This observation may be attributed to the relaxation of polymer chains in the gel electrolyte, which affects the interface with the MWCNTs at different slicing speeds. The relaxation of polymer chains is limited at higher slicing speeds; thus, a better interface between the MWCNT and gel electrolyte is formed, and the device has a lower internal resistance. This phenomenon was also verified by the decreasing internal resistance drop in the galvanostatic charge-discharge curves with increasing slicing speeds (Figure 3a). The specific capacitance reached a plateau at a slicing speed of 20 mm s⁻¹. Therefore, a slicing speed of 20 mm s⁻¹ was selected for further studies.

The introduction of PANI increased the specific capacitance of the supercapacitor. For the MWCNT/PANI composite electrodes, reversible charge-discharge performances at a variety of scan rates and current densities were achieved (Figure 3c), and a higher specific capacitance of 240 F g⁻¹ (145.5 F cm⁻³) was achieved. The introduction of PANI increased the specific capacity by approximately 20 times compared to bare MWCNT electrodes. The performance enhancements were attributed to the high conductivity and rapid electron transport that arises from the incorporation of PANI in the porous MWCNT network, the pseudocapacitance associated with the uniformly coated PANI on the surfaces of MWCNTs, and the stable interfaces between the different components to retain high specific capacities after slicing.

For the MWCNT/PANI composites, with the increasing thickness from 10 μ m – 60 μ m, the galvanostatic charge-discharge was compared at a current density of 0.50 A g⁻¹ (Figure 3d). The specific capacitances remained almost unchanged, with a maximum value, at 40 µm, of 248.8 F g⁻¹ (150.8 F cm⁻³) (Figure 3e). The cyclic stability of the thin supercapacitor was verified by cyclic charge-discharge characterization, and the specific capacitance maintained by 96.0% of the maximum value after 2000 cycles. The energy and power densities reached 3.10 mW h cm⁻³ and 0.99 W cm⁻³, respectively, which are comparable to the previous reports on miniature energy storage devices and commercial counterparts (Figure 3f).^[4,5,15,22].

The slicing method shows several unique features that are favorable for practical applications. First, the individual variation of the obtained thin supercapacitors was small. For 22 thin supercapacitors produced under the same conditions, the specific capacitance and internal resistance only varied by 8.8% and 11.6%, respectively (Figure 4a-c). Second, the thin supercapacitors exhibit a low areal density, which is comparable to the state-of-theart thin energy storage devices and is promising for lightweight electronic devices.^[24] Third, they have high flexibility, which is favorable for flexible electronics. The specific capacitance maintained 91% of its maximum value with increasing bending angles from $0^{\circ} - 180^{\circ}$. It recovered 96% of the specific capacitance after bending at 90° for 300 cycles. The slicing method also enables tunable connectivity of the devices to tune the output voltage and energy. For example, a thin supercapacitor with three units can be connected in series or parallel (Figure 4d), and the output voltage and discharge time were accordingly increased by three times (Figure 4e). As a proof-of-concept lightweight, thin, and flexible power source, a supercapacitor with three serial units was fixed on a fingernail (Figure 4f) to light up a commercial LED (Figure 4g).

CONCLUSIONS

In conclusion, a general and effective slicing method has been developed for the fabrication of thin supercapacitors with low cost and uniform thicknesses. The thin supercapacitors exhibit uniform surfaces, well-formed interfaces, and well-controlled thicknesses. A high specific capacitance of 248.8 F g⁻¹ (150.8 F cm⁻³) was achieved with tunable output voltage and energy. The thin supercapacitors are demonstrated to be lightweight, thin, and flexible power sources to power commercial electronics. This slicing method is also compatible with the fabrication of a variety of other devices including, sensors, transistors, solar cells, and batteries for largescale production and high performances.



Figure 4: a) Photograph of thin supercapacitors with a thickness of 20 µm and a length of 5 mm (0.2 in.) for each unit. b) Histogram of the specific capacitance of 22 thin supercapacitors fabricated with the same conditions. c) Comparison of the specific capacitance and internal resistance of the 22 thin supercapacitors. d) Schematic illustration of three supercapacitors units connected in series and parallel. e) Galvanostatic charge-discharge curves of one unit, three units connected in series, and three units connected in parallel. Photographs of (f) three units connected in series and placed on a fingernail (g) powering a red LED.

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03 Boosted UV Photodetection Performance in Chemically Etched Amorphous Ga₂O₃ Thin-Film Transistors

Zuyin Han, Huili Liang, Wenxing Huo et al.

ABSTRACT

Bottom-gate amorphous gallium oxide (Ga_2O_3) $(a-Ga_2O_3)$ thin-film transistors (TFTs) were fabricated to boost their UV photodetection properties. A simple chemical-etching solution was employed that is easy to use, low cost, and compatible with traditional lithographic processes to selectively etch a-G a_2O_3 films. The a-G a_2O_3 channel etched device, on silicon, effectively suppresses gate leakage current. Further, a patterned a-Ga₂O₃ TFT on guartz shows excellent n-type TFT performance with a high on/off ratio of approximately 10⁷. It is also applied as a phototransistor, to diminish the persistent photoconductivity (PPC) effect while keeping a high responsivity (*R*). Under 254 nm UV illumination, the $a-Ga_2O_3$ phototransistor demonstrated a high light-to-dark ratio of 5×10^7 , a high responsivity of $R = 5.67 \times 10^3$ A W⁻¹, and a high detectivity of 1.87×10^{15} Jones. The PPC phenomenon in a-Ga₂O₃ UV phototransistors was effectively suppressed by applying a positive gate pulse, which significantly shortens the decay time to 5 ms and enables possible imaging applications.

INTRODUCTION

Amorphous galium oxide (Ga_2O_3) (a-Ga_2O_3) has attracted increasing attention for its wide range of applications in deep ultraviolet (UV) photodetection, such as confidential space communication, imaging, flame detection, and missile warning systems. ^[1-4] Two-terminal Ga_2O_3 photodetectors (PDs) are the most commonly investigated, but their slow response speed, caused by persistent photoconductivity (PPC), ^[5,6] impedes their further application. ^[7] PPC occurs in most oxide semiconductor materials because of the large quantity of oxygen vacancy (V_o) defects and the high density of trap states. ^[8,9]

Three-terminal PD, or phototransistors, have an additional terminal-gate to control the channel carriers' transportation behavior are regarded as an alternative solution to improve the PD performance.^[10,11] Phototransistors have the

intrinsic gain of transistors and regular photoconductors, which makes it possible to achieve high light-to-dark current ratios and responsivity (R).^[11,12] PPC can be eliminated by exerting a gate pulse, as demonstrated by Jeon et al. in a three-terminal photosensor array.^[5] For a-Ga₂O₃ UV PD or imaging applications, research is needed to suppress PPC and raise the response speed while retaining a R. The controllable and selective etching of a-Ga₂O₃ channels to metals and other oxides is critical to achieving a low gate leakage current and favorable transfer characteristics. [13,14] Wet chemical etching of β -Ga₂O₃ has been demonstrated by using phosphoric acid (H_3PO_4) and sulfuric acid (H₂SO₄). ^[15,16] However, these strong acids readily corrode metals and oxides, which makes device fabrication difficult.

In this study, we present bottom-gate a-Ga₂O₃ thin-film transistors (TFTs) and phototransistors, where the a-Ga₂O₃ channels were selectively etched using tetramethylammonium hydroxide (TMAH) aqueous solution. This new etching method is low cost, simple, safe, and is compatible with conventional lithographic techniques. For the bottom-gate Ga₂O₃ TFT on silicon, the patterned channel device exhibits superior transistor characteristics compared to the unpatterned one. A bottom-gate a-Ga₂O₃ phototransistor with interdigitated source/ drain (S/D) electrodes was prepared on quartz and used to detect deep UV rays. It demonstrated typical transistor output and transfer characteristics with a high on/off ratio of approximately 107. Meanwhile, excellent photodetector performance was demonstrated under a 254 nm UV illumination, including a high light-to-dark ratio of 5×10^7 and R = 5.67 \times 10³ A W⁻¹. By applying a positive gate pulse, PPC in the a-Ga₂O₃ phototransistors is effectively eliminated with a fast decay in 5 ms.

METHODS

Common-gated a-Ga₂O₃ TFTs were fabricated on silicon dioxide (SiO₂) (300 nm)/Si substrates. An a-Ga₂O₃ channel layer (25 nm) was deposited by RF-sputtering using a Ga₂O₃ ceramic target (99.999% pure) at room temperature and patterned by UV-lithography followed by wet chemical etching in a TMAH solution. The ITO (100 nm) S/D electrodes were prepared by UV-lithography and lift-off process, where the film deposition was carried out in a sputtering chamber. Bottom gate staggered a-Ga₂O₃ TFTs were fabricated on quartz substrates with interdigitated S/D electrodes. Cr film (35 nm) was deposited by RF-magnetron sputtering and wet etched after the lithography to form the bottom gate electrode. Then, aluminum oxide (Al_2O_{3}) (110 nm) was grown on the gate metal at 200 °C (392 °F) in the ALD system and patterned by the combined process of UV-lithography and wet etching in an H₃PO4 solution. After that, a 25 nm a-Ga₂O₃ layer was sputtered, which is also patterned into discrete rectangles with dimensions of 175 μ m × 600 µm. Next, interdigitated S/D electrodes are defined by UV-lithography. The S/D electrodes have 15 pairs of fingers with 10 µm in width, 10 μ m in spacing gap, and 145 μ m in length. At last, a sequential deposition of tin (Ti) and gold (Au) layers were deposited in the RF-magnetron sputtering system with a thickness of 20 nm and 80 nm, respectively, which are further patterned by the following lift-off process.

Film thickness was measured by a stylus profiler (KLA-Tencor P-6 Stylus Profiler). The surface morphology was evaluated by atomic force microscopy (AFM, Bruker Dimension EDGE), laser scanning confocal microscope (Olympus® LEXT™ OLS5000 system), and scanning electron microscopy (SEM, Zeiss Sigma 300). The electrical properties were analyzed using a Keithley 4200 and a Keithley 6487. A handheld UV 254 nm lamp (ZF-5) and a xenon lamp with Omni-λ 180i grating spectrometer were used.

RESULTS AND DISCUSSION

The etching behaviors of two a-Ga₂O₃ samples were first investigated using different TMAH concentrations and temperatures. The a-Ga₂O₃ films are labeled as S1 and S2, which are sputtered with oxygen (O₂) and without O₂ flux, respectively. Both of the samples are amorphous. S1 and S2 have different densities, determined from X-ray reflection spectra (XRR), which are 5.32 g cm⁻³ (332 lb ft⁻³) and 4.84 g cm⁻³ (302 lb ft⁻³), respectively. The density affects the etching rate because of their different Vo defect densities. ^[8] The etching rates of S1 are slower than S2, which are attributed to its higher density and hence denser structure.

The selective etching ability of a TMAH solution is critical for the fabrication of TFTs. The amorphous Al₂O₃ was immersed in a 0.048% TMAH solution at 27 °C (80.6 °F) for 140 s, the depth profile of Al₂O₃ was almost unchanged, suggesting that it is hardly etched by TMAH at this low concentration. A slight etching of Al₂O₃ does occur, at a rate of 0.72 nm s⁻¹, in a 0.24% TMAH solution at 60 °C for 15 s. Thus, a selec-



Figure 1: AFM images of a) unetched $a-Ga_2O_3$ film (S2), b) etched $a-Ga_2O_3$ film (S2), c) unetched $a-Al_2O_3$ film, and d) etched $a-Al_2O_3$ film.



Figure 2: Laser scanning confocal microscope images of $a-Ga_2O_3$ film etched with a) TMAH solution and b) H_3PO_4 solution.

tive etching rate ratio of $a-Ga_2O_3$ (S2) to Al_2O_3 of 17:1 in the 0.24% TMAH solution at 60 °C (140 °F) was achieved, which provides an adequately wide and easily controllable operation regime for the fabrication of $a-Ga_2O_3$ TFTs.

The a-Ga₂O₃ and Al₂O₃ surface morphologies, after being etched, is revealed by AFM (Figure 1). The root-mean-square (RMS) surface roughness of the as-deposited a-Ga₂O₃ (Figure 1a) film is 0.55 nm, which is slightly smaller than the 1.24 nm after etching (Figure 1b). In Figure 1c,d, the RMS values are 0.34 nm and 0.38 nm for unetched and etched Al₂O₃ films, respectively, indicating that the Al₂O₃ surface is uniformly etched by TMAH solution under this condition.

To further corroborate the effect of TMAH solution on the $a-Ga_2O_3$ patterns, 400 nm thick Ga_2O_3 films were patterned and etched into interdigitated features by etching with TMAH and H_3PO_4 solutions. Figure 2a,b shows the corresponding 3D laser scanning confocal microscope images collected in reflection mode, where well-defined

patterns can be clearly seen in both cases. The cross-sectional views show the same trapezoidal structure, which is favorable for metal deposition. The ratios of the top to the bottom edges of the trapezoids are similar, demonstrating that the etching effect of TMAH is comparable with H_3PO_4 . Thus, considering that TMAH barely etches metal or Al_2O_3 , it is more preferred than H_3PO_4 for the fabrication of multi-component devices.

Based on the above-mentioned wet chemical etching technique using TMAH solutions, common bottom-gate TFTs with patterned and unpatterned a-Ga₂O₃ channels were fabricated on commercial SiO₂/Si substrates (Figure 3a). The electrical characteristics are measured at a source-drain voltage (VDS) of 10 V with the source-gate voltage (VDS) of 10 V with the source-gate voltage (VGS) from -100 V – 200 V (Figure 3b). The TFT with patterned a-Ga₂O₃ channel exhibits a typical n-type transfer curve. ^[17,18] The gate current (I_{GS}), generally defined as leakage current, is very low, about 10⁻¹⁰ A for the entire V_{GS} range. Conversely, the TFT with unpatterned a-Ga₂O₃ channel shows an abrupt drop of the drain



Figure 3: a) Schematic structures of the TFTs. b) $I_{DS}-V_{GS}$ curves and $I_{GS}-V_{GS}$ curves. c) Equivalent circuit of a-Ga₂O₃ TFT without channel patterned.

current (I_{DS}) in the transfer curve at a specific V_{GS} , where the I_{GS} begins to increase dramatically, indicating that the channel electrons start to transport vertically through SiO₂ layer and reach the gate electrode at a positive V_{GS} . The abnormal curves imply that it is beneficial to use a patterned a-Ga₂O₃ channel layer.

Next, an Al_2O_3 dielectric layer was used to fabricate $a-Ga_2O_3$ TFT with a bottom-gate staggered structure on quartz substrates. The interdigitated configuration is used to separate photogenerated carriers effectively.^[1,19] A winding gate electrode was designed with a 1.5 µm overlap at the edge of the S/D electrodes (Fig-



Figure 4: a) Schematic structure of the a-Ga₂O₃ phototransistor on quartz. b) $I_{DS}-V_{GS}$ curves, and c) $I_{DS}-V_{DS}$ curves. d) Time-dependent photoresponse curves. e) $R-V_{GS}$ curve. f) Normalized photoresponsivity spectrum.

ure 4a). Figure 4b shows the I_{DS} – V_{GS} transfer curves at different VDS in the dark and under 254 nm light illumination. The on-state I_{DS} increases as V_{DS} increases from 0.1 V to 10 V, and the off-state IDS remains low. The device exhibits decent electrical performance, such as a high on/off ratio of about 10⁷, a low subthreshold swing of 0.65 mV dec⁻¹ and a moderate positive threshold voltage (V_{th}) of 5 V. Under 254 nm light, the I_{DS} increases in the depletion region compared with the in the dark. The on-state photocurrent also increases as V_{DS} increases from 0.1 V to 10 V. At V_{DS} = 10 V and V_{GS} = 4 V, a high photocurrent of about 10 4 A is obtained, leading to a large light-to-dark current ratio of 5×10^{7} .

The ultrahigh rejection ratio is reasonable because the depletion "off" state in the dark is reversed into an "on" state due to the presence of numerous photogenerated electrons. ^[20] Figure 4c demonstrates the output curves of the same device with an excellent linear and saturation performance, indicating a good ohmic contact between the Ga₂O₃ and Ti/ Au. Time-dependent photoresponse behavior was evaluated with $V_{GS} = 10 V$ (Figure 4d). The I_{DS} increases as V_{DS} varies from 1 V – 20 V. Furthermore, the device demonstrates a relatively slow response to the periodic UV illumination. Figure 4e shows the responsivity (R)as a function of V_{GS} at V_{DS} = 10 V. R is calculated according to the following equation:

$$R = \frac{(I_{\text{photo}} - I_{\text{dark}})}{PS}$$

where I_{photo} is the photocurrent, I_{dark} is the dark current, P is the light intensity, and S is the illumination area. As V_{GS} increases from –15 V– 10 V, R increases to 5.67 × 10³ A W⁻¹. Based on this responsivity value, the detectivity (D^*) expressed as:

$$D^* = \frac{RS^{1/2}}{(2qI_{dark})^{1/2}}$$

is calculated to be 1.87×10^{15} Jones. A normalized photoresponse spectrum has been measured at V_{DS} = 20 V and V_{GS} = 10 V and shows a peak at 285 nm and a long tail until 360 nm. (Figure 4f)

Next, the suppression of PPC with the pulse gate voltage was investigated. A strong PPC remains for dozens or even hundreds of seconds in the a-Ga₂O₃ phototransistor working in a quasi-two-terminal configuration with V_{GS} = 0 V, (Figure 5a), which severely hinders its practical applications. To diminish the PPC, a positive 20 V gate bias with a pulse width of 850 ms is applied. The I_{DS} curve shows an instantaneous sharp peak and then immediately recovers to about 10^{-10} A once the gate voltage is reset to 0 V, suggesting that the PPC phenomenon is suppressed (Figure 5a,b). The decay time τ_d , defined as the time during which the current decays from 90% to 10%, was 5 ms.



Figure 5: a) Suppression of PPC with a positive gate pulse. b) I_{DS} Decay time.

CONCLUSIONS

In this work, a highly selective etching solution was developed for the preparation of patterned a-Ga₂O₃ films using TMAH. A distinct influence of the chemical etching on device performance is investigated by comparison of two common bottom-gate TFTs with patterned and unpatterned a-Ga₂O₃. Furthermore, a bottom-gate a-Ga₂O₃ TFT was fabricated, with interdigitated S/D electrodes. The TFT shows typical n-type oxide semiconductor TFT transfer curves with a high on/off ratio of approximately 10⁷, and excellent output characteristics. The device demonstrates a good response to UV 254 nm light, such as a high light-todark ratio of 5×10^7 and responsivity of 5.67 \times 10³ A W⁻¹. Also, the PPC in a-Ga₂O₃-based phototransistors is effectively suppressed by applying a positive gate pulse with a decay time as low as 5 ms. These results suggest that the chemically etched a-Ga₂O₃ phototransistor is promising for high-performance UV photodetection and imaging applications.

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04

Multiscale and Uniform Liquid Metal Thin-Film Patterning Based on Soft Lithography for 3D Heterogeneous Integrated Soft Microsystems: Additive Stamping and Subtractive Reverse Stamping

Min-gu Kim, Choongsoon Kim, Hommood Alrowais et al.

ABSTRACT

The use of intrinsically soft conductors, such as liquid eutectic gallium—indium alloy (EGaIn), has enabled the fabrication of bioinspired soft electronics. The fabrication of EGaIn thin films with high resolution and size scalability is one of the primary technical hurdles. Soft lithography using wetting/nonwetting surface modifications and 3D heterogeneous integration can address these challenges. This study demonstrates multiscale EGaIn thin-film patterning by utilizing additive stamping for large-scale (mm–cm) soft electronics and subtractive reverse stamping for microscale (µm–mm) soft electronics. These structures can be integrated to fabricate several functional soft microsystems.

INTRODUCTION

Bioinspired soft functional material synthesis ^[1,2] and manufacturing technology ^[3,4] for soft electronics has applications ranging from entertainment to healthcare. ^[5,6] Unlike conventional solid-state electronics, soft electronics are lightweight, stretchable, reconfigurable, and biocompatible for skin-mountable and wearable sensors. ^[7,8] Flexibility and stretchability are achieved by using either 3D solid metal patterns ^[9,10] or elastic polymer matrices with embedded conductive nanomaterials. ^[11,12]

An alternative approach to realize soft microsystems is to use intrinsically soft conductors, e.g., liquid eutectic gallium–indium alloy (EGaIn). EGaIn-based soft electronics are nontoxic, mechanically stable, and highly stretchable. Also, the low melting temperature (< 15 °C (59 °F)) and negligible vapor pressure facilitate room-temperature and ambient pressure manufacturing. ^[13–15] Moreover, thanks to the formation of a thin oxide layer on the EGaln surface, ^[16,17] the formed structures maintain their mechanical shapes on a soft elastomeric substrate, such as poly(dimethylsiloxane) (PDMS).

A broad range of patterning methods based on lithography-enabled stamping and stencil printing, injection, as well as additive and subtractive direct write/patterning processes have been implemented for EGaln microsystems. ^[18–24] Limitations of lithography-defined stencils are the relatively low resolution, rough EGaln surface, and excessive EGaln loss during the stencil lift-off process. Subtractive direct patterning techniques using laser ablation ^[25,26] or electrochemical reduction ^[27,28] enable an inexpensive and facile approach to pattern fine EGaln lines, but the serial process makes EGaln removal slow in the case of patterning small EGaln features on large substrates. Further, manually spreading EGaln using a roller results in rough surfaces with holes in the EGaln film. ^[18] Direct write and injection techniques address this issue, ^[29–32] but the resolution is limited. Microfluidic injection ^[33,34] and vacuum filling ^[35,36] provide high resolution, but the microchannels require relatively large thicknesses. Using a microtransfer deposition process based on soft lithography, ^[37] EGaln features > 2 µm can be achieved, but the technology suffers from residues formed outside of the channel areas.

Soft lithography offers a simple, fast, and low-cost way to pattern multiscale EGaln films. However, the surface oxide layer on EGaln interferes with uniform wetting on soft elastomeric substrates. Stamp lithography is often regarded as the lowest resolution and



5.5 mm

Figure 1: Schematic illustration of the multiscale and uniform EGaIn thin-film patterning process by utilizing a) subtractive reverse stamping for microscale and high-density EGaIn lines embedded in a selectively chemical-surface-modified PDMS microchannel and b) additive stamping for centimeter-scale and large-area EGaIn patterning on a physical-surface-modified PDMS substrate.

least reliable technique among the additive printing methods. ^[18,19,38] By utilizing chemical and physical surface modification of the elastomeric substrates, ^[39,40] the PDMS surfaces can be modified to have selective nonwetting or wetting properties. The nonwetting characteristics of chemically modified PDMS surfaces hinder the formation of EGaln residue, while the uniform wetting characteristics of physically modified PDMS surfaces assist in the formation of thin and smooth films.

Recently, we demonstrated high resolution, uniform, and residue-free EGaln patterning, ranging from single micrometer to millimeter scales, by utilizing a chemical surface modification and residue transfer process using a reverse stamping approach. [41] Building on our previous work, [41-44] this study presents multiscale and uniform EGaIn thinfilm patterning by utilizing additive stamping for largescale (mm-cm) soft electronics and the subtractive reverse stamping for microscale (µm-mm) soft electronics. By combining these complementary patterning techniques using 3D heterogeneous integration, fabricated and optimized soft electronic components built with different patterning processes can be integrated to form high-density and multifunctional soft microsystems.

METHODS

Figure 1 illustrates the complementary multiscale EGaln thin-film patterning processes based on soft lithography. The underlying liquid metal patterning processes mainly consist of three steps: 1) microtransfer molding of EGaln, 2) EGaln transfer using subtractive reverse stamping or additive stamping, and 3) sealing and interconnection. Chemical surface modification of the PDMS mold (for the subtractive approach) or the PDMS stamp (for the additive approach) using toluene is performed to increase the hydrophobicity. The PDMS mold/stamp is then coated by pressing onto a donor PDMS substrate coated with EGaln.

For the subtractive approach (Figure 1a), the PDMS stamp is reverse stamped to remove EGaln residue on the protruding surfaces to a sacrificial PDMS layer. The reverse stamping process yields fine, uniform, and thin EGaln lines inside of the PDMS channels without residues on the surrounding protruding surfaces. Information). The subtractive approach showed size scalability from 2 µm to 1 mm – 2 mm in line width. ^[41]

For the additive stamping approach, a PDMS stamp wet with EGaln is stamped onto a



Figure 2: SEM images of a) paper, b) standard PDMS, and c) paper-textured PDMS. d) 3D laser scanning confocal microscopy image of the paper-textured PDMS surface.

paper-textured PDMS substrate (Figure 1b). The paper texture, comprised of randomly distributed micro cellulose fibers (Figure 2a), is transferred to a PDMS surface using a conventional PDMS casting method. The resulting paper-texture PDMS exhibits a surface microstructure which allows it to be wet by EGaln (Figure 2b–d). As a result, continuous EGaln films can be transferred to paper-textured PDMS with multiple stamping steps.

Surface characterizations were performed using an Olympus[®] LEXT[™] OLS4000 3D laser scanning confocal microscope and scanning elec-



Figure 3: a) Measured EGaIn width as a function of designed stamp width and b) resulting film thickness as a function of patterned EGaIn width. c,d) Patterned EGaIn films on standard and paper-textured PDMS surfaces and a cross-sectional view of patterned EGaIn film on paper-textured PDMS after sealing with an additional PDMS layer. e) Reflection mode scanning laser confocal microscopy characterization of the EGaIn thin film as a function of the number of stamping steps (*n*).



Figure 4: a) Soft, passive components fabricated using additive stamping, including a resistor, planar spiral inductor, and interdigitated capacitor. b) Soft circuit with embedded LEDs (5 × 5 array) operated under bending (r = 10 mm) and stretching ($\varepsilon = 50\%$) deformation.



Figure 5: Demonstration of 3D heterogeneous integration and resulting performance of soft LC resonator.

tron microscopy (SEM, Hitachi S-3700N Variable Pressure SEM). Electrical characterizations of the soft, passive components, circuits, and LC resonator were performed using a multimeter (Hewlett Packard 34401A), a source meter (Keithley 2636A), and an LCR meter (Agilent 4284A). For mechanical stretching and bending characterizations, a linear motion stage and circular glass cylinders (radius: 10 mm (0.4 in.)) were prepared, respectively. Thermal characterizations of the soft heater were performed using a source meter (Keithley 2636A) to supply power, and temperature increases were recorded using an IR camera (FLIR T640).

RESULTS AND DISCUSSION

Figure 3a,b shows the measured EGaIn width as a function of the stamp width and the resulting film thickness as a function of the patterned EGaIn width, respectively. Figure 3c,d shows the non-uniform patterned EGaIn films deposited on a standard PDMS surface and a smooth uniform EGaIn film on paper-textured PDMS surface. PDMS stamps were stamped five times on paper-textured PDMS substrates to achieve smooth and uniform films. Figure 3e shows the SEM and 3D scanning laser confocal microscopy reflection mode images of stamped EGaIn, showing the evolution of the height variation with successive stamping. The additive stamping process decreases the surface roughness (Ra) with an increasing number of stamping steps, which indicates that the stamped EGaIn film is getting smoother. The random, micrometer-sized features, as characterized by scanning confocal laser microscopy in reflection mode, on the paper-textured PDMS surface (Figure 2b) were partially wetted during the initial one to two stamping steps, ultimately filling the grooved areas with EGaIn. After stamping five times, the surface structures of the paper-textured PDMS were entirely covered with EGaIn, showing a uniform and smooth EGaIn thin film.

Using the additive stamping process, soft, passive components and circuits were fabricated, and their electrical and mechanical characteristics were investigated. Figure 4a shows a soft resistor, planar spiral inductor, and interdigitated capacitor, all having a 1 mm (0.04 in.) line width and 1 mm (0.04 in.) line spacing. Figure 4b shows a simple circuit comprised of a 5 × 5 array of light-emitting diodes (LED). A constant current was applied to the LED array, which was subjected to bending (bending radius, r = 10 mm (0.4 in.)) and stretching (strain, ε) deformation. The soft circuit withstood the bending and strain deformations (up to $\varepsilon = 50\%$) while maintaining its functionality.

By combining the proposed multiscale EGaIn thin-film patterning techniques via 3D heterogeneous integration, more complex soft microsystems were fabricated. Three different soft functional microsystems were fabricated: i) a soft inductor-capacitor (LC) resonator, ii) a fingertip-mountable, soft oximeter, and iii) soft heaters with localized or distributed heating. Figure 5 shows the LC resonator. The interdigitated capacitor was fabricated using subtractive reverse stamping, and its areal capacitance was 13.2 pF cm⁻², which is roughly nine times higher than what would be achievable with additive stamping. The planar coil



Figure 6: a) Demonstration of a fingertip-mountable soft pulse oximeter. b) Circuit diagram; fabrication and electric component integration of c) soft sensor layer and d) soft circuit layer. e) 3D-integrated microsystem mounted on a fingertip. Measured PPG waveforms of IR LED and red LED using f) PCB-based rigid sensing system and g) PDMS/EGaln-based soft sensing system.



Figure 7: Demonstration of soft heaters for a) localized and b) distributed heating applications. c) Simulated and measured hot-spot temperature as a function of applied heating power.

inductor, as well as the readout coil, were fabricated using additive stamping. After 3D integration of the LC components using liquid-metal filled vias, the soft microsystem was wirelessly interrogated using a readout coil to collect the resonance frequency. The measured resonance frequency was 276 MHz, which also agreed well with the calculated value, and the Q factor was \approx 20 (Figure 5b).

A fingertip-mountable, soft, and 3D-integrated biological sensor, comprised of a soft sensing layer with a commercial pulse oximeter and a soft interfacing circuit layer, is demonstrated for noninvasive and real-time heart rate (HR) and blood oxygen monitoring (Figure 6a). This soft sensor layer is fabricated using subtractive reverse stamping to connect the integrated pulse oximeter (MAX30100, Maxim Integrated Products Inc.), while additive stamping is utilized to fabricate the soft printed circuit board for the interfacing circuit (Figure 6b–d). These soft sensor and circuit layers are then vertically interconnected through soft vias (Figure 6e). The photoplethysmogram (PPG) waveforms using an IR LED and a red LED, and the extracted HR and saturation of peripheral oxygen (SpO₂) using the PDMS/ EGaln-based soft sensing system are shown in Figure 6f, g. The results were comparable to a rigid PCB-based sensing system.

Finally, soft heaters based on EGaIn thinfilm resistors are demonstrated for localized and distributed heating applications. For the localized heating applications (Figure 7a), a 50 µm wide heating resistor fabricated using subtractive reverse stamping and was vertically integrated on a soft circuit. For large area heating applications (Figure 7b), a 1 mm (0.04 in.) wide serpentine heating resistor was fabricated using additive stamping. Figure 7c shows the measured and simulated hot-spot temperature as a function of the applied power. To reach a temperature increase of $\Delta T \approx 10 \text{ °C}$ (50 °F), the vertically integrated microheater requires 65 mW, while the serpentine-shaped heater heats a larger area but requires 113 mW. Compared to other heaters, ^[45-47] the fabricated soft heaters using thin-film resistors showed 8 times higher heating efficiency. In addition to efficient heating, the soft heater provides flexibility and stretchability for wearable and skin mountable electronics applications.

CONCLUSIONS

This study reports the multiscale and uniform, thin-film patterning of EGaln using soft lithography by utilizing subtractive reverse stamping for high-density microscale patterns and additive stamping for centimeter-scale patterns. Considering the size scalability of the thin-film patterning and the possibility to heterogeneously integrate structures fabricated with either technique, soft electronic components can be fabricated and integrated to form soft and flexible multifunctional microelectronics.

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Introduction: Flexible Thin-Film Electronics

Lawrence A. Renna

Alessandro Volta created the first electrical circuit in 1800 using salt-water solutions connected by pieces of metal. Volta went on to invent many electronic systems, most notably the Voltaic Pile (the first battery). ^[1] Fast-forward and electronics are ubiquitous throughout our lives. Most electronic devices are composed of rigid circuit boards containing electronic components (e.g., transistors, resistors, and capacitors), and printed metallic interconnects. Now, flexible electronics are currently being developed for next-generation devices. Flexible electronics can be used for an incomprehensible number of applications, ^[2] but some include, foldable displays, conformal photovoltaics, batteries, power generators, wearable sensors, soft robotics, and bioelectronic interface applications. ^[3, 4]

1. FLEXIBLE METLALIC THIN-FILM CONDUCTORS

Flexible electronics require patterned conducting materials that can withstand strain without losing conductivity to enable functionality for a variety of applications. To achieve conducting pathways, or interconnects, different materials can be used including but not limited to conducting polymers (e.g., PEDOT:PSS), ^[5, 6] carbon materials (e.g., graphene, CNTs), ^[7, 8] oxides (e.g., ITO), ^[9] liquid metal (e.g., EGaln), ^[10, 11] metal nanowires, ^[12] and metallic thin films. ^[13–16]

Often, to achieve conducting structures, small islands of rigid electronics are assembled on to a flexible polymer substrate and connected using thin-film metallic interconnects or electrodes. The mechanical properties of the metal layers and their adhesion to the flexible substrate, especially during strain, are of the utmost importance to their functionality. The failure of these layers is either via i) fracture through the thickness of the layer or ii) the metallic layers delaminate from the substrate. ^[16] Thus the study of metallic interconnects and their failure during strain or bending is imperative to develop flexible electronic devices.

The through-thickness fracture of metallic interconnects can be studied by tensile strain testing and bending experiments. The deformation of metallic thin films on flexible substrates has been examined by tensile testing and monitoring the effects by X-ray diffraction and microscopy. ^[17] ^[18] For example, Gruber et al. studied the cracking behavior of copper (Cu) films on polyimide (PI) with tantalum (Ta) interlayers. The fracture toughness of the Cu films increases with Cu film thickness and

decreases with increasing Ta interlayer thickness. When the Cu films were thinner than 70 nm, they exhibited inherent brittle fracture.

Furthermore, the mechanical failure of brittle, thin films on a flexible substrate, when bending, can be observed by optical microscopy. Glushko et al. demonstrated the variable mechanical cracking of printed silver (Ag) interconnects via cyclic tensile, compressive, and mixed tensile compressive bending strains. Conversely, evaporated Ag thin films showed no fracture dependence on the type of strain. ^[19]

The adhesion of metallic thin film interconnects to the flexible substrate is also critical to their performance. ^[16] Gold (Au) or Ag are ideal materials for interconnects because they are ductile, have a low electric resistance, and can be easily deposited and patterned. However, these metals sometimes delaminate from flexible polymer substrates. The delamination typically manifests as buckling from the substrate. Therefore, titanium (Ti), tantalum (Ta), or chromium (Cr) interlayers are used to improve the adhesion of metallic thin films to the polymer substrate. Confocal laser scanning microscopy (CLSM) can be used as a tool to measure the buckling of metallic thin films during compression-induced delamination.

As shown in the digest article "Thin Film Adhesion of Flexible Electronics Influenced by Interlayers," the adhesion properties of Au and Au/ Ta thin films on PI, under compressive strain, was investigated. ^[16] CLSM was used to measure the buckling dimensions under compressive strain. The dimensions of the buckles can be used to calculate the critical buckling and driving stresses, using the Hutchinson and Suo model. The studies show that Au thin films spontaneously buckle, while a compressive strain is required to delaminate the Au/ Ta film, indicating larger adhesion energy.

Further Reading:

https://onlinelibrary.wiley.com/doi/ abs/10.1002/admt.201700277 https://onlinelibrary.wiley.com/ doi/10.1002/aenm.201700535

Appl. Note: https://www.olympus-ims.com/en/ applications/electro-mechanical_behavior_of_ thin_films/

Appl. Note: https://www.olympus-ims.com/en/ applications/quantitative_investigations_of_the_ interconnect/

2. CONDUCTIVE POLYMER MEMBRANES

Flexible electronics can be used for wearable devices for applications such as movement sensors, biological sensors, triboelectric nanogenerators, flexible power supplies, and actuators. [20] Obtaining flexible conductors that can withstand high strain and has low resistance is a challenge in the fabrication of flexible electronic devices. Moreover, an additional requirement for wearable electronics, especially those in contact with skin, is that they have relatively high porosity compared to more established flexible electronics. This is because the comfort of wearable devices is contingent on air permeability. Attaining flexibility, elasticity, high conductivity, high mechanical integrity, and porosity is an active research area.^[12]

Flexible electrodes are generally composed of an elastic substrate as the elastomer to support bending, stretching, and twisting. However, these materials are nonporous and do not provide breathability. One solution to the lack of air permeability of flexible electronics is to prepare conductive polymer membranes. Conductive polymer membranes are composed of a network of stretchable polymer fibers and conductive additives. The network of polymer fibers is inherently porous and allows for gas permeability. Methods of fabrication include the inclusion of conductive additives into yarns, fabrics, and breathable ionic membranes, [21] coating of textiles, ^[22] using cellulosic templates, electrospraying, ^[22] electro2hydrodynamic direct2writing, ^[23] and electrospinning polymer fibers. [12, 24]

In the article digest "Breathable and Flexible Polymer Membranes with Mechanoresponsive Electric Resistance," [12] the authors demonstrate a flexible, highly conductive membrane with inherent porosity to allow for gas permeability. The membrane was fabricated by first electrospinning polyurethane (PU) to form polymer nanofiber mats. Conductive Ag nanowires (AgNWs) are dispersed onto a membrane via a filtration method. Finally, a sandwich is made with the AgNWcoated PU membrane and another PU membrane. Polycaprolactone fibers were used to improve the adhesion of the sandwich. The resulting membranes had a low sheet resistance, showed excellent stability to mechanical strain, and allowed gas permeation.
Further Reading: https://onlinelibrary.wiley.com/doi/ abs/10.1002/adma.201908496

https://onlinelibrary.wiley.com/ doi/10.1002/smll.201703521

3. FLEXIBLE MICROPILLAR ELECTRODE ARRAYS

Flexible electronics have also shown promise in bioelectronic interface applications. Bioelectronic electrodes are essential to investigate the relationship between electricity and biology (electrophysiology). ^[25, 26] Bioelectronic electrodes can be utilized for both bioimpedance and biopotential measurements. Forming intimate interfaces between electrodes and biological matter (e.g., neural tissue) are important to achieve high fidelity biological to electrical signal transduction. ^[26]

For example, neural electrode techniques have considerably improved our ability to understand brain function and have become a tool for the clinical diagnosis and treatment of neurological disorders. Creating tight interfaces, and good electrical contact, between conventional subdural electrodes and neural tissues, is challenging due to their large mechanical mismatch. Thus, flexible electronics are well suited for neural electrode applications. Fabrication of flexible bioelectronics typically uses metal evaporation, atomic layer deposition, photolithography, and transfer printing, and inkjet printing.^[25, 27] Nonetheless, conventional flexible substrates such as PI and polydimethylsiloxane (PDMS) still have moduli much higher than neural tissue.^[26]

To address this issue, Du et al. prepared novel flexible micropillar electrode arrays (μ PEAs) based on a biotemplate method, which is described in the article digest "Flexible Micropillar Electrode Arrays for In Vivo Neural Activity Recordings." ^[26] The μ PEAs were prepared by using a lotus leaf to create a template that was filled with a flexible material and coated in Au for conductivity. Each electrode contained many hierarchical micropillars, which contained surface nano-scale wrinkles (**Figure 1**). The μ PEAs were engulfed by the neural tissue, forming a low impedance interface, which allows for *in vivo* multichannel recordings with a high signal-to-noise ratio.

Further Reading:

https://onlinelibrary.wiley.com/doi/ full/10.1002/advs.201700625

https://onlinelibrary.wiley.com/doi/ abs/10.1002/admt.201900566

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Figure 1: 3D confocal image of spatially patterned micropillars on PI substrate.

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05 Film Adhesion of Flexible Electronics Influenced by Interlayers

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ABSTRACT

As flexible electronics emerge for applications such as medical sensors and foldable displays, there is a need to understand the interfacial behavior between the conducting elements and the compliant polymer substrate that the devices are prepared on. Compression-induced delamination is a technique that uses the buckling dimensions to evaluate the interfacial adhesion of materials on flexible substrates quantitatively. This study shows that spontaneous buckles are formed in gold (Au) films, which are deposited without an interlayer. Conversely, external loading is required to delaminate the Au film with the tantalum (Ta) adhesion layer indicating higher adhesion energy.

INTRODUCTION

Flexible devices and sensors are an emerging field in the electronics sector used for various applications, such as foldable displays ^[1,2] and neural electrodes. ^[3,4] The primary goal in the design of flexible electronics is to achieve significant strain (>10%) without losing electronic functionality. Many designs to achieve this goal consist of small islands of rigid electronics placed on a flexible polymer substrate and connected using metallic lines. In this design, the adhesion between the lines and the underlying substrate is of great importance to device reliability.

The failure of flexible electronic materials occurs via two mechanisms; the fracture of the metallic conducting components through thickness crack formation or the metallic layers delaminate from the substrate. Several testing techniques have been used to analyze cracking failure, the most popular being tensile straining ^[5–9] and bending. ^[10–13] The techniques used to evaluate the adhesion of thin films to rigid substrates have advanced our understanding of adhesion and its mechanisms. ^[14– 19] These methods work well for films on rigid substrates; however, flexible electronics present more challenges, and the methods and models for rigid substrates cannot always be employed. Therefore, tensile-induced delamination ^[20,21] or compression-induced buckling methods ^[22,23] have been developed to this end. These techniques work well for brittle films, ^[24–26] but require an extensive amount of straining for ductile films ^[27] or an overlayer to induce delamination at lower levels of strain. ^[28,29]

Noble metals, such as Au or Ag, are the materials of choice for the connecting lines between the semiconducting islands. It is advantageous to use these metals because they are ductile, have a low electric resistance, and can be easily deposited and patterned. Unfortunately, these metals, sometimes, have trouble adhering to the polymer substrates used in flexible electronics. Therefore, interlayers, like titanium (Ti), tantalum (Ta), and chromium (Cr), are used to improve the adhesion of the noble metal to the polymer substrate. [26,27,30] Since the conducting metals used are ductile, methods that can induce defined areas of delamination are desired to determine the effect of interlayers on adhesion energy. Buckling-based techniques are ideal because plastic deformation is minimized, and buckle delamination is well understood. [31-33] Spontaneous buckling can occur when the residual stress of the film is large and compressive, typically in the range of 0.5 GPa – 2 GPa, but typically does not occur on polymer substrates because the substrate can accommodate the film stress by macroscopically bending. Conversely, tensile-induced delamination is effective at creating buckles in a ductile film system of 50 nm Cu with a 10 nm Cr interlayer. [26]

In this work, compression-induced delamination will be used to cause a 300 nm Au film to buckle upon unloading rather than during loading. Buckling during tensile unloading was compared to spontaneous buckling and used to measure the adhesion energy. With the proper utilization of the different buckling phenomena, the adhesion energy of the interface and how much the addition of interlayers improves adhesion can be quantified.



Figure 1: Optical micrograph of the Au–Ta film on PI, unloaded after strained to 15%. The straight buckles formed perpendicular to the straining direction (arrow).

METHODS

Au films (300 nm thick) were sputter-deposited with and without a 10 nm Ta interlayer using a DC Magnetron system onto 50 mm thick Kapton polyimide (PI) substrates. ^[3,34] The Ta film was used as an interlayer to improve the adhesion between Au and PI.

To measure the buckle dimensions, two different devices were used-atomic force microscopy (AFM, Veeco Dimension AFM) and 3D confocal laser-scanning microscopy (CLSM, Olympus[®] LEXT[™] OLS4100 microscope). The CLSM measurements were performed using a laser-wavelength of λ = 405 nm. Because its maximum lateral image size is 80 µm × 80 µm and the vertical limit is 6 mm, the AFM was used only to image smaller buckles. The CLSM can be used to measure all buckle sizes since its vertical limit depends on the distance of the objective to the sample. Gwyddion was used to analyze the images and measure the dimensions of the buckles. ^[35] Additionally, focused ion beam (FIB) crosssectioning and scanning electron microscopy (SEM) was used to characterize the buckles.

The buckle dimensions are directly related to the critical buckling stress and the delamination stress of the film at the interface. The stresses and the interfacial fracture energies can be calculated using the well-known Hutchinson and Suo model.^[31] The method is based on the Euler beam theory. The critical buckling stress, ob, and the driving stress, ob, can be calculated by using **Equations (1)** and **(2)**.

$$\sigma_{\rm b} = \frac{\pi^2 E}{12(1-v^2)} \left(\frac{h}{b}\right)^2$$
(1)

$$\sigma_{\rm d} = \sigma_{\rm b} \left[\frac{3}{4} \left(\frac{\delta}{h} \right)^2 + 1 \right] \tag{2}$$

where δ is the buckling height, *b* is the half buckle width, *h* is the film thickness, *E* is the film's elastic modulus, and v is its Poisson's ratio. The critical buckling stress is the stress necessary to cause film delamination, and the driving stress propagates the buckles. The interfacial fracture energy, $\Gamma(\Psi)$, for spontaneous buckles is given by **Equation 3** and is used to calculate the adhesion energy of the interfaces.

$$\Gamma(\Psi) = \left[\frac{(1-\upsilon^2)h}{2E}\right] (\sigma_{\rm d} - \sigma_{\rm b}) (\sigma_{\rm d} - 3\sigma_{\rm b})$$
(3)

RESULTS AND DISCUSSION

The Au films on PI (without Ta) delaminated spontaneously at the metal-polymer interface in the form of straight-sided and telephone cord buckles due to the high compressive residual stress in the films, whereas, the Au–Ta films on PI did not delaminate. The typical height and length of the spontaneously formed buckles were on the order of hundreds of nanometers to a few micrometers, respectively.

Therefore, a loading-unloading experiment was performed on the Au–Ta films on Pl to create buckles to access the adhesion energy. After straining to a maximum strain of 15% and unloading, straight buckles perpendicular to the straining direction were observed (**Figure 1**). Typically, buckles form parallel to the straining direction when tensile-induced delamination is used because compressive stress builds up due to the difference in the Poisson's ratio between film and substrate. ^[20,36] The appearance and spacing of the buckles perpendicular to the straining direction are similar to the cracking of brittle films under tension.

To determine the amount of strain required to cause buckling, incremental load-unload testing was. The loading varied between 2% and 14% strain, while the unloading segments always went to 2N. Optical micrographs were taken at the peak strains and every 1% decreasing strain during unloading (Figure 2a-k). As shown in Figure 2a at 0% strain, no buckles are observed. Upon straining, the film is mostly flat, however small buckles parallel to the straining direction are visible at a preexisting defect in the film. Upon unloading, buckles perpendicular to the straining direction are observed. At lower strains, they are mostly clustered at a series of scratches, but with the increasing strain, the buckles encompass the entire visible area. With each increasing load step, existing interface cracks grow, or more are nucleated which, in



Figure 2:In situ optical incremental load-unload experiment. The arrow in (a) indicates the straining direction. In (a), (b), (d), (f), and (h), the film is under tension, in (c), (e), and (g), the film is in an unloaded state, and (i)–(k) is a series during unloading. The buckle spacing decreases with decreasing strain (buckle density increases) and reaches saturation spacing at approximately 7% unloading strain (l). Note that the x-axis in (l) is reversed.

turn, produces more buckles upon unloading. **Figure 2**i–k shows how buckles form and that the density increases during the removal of the tensile load. Finally, **Figure 2**I shows the measured buckle spacing as a function of the unloading from 14% strain. The buckle spacing during unloading follows the same trend as crack spacing during tensile loading, where the spacing decreases until a plateau is reached at approximately 7% unloading strain. Therefore, it was determined that approximately 6% – 8% maximum strain is required to cause delamination upon unloading.

The spontaneous buckle dimensions were measured by AFM (Figure 3a) and CLSM (Figure **3**b) to calculate the adhesion energy of the Au film on PI. Figure 3b shows that the delamination starts as single straight-sided buckles and then continues to propagate as telephone cord buckles. This is a common delamination process in biaxially stressed films with spontaneous buckles because of the large shear stress. [37,38] The buckles in the white box (Figure 3b) are the same as in Figure 3a. The same seven single buckles were measured with both imaging methods. CLSM can image a larger area, and it is possible to measure more buckles from a single image. The height of the buckles varies, and the telephone cord buckles are much taller than the single buckles, more than 5 µm in height. Therefore, AFM cannot measure most of the telephone cord buckles due to the maximum deflection limit of the cantilevers. The sample height for the CLSM is only limited to the distance of the objective to the sample, which is a few millimeters. The

marked profiles indicate where the cross-sections have been taken. In **Figure 3**c, the cross-sections of the same buckle measured with the two different methods and shows that the buckle profiles are in good agreement.

Using the elastic properties of $E_{Au} = 77$ GPa and the Poisson's ratio $v_{Au} = 0.44$ of gold, the stresses calculated from the data of both imaging techniques with the Hutchinson and Suo model ^[31] are in good agreement. For example, when AFM measurements are used to calculate the critical buckling stress, the value is $\sigma_{\rm b}$ = 76 ± 24 MPa, compared to the CLSM where $\sigma_b = 74 \pm 23$ MPa is determined. The $\Gamma(\Psi)$ of the spontaneous buckles were calculated from the values measured by AFM and CLSM and are $\Gamma(\Psi) = 0.7 \pm$ 0.3 Jm⁻² and $\Gamma(\Psi) = 0.8 \pm 0.3$ Jm⁻², respectively. The interfacial adhesion values are similar to that for the same interface measured with four-point bending (0.8 Jm⁻²).^[3]

Because the compression-induced buckles were quite large, only CLSM was used to measure the buckle dimensions (**Figure 4**). The buckle heights are almost three times larger than the spontaneously formed buckles of Au–PI. FIB cross-sectioning was used to determine that the Ta–PI interface fails (**Figure 5**). The critical buckling stress was calculated by **Equation 1** to be approximately 350 MPa. Using **Equations 1 – 3** and the elastic properties of Au, the adhesion energy of the Au– Ta films on PI were determined to be $\Gamma(\Psi) =$ 11.2 ± 2.2 Jm⁻², which is much higher than the Au film on PI without the Ta interlayer.



Figure 3: (a) AFM height image of the gold film with two spontaneous buckles. (b) CLSM image of an area with the same buckles as in the AFM image. (c) Cross-section of the same buckle taken at approximately the same position

CONCLUSIONS

In this study, the delamination behavior of the Au–PI film system with and without a Ta interlayer was examined using spontaneously produced buckles and compression-induced buckling. Incremental tensile straining was used to induce buckling of the Au–Ta films on PI. After 6% – 8% applied strain, buckles perpendicular to the straining direction formed during unloading. In situ optical microscopy revealed that after 6% – 8% applied strain, compressive stress significant enough to induce buckling develops due to the elongation of the Au film during straining. The film elongates because the Au film plastically deforms via uniform necking across the whole film. Necking occurs on account of the good adhesion between the film and substrate, which helps to suppress catastrophic failure. This uniform deformation is in contradiction to the original theory that when a film delaminates from the substrate and becomes freestanding, plastic deformation will localize only at freestanding buckled areas. The Ta interlayer's improved adhesion provides the Au-PI interface, and the formation of the buckles perpendicular to the straining direction were crucial factors necessary to determine how film deformation and delamination are connected. With this new understanding, the lifetime and reliability of flexible electronics can be extended.



Figure 4: (a) CLSM image of an area with the same buckles as in the AFM image. (b) Cross-section of the buckle taken indicated by the black line in (a).



Figure 5: FIB cross-section of a buckle indicating that the Ta–PI interface failed as well as demonstrating that localized necking concentrated at the top of the buckle does not occur.

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06 Breathable and Flexible Polymer Membranes with Mechanoresponsive Electrical Resistance

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ABSTRACT

Flexible low-resistance membranes that tolerate very high deformability, produce low joule heating, and allow the passage of gases for human comfort are desired for wearable devices. Herein, a network of silver nanowires (AgNWs) between two highly porous electrospun thermoplastic polyurethane (TPU) membranes is presented. The membranes are mechanically robust (both for bending and stretching) and can withstand large strain before breakage (> 700%). The sheet resistance is as low as <0.1 Ω sq⁻¹, and only increases to 1.6 Ω sq⁻¹ upon stretching to 100% strain. The combination of polymer elasticity and the AgNW network structure provides a reversible change in resistance beyond 100% strain. This flexible, sandwich-like, electrically conductive membrane is a promising candidate for smart wearable devices and soft robotics.

INTRODUCTION

Traditional electronics are typically composed of intrinsically heavy and rigid materials, like silicon, metals, and glass, which have minimal flexibility, stretchability, bendability, twistability, and impact resistance. There is a need for flexible and deformable circuits and electrodes with low electric resistance that maintain performance even in a strained state for lightweight, wearable, and flexible electronic devices. ^[1–3] Efforts to construct flexible circuits and electrodes with low resistance focused on elastomeric electrically conductive materials. ^[4–10] These materials are promising for a variety of applications; ^[11–17] however, obtaining flexible conductors with both high strain properties and low resistance is still a challenge. ^[18] Further, porosity is an essential requirement for the comfort of wearable electronic devices that contact skin to allow air for permeability.

Presently, flexible electrodes are composed of an elastic substrate, such as polydimethylsiloxane (PDMS), ^[19–20] thermoplastic polyurethane (TPU), ^[21] and electrically conductive materials. ^[22–26] Low-resistance electrodes provide the advantages of less energy loss and reduced joule heating. Silver is an excellent material for electrodes and is often used for flexible electrodes with low resistance. ^[27] In our previous work, we prepared electrospun polymer membranes with a metal-like conductivity of 7.5×10^5 S m⁻¹ using a very low content (3.35 vol. %) of silver nanowires (AgNWs). ^[6] However, this kind of electrically conductive membrane is bendable but not sufficiently stretchable and is inherently nonporous.

Electrospinning is a promising technique for fabricating porous substrates with high conductivity, flexibility, and air permeability. The ability to electrospin many different polymer types also provides the advantage of tuning the membrane's mechanical characteristics. For example, electrospun polyamide nanofiber nonwovens embedded with AgNW networks showed 50% stretchability and a sheet resistance of 8.2 Ω sq⁻¹. ^[28] Electrospun polyurethane nonwoven porous substrate coated with AgNW provided a highly stretchable membrane (more than 300%) with high conductivity. ^[29]

Herein, we present a flexible and breathable polymer membrane with bending and stretching stability and very low electrical resistance. We also provide important fundamental studies on island formation, anisotropy, hot spots, and thermal transport in such structures. We present a simple and scalable preparation method for making such membranes. We use a network of AgNWs as conductive layer sandwiched between two porous electrospun TPU nanofibrous networks. We improved the interface stability with short polycaprolactone (PCL) fibers dispersed in between the AgNWs. Our membranes show a sheet resistance as low as <0.1 Ω sq⁻¹. The resistance does not significantly increase upon deformation (twisting, bending, and stretching to approximately 100% strain). We also show a reversible change in the resistance upon stretching or bending with more than 100% strain for several cycles. The AgNW networks reversibly break and reform during stretching and releasing, respectively. These membranes are breathable, which allows the exchange of gases. Lastly, the membranes have a lower thermal conductivity compared to other porous polymers, despite their electrical conductivity. These membranes are a promising material for electrodes in smart textiles and other wearable devices.

METHODS

The concept for the preparation of flexible and breathable electrically conductive membranes is illustrated in **Figure 1**. First, we prepared TPU nanofiber nonwovens via elec-



Figure 1: Schematic of preparing the TPU-AgNW/PCL-TPU membrane by sandwiching a network of AgNWs between TPU layers.

trospinning. We then used the porous TPU membranes as a filter for the filtration of AgNWs (17 mg mL⁻¹, 126 \pm 10 nm in diameter, and 18 \pm 4 µm in length) mixed with a PCL short-fiber dispersion (1 mg mL⁻¹, average aspect ratio \approx 1000). Another layer of TPU nanofibers was electrospun on top of the AgNWs and PCL short fibers. To induce thermal annealing, the achieved sandwich-like, electrically conductive nonwovens were pressed between two glass plates and heated at a temperature of 75 °C (167 °F) for 30 minutes to melt the PCL fibers and bond the two layers of TPU nonwovens and AgNWs together.

A Zeiss LEO 1530 was used for scanning electron microscopy (SEM) characterization of the AgNWs and their corresponding networks. Energy dispersive X-ray analysis (EDX) was performed using a Zeiss Ultra Plus (V = 10 kV). Optical microscopy was performed using an Olympus[®] LEXT[™] OLS5000 confocal laser scanning microscope. A 100 × magnification lens with a working distance of 300 μ m was used. Image analysis was conducted with Matlab.^[30] The gas permeability test was performed with a homemade unit. ^[5] Tensile tests were carried out using a tensile tester (ZwickiLine Z0.5; BT1-FR0.5TN. D14). Sheet resistance measurements (four-point measurements) were performed using a Keithley 2420 high-current source meter coupled with a Signatone SYS-301. A digital multimeter (EMOS Multimeter EM391) connected to measure the sample with a bronze conductor was employed to measure the stretching resistance and bending resistance. Thermography imaging was performed with an Infratec VarioCAM HD research IR camera. Thermal diffusivity was measured with our own, self-built Lock-In thermography setup. [31-32]



Figure 2: a,c) Photograph and b,d) SEM image of the electrospun TPU nonwoven and TPU with AgNWs and PCL, respectively. e) Photograph of TPU-AgNW/PCL-TPU. f) Cross-section of EDX overlayed SEM image of TPU-AgNW/PCL-TPU. g) Cross-section SEM of TPU-AgNW/PCL-TPU and h) TPU-AgNW –TPU.

RESULTS AND DISCUSSION

The TPU nonwovens consist of randomly oriented fibers (the 2D order parameter is around 0.1) with an average diameter of 1.6 \pm 0.5 µm (**Figure 2**a,b). After filtration, the AgNWs and short PCL fibers generated a double network-type structure due to percolation (**Figure 2**c,d). Afterward, we covered the AgNW/ PCL layer with another layer of TPU nonwoven by electrospinning. Finally, we hot pressed the three-layer stack at 75 °C (167 °F) for 30 minutes to melt the PCL and increase the adhesion of the layers (**Figure 2**e). The resulting three-layer membranes are designated as TPU-AgNW/PCL-TPU. We checked the presence of an AgNW layer sandwiched between the two TPU layers with PCL short fibers by EDX (**Figure 2**f). The cross-sectional SEM images of TPU-AgNW/PCL-TPU and TPU-AgNW-TPU (without the use of PCL short fibers for comparison) are shown in **Figure 2**g,h, respectively. The PCL short-fiber dispersion acts as a glue between the AgNW network and the TPU. The TPU-AgNW/PCL-TPU membranes also possess good gas (CO₂) permeability.



Figure 3: a) Stress–strain curves of sandwich membranes with different amounts of AgNWs. b) Resistance of membranes with different amounts of AgNWs with different strains. c) Optical microscopy images of TPU-2.0AgNW/PCL under different stains. (scale bar: 500 μ m) d) EDX-SEM image of TPU-2.0AgNW/PCL at 100% strain. (scale bar: 50 μ m) Ag is indicated in purple. e) Thermography images upon stretching (scale bars: 3 mm).

Different amounts of the AgNW dispersion were used to investigate the influence of the AgNW concentration on the air permeability and electrical properties. The sheet resistance was $6.1 \pm 0.3 \times 10^8 \Omega \text{ sq}^{-1}$ without an AgNW layer. The sheet resistance decreased to 0.09 $\Omega \text{ sq}^{-1}$ with 8.5 wt.% AgNWs. Even the use of a small amount of AgNWs (1.2 wt.%) significantly decreased the resistance to $\approx 1 \Omega \text{ sq}^{-1}$. Further reduction in the amount of AgNW to ≈ 0.5 wt% led to a sharp increase in the sheet resistance (2.4 \pm 3.1 \times 106 $\Omega \text{ sq}^{-1}$). This result indicates that the percolation threshold of AgNW is 0.5 wt.% – 1.2 wt.%.

The sandwich membranes exhibited a breaking stress of \approx 8 MPa. The TPU without AgNWs had breaking stress of \approx 10 MPa. The membranes with different amounts of AgNWs can be stretched to over 700% (Figure 3a). The membranes showed 10% and 30% creep after stretching for 100 cycles to 50% and 100% strain, respectively. We measured the resistance as a function of % strain (Figure 3b). TPU-AgNW/PCL-TPU can tolerate considerable strains with a moderate increase in resistance depending upon the amount of AgNWs. The sample with the highest content of AgNWs (8.5 wt.%) changed its resistance by only two orders of magnitude at a strain of \approx 150%. In contrast, the sample with the fewest AgNWs (1.2 wt.%) showed a comparable increase in resistance already at a strain of only 60%.

Figure 3c shows the optical microscopy images of the AgNW layer after 0%, 100%, and 150% stretching and recovering to 0% again for the sample with 8.5 wt% AgNWs. When the membrane was stretched up to 100%, few cracks could be observed in the AgNW layer. However, upon further stretching to approximately 150%, large cracks (bright area), in an island-like fashion, were observed, causing a significant increase in resistance. The formation of island-like structures is confirmed by EDX measurement (Figure 3d). The separated islands and cracks restricted the flow of electricity and created hot spots due to joule heating at the bottlenecks. Such hotspots can be imaged by infrared thermography when applying a DC current (Figure 3e).

We employed direction-dependent lock-in thermography to gain a better insight into the composite morphology. Using a line laser as a heat source, we can probe the overall thermal diffusivity in such a composite sample along different orientations relative to the stretching direction. We see in **Figure 4**a–c that the TPU fibers align parallel to the stretching direction. Image analysis of these laser scanning microscopy images reveals that the fiber orientation is already complete at a strain of $\approx 100\%$.

The 2D order parameter (S2D) measures how well the fibers are aligned. The order parameter is given by **Equation 1**.

$$S_{2D} = \frac{2}{N} \left[\sum_{(i=1)}^{N} (\cos(\alpha_i - \bar{\alpha}))^2 \right] - 1$$
(1)

where N is the number of stretched fiber orientations in the SEM image, α_i is the angle between the *i*th fiber and the horizontal axis, and $\bar{\alpha}$ is the average angle. ^[30] The S_{2D} of pure TPU remains constant at a value close to 1.0 after 100% strain (Figure 4d). For pure TPU, the thermal diffusivity increases along the stretching direction and decreases perpendicular to it (Figure 4e,f). Since TPU is a thermal insulator, the absolute thermal diffusivity remains at a low level. Heat travels along these oriented fibers faster than perpendicular to it, resulting in a high anisotropy ratio (Figure 4g). For AgNW-TPU, some degree of anisotropy evolves (Figure 4h,i), but the overall thermal diffusivity decreases compared to the unstretched state. Simultaneously, for AgNW-TPU samples, we find an evolution of anisotropic heat spreading (Figure 4g). Overall, the stretching of the AgNW-TPU sample leads to a smaller amount of anisotropy compared to the pure TPU network structure (Figure 4g).

The membranes showed excellent stretchability and bending stability. The samples were subjected to 100 cycles of stretching and bending. The resistance change (RC) can be described by **Equation 2**:

$$RC = \frac{R}{R_0}$$
(2)

where R is the time-dependent resistance and R_0 is the initial resistance measured after stretching and bending tests. The RC of the sample with 1.2 wt% of AgNWs significantly increased after only 60 stretching cycles; the RC was >20 000 under 50% strain. However, the same sample showed much better bending stability (bending curvature from 0° to 150°) without a significant change in resistance. The RC of TPU-0.25AgNW/PCL-TPU after 100 bending cycles was merely 1.32. The sample TPU-2.0AgNW/PCLTPU with a dense network of AgNWs showed both excellent bending and stretching stability. No significant change in the RC was observed for bending tests. During strain testing, RC increased by only a factor of ≈ 20 after 100 cycles.

CONCLUSIONS

In conclusion, we have demonstrated a new strategy to fabricate sandwich-like electrically conductive membranes with very low electric resistance. Our material consists of an AgNW network sandwiched between two porous electrospun TPU nonwovens. PCL short fibers act as glue and provide a robust interface between the three layers. Our membranes show excellent bending and stretching stability, high stretchability, and very low initial electric resistance ($<0.1 \Omega \text{ sq}^{-1}$). Additionally, the membrane possesses gas permeability and low thermal diffusivity. Furthermore, the material has the potential to be integrated into smart wearable devices.



Figure 4: a–c) Laser scanning microscopy images of TPU fibers (scale bars: 50 µm). The fibers align in the stretching direction (white arrows) with increasing strain, S. d) The 2D order parameter for the fiber orientation derived from laser scanning microscopy images with increasing strain. e) Temperature amplitude as a function of position on the surface of a pure TPU. f) Thermal diffusivity as a function of direction (0° is horizontal) and strain for a pure TPU (f). Anisotropy ratios for the thermal diffusivity. g) The pure TPU shows a stronger anisotropy than the TPU-2.0AgNW/PCL-TPU. h) Temperature amplitude as a function of position on the surface of TPU-2.0AgNW/PCL-TPU film with 0% strain. i) Thermal diffusivity as a function of direction (0° is horizontal) and strain for TPU-2.0AgNW/PCL-TPU film.

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07 Super-Resolution Microscopy by Movable Thin Films with Embedded Microspheres

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ABSTRACT

Microsphere-assisted imaging has emerged as a simple technique to obtain optical super-resolution. This work addresses the methodology of the resolution measurements and the limited field-of-view provided by each sphere. It is suggested that a standard method of resolution analysis in far-field microscopy based on convolution with the point-spread function can be extended into the super-resolution area. This provides a unified approach to resolution measurements. To develop surface scanning functionality, high-index barium titanate glass microspheres were embedded in polydimethylsiloxane (PDMS) thin films. It is shown that such films adhere to nanoplasmonic structures' surface so that the tips of embedded spheres experience the objects' optical near-fields. Based on rigorous criteria, a resolution of approximately $\lambda/6 - \lambda/7$ (where λ is the illumination wavelength) is demonstrated for arrays of gold (Au) dimers and bowties. Such films can be translated along the surface of investigated samples after liquid lubrication. It is shown that after lubrication, the resolution is diffraction-limited; however, the super-resolution gradually recovers as the lubricant evaporates. It is shown that such films adhere to nanoplasmonic structures' surface so that the tips of embedded spheres experience the objects' optical near-fields. Based on rigorous criteria, a resolution of approximately λ /6 – λ /7 (where λ is the illumination wavelength) is demonstrated for arrays of gold (Au) dimers and bowties. Such films can be translated along the surface of investigated samples after liquid lubrication. It is shown that after lubrication, the resolution is diffraction-limited; however, the super-resolution gradually recovers as the lubricant evaporates.

INTRODUCTION

Imaging by dielectric microspheres has emerged as a surprisingly simple way to obtain super-resolved images of nanoscale structures. ^[1–9] The method involves bringing a dielectric microsphere in contact with the investigated structure so that the microsphere experiences the object's optical nearfield and creates a magnified virtual image that can be viewed by a standard microscope. Initially, the method has been demonstrated for micrometer-scale, low-index (n_s = 1.46) silica spheres in air. [1] After that, this method was advanced by using highindex spheres ($n_s > 1.8$) submerged in a liquid or embedded inside elastomeric slabs, [3] which improved the quality of images. [4, 8]

Based on a solid-immersion concept, the maximal diffraction-limited resolution available for high-index ($n_s \sim 2.0$) barium titanate glass (BTG) microspheres can be estimated as $\sim \lambda/4$. Thus, the optical super-resolution by high-index spheres should be defined as a resolution better than $\sim \lambda/4$. One of the well-known approaches to experimentally measure super-resolution values is using "point" objects. [10] The image of an object is defined as a point-spread function (PSF) of the optical system. The PSF width represents the system's optical resolution. This concept is widely used in fluorescent (FL) microscopy, such as stimulated emission depletion (STED) [11] and other methods where bright "point" objects are readily available in the form of dye molecules or quantum dots.

To measure the resolution of microsphere-assisted imaging, researchers often select arrays containing features with recognizable shapes. $^{[1-9]}$ The basic idea of this approach is that the resolution of the optical system is equal to the characteristic dimensions of the minimum feature sizes that can be discerned. Different features have been studied by the microsphere-assisted technique that resulted in a broad range of resolution claims from $\lambda/6$ to $\lambda/17$. $^{[1, 4-7, 9]}$

In this work, we show that this approach can result in significantly overestimated resolution values. To solve this problem, we developed a resolution analysis based on a standard procedure of convolution with PSF, with subdiffraction-limited values allowed. A similar approach has been used previously to provide one-dimensional (1D) treatment with rectangular functions. ^[8] In the present work, we generalized this approach for 2D PSF and objects with arbitrary shape.

Furthermore, we developed a different approach to the field-of-view (FOV) limitations based on the incorporation of BTG spheres in polydimethylsiloxane (PDMS) thin films (or coverslips), as illustrated in **Figure 1**. The critical element of the coverslips' design is a planar array of high-index BTG microspheres with a broad range of diameters ($2 < D < 53 \mu m$) held in the nanometer-scale proximity to the bottom surface of the coverslips. Once the coverslip is attached to a nanoplasmonic structure, the tips of microspheres can experience the object near-fields, leading to the possibility of super-resolution imaging. We show that the PDMS coverslips are naturally adherent to



Figure 1: (a,b) SEM of the 2D arrays of golden dimers and bowties, respectively. (c) Schematic of the setup. (d-f) Step-by-step fabrication of coverslips with embedded spheres. (g) Photograph of the coverslips. (h) Microscopic image of the coverslip's bottom surface. (i) Mapping at the bottom surface by atomic force microscopy.

various substrates, providing imaging of Au dimers and bowties with $\lambda/6 - \lambda/7$ resolution. After surface lubrication with isopropyl alcohol (IPA), the coverslips can be translated along the surface. The ability to simultaneously capture images through the 2D array of spheres during wide-field microscopy allows precise alignment of microspheres with the objects of studies. We show that just after lubrication, the resolution is diffraction-limited. However, as the lubricant evaporates, the resolution gradually increases beyond the diffraction limit.

METHODS

As objects for imaging, we used arrays of Au dimers and bowties illustrated by scanning electron microscopy (SEM) images in **Figure 1**a and **Figure 1**b, respectively. ^[8] The BTG spheres with larger barium (Ba) content have an index of $n_s \sim 1.9$, and the spheres with a larger titanium (Ti) content have an index of $n_s \sim 2.1$ for the red portion of the visible region. Imaging was performed by an Olympus[®] LEXT[™] OLS4000 scanning laser confocal microscope operating at $\lambda = 405$ nm.

To fabricate the coverslips with embedded spheres, we used a three-step process ^[12] schematically illustrated in **Figure 1**d-f. This process bears some similarities with previously developed technology of embedding polystyrene microspheres in the PDMS membranes for applications in projection lithography. ^[13] First, the BTG spheres were deposited on the surface of a microscope slide, where they formed a disordered monolayer. Then, a PDMS layer was cast over the spheres. It was cured at 90 °C (194 °F) for one hour. The photograph of this layer at the top of the microscope slide is presented in **Figure 1**g. Finally, this thin layer was lifted from the substrate with tweezers and used as a coverslip in super-resolution studies.

RESULTS AND DISCUSSION

The microsphere-assisted imaging demonstrates significantly improved resolution. The virtual image of a dimer in **Figure 2**a obtained through the 5 µm BTG sphere embedded in the PDMS coverslip is shown in **Figure 2**b. The virtual image of a bowtie in **Figure 2**e obtained through the embedded 53 µm BTG sphere is shown in **Figure 2**f. Irradiance profiles along the x-axis of dimers and bowties are illustrated using red as color in **Figure 2**d and **Figure 2**h, respectively. The saddle-topeak ratios of these profiles, 0.16 and 0.35, respectively, are significantly smaller than that assumed in various classical definitions of resolution of two-point sources ^[14,15].

An attempt to define resolution based on the observation of minimal discernable features can lead to misleading results if, for example, we interpret the saddle point as a manifestation of a resolution of ~15 nm gap in bowties, which would imply a resolution above $\sim\lambda/27$. As we show below, the image reconstruction with the Gaussian PSF



Figure 2: (a,e) SEM image of the Au dimer and bowtie, respectively. (b,f) Images of dimer and bowtie obtained through the 5 μ m and 53 μ m BTG microsphere, respectively. (c,g) Calculated convolutions of the idealized dimer and bowtie with the 2-D PSFs with FWHMs of λ /7 and λ /5.5, respectively. (d,h) Comparison of the measured and calculated irradiance cross-sectional profiles.

with the width $\sim \lambda/5.5$ allows obtaining a high-quality fit to the experimental results.

We treated the super-resolved images based on an analogy with the classical theory ^[16] where the image, l(x, y), is considered as a convolution of a diffraction-limited PSF and the object's intensity distribution function, O(u, v). This can be expressed in the standard integral form by **Equation 1**:

$$I(x,y) = \iint_{-\infty}^{\infty} O(u,v) PSF\left(u - \frac{x}{M}, v - \frac{y}{M}\right) du dv \quad (1)$$

in which the integration is performed in the object plane where the coordinates (xo, yo) are linearly related to the image plane via the magnification M as $(x_0, y_0) = (x_i/M, y_i/M)$. We used a Gaussian function for PSF (x_0, y_0) with the full width at half maximum (FWHM) being a fitting parameter. Based on the Houston criterion, fitted values of the FWHM in the object plane were considered a resolution of the system. To enable the super-resolution

analysis, we allowed subdiffraction-limited FWHM values; however, we kept the same basic **Equation 1** for image reconstruction.

Images calculated with 2D PSFs with FWHMs $\sim \lambda/7$ and $\sim \lambda/5.5$ are presented in **Figure 2**c and **Figure 2**g for dimers and bowties, respectively. An excellent agreement with experimental images was found. Blue dashed lines represent the calculated intensity profiles along the x-axis. They are also found to be in good agreement with the experiment.

To align embedded spheres with various objects, we developed a technique based on lubrication and locomotion of the entire PDMS thin film containing BTG spheres, as illustrated in **Figure 3**. The lubrication was provided by using IPA with $n_s = 1.37$. The locomotion of the coverslip was performed by a tapered stainless steel microprobe inserted in the PDMS connected with a hydraulic micromanipulation controller, providing ~1 µm precision of the translation.



Figure 3: (a,b) Translation of the coverslip lubricated with IPA, and (c) the dimers are seen near the array's edge. (d) Experimental setup.

The translation and imaging through the coverslip immediately after its lubrication and application to the sample surface are illustrated in Figure 3a-c. Initially, the 16 μm BTG microsphere is located approximately 40 µm away from the border of the nanoplasmonic array (Figure 3a). As a result of the shift of the coverslip by ~40 μ m, this sphere is aligned with the edge of the array (Figure 3b). The virtual image of the array was obtained by the $20 \times (NA = 0.4)$ objective lens by focusing deeper in the structure (Figure 3c). The diffraction-limited resolution of the microscope objective can be estimated as $d = 0.515\lambda/$ NA ~ 700 nm. However, experimentally, the 700 nm and 350 nm periods of the arrays can be discerned in the virtual image (Figure 3c). Immediately after lubrication, the internal structure of the dimers cannot be resolved.

Achieving super-resolution in such a situation requires reducing the thickness of the IPA layer due to its evaporation, as schematically illustrated in **Figure 4**a. Using geometrical optics, it can be shown that the lateral image magnification (M) is related to the gap (g) separating the spheres from the object by **Equation 2**:

$$M(n',r,g) = \frac{n'}{2(n'-1)(\frac{g}{r}+1)-n'}$$
(2)

where *r* is the radius of the sphere, and $n' = n_{sp}/n_0 \sim 2.0/1.37 \approx 1.46$ is the refractive index contrast between the sphere and object space. The dependence of M on the normalized gap (g/r) calculated using **Equation 2** is illustrated for n' = 1.5 by the black line in **Figure 4**b. In the limit of g << r, **Equation 2** leads to $|M| \sim |n_i/(2-n')| \sim 3$. The dynamical behavior of *M* as IPA evaporates was studied (**Fig**-



Figure 4: (a) Schematic illustration of the IPA layer evaporation. (b) Dynamical measurements of M (c) SEM image of the dimer array. Virtual images through the same sphere (d) after lubrication, (e) after 10 min, (f) after 72 hours.

ure 4d-f). The magnification (*M*) of the virtual image created by the 16 µm sphere embedded in a PDMS coverslip was determined using a comparison with the real image of the surface of the structure outside the microsphere ^[4]. The experimental results demonstrate a reduction of magnification from M ~ 5.4 measured in the first minute (**Figure 4**d) to M ~ 3.1 after 72 hours (**Figure 4**f).

The dimers were barely resolved within the first minute after lubrication and application of the coverslip (**Figure 4**d). However, the structure of individual dimers became much better visible in the images obtained later in the course of evaporation of the IPA layer, as seen in the magnified images after drying for 10 min and 72 hours (**Figure 5**a,c). Irradiance profiles along the x-axis of dimers are illustrated in **Figure 5**b and **Figure 5**d, respectively.

Using a PSF-based image fitting procedure described previously, we calculated intensity profiles along the x-axis, represented by

blue dashed lines. They demonstrate excellent agreement with the experimental intensity profiles at the FWHM of the Gaussian PSF fitting function at ~ λ /4 and ~ λ /5.5. These results show that the super-resolution provided by the embedded BTG microspheres gradually increases as the IPA layer evaporates. The resolution values obtained after 72 hours (~ λ /5.5) almost reached the level of resolution obtained in structures without lubrication (~ λ /6- λ /7).

CONCLUSIONS

We showed that the observation of minimal discernible features in the optical images of extended objects (which cannot be approximated as point-sources) could result in overestimated resolution values. It is shown that a more consistent way of defining optical super-resolution is based on a standard procedure of convolution with PSF with widths smaller than the diffraction limit. We demon-



Figure 5: (a) Image of an Au dimer after 10 minutes of the IPA evaporation. (b) Comparison of the measured and calculated irradiance profiles. (c,d) Same as (a,b), respectively, but after drying for 72 hours.

strated that $\sim\lambda/6-\lambda/7$ resolution could be systematically achieved in the images of nanoscale metallic dimers and bowties. Another bottleneck problem of this technology is based on a limited FOV of virtual imaging through individual spheres. In this work, we developed a technology of fabrication of transparent elastomeric PDMS thin films containing hundreds of embedded high-index BTG microspheres. Such films or coverslips can be considered as a new optical component for super-resolution microscopy.

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08 Flexible Micropillar Electrode Arrays for In Vivo Neural Activity Recordings

Mingde Du, Shouliang Guan, Lei Gao et al.

ABSTRACT

Flexible electronics that can form tight interfaces with neural tissues hold great promise for improving the diagnosis and treatment of neurological disorders and advancing brain/machine interfaces. Here, the facile fabrication of a novel flexible micropillar electrode array (µPEA) is described based on a biotemplate method. The flexible and compliant µPEA can readily integrate with the soft surface of a rat cerebral cortex. Moreover, the recording sites of the µPEA consist of protruding micropillars with a nanoscale surface roughness that ensures tight interfacing and efficient electrical coupling with the nervous system. As a result, the flexible uPEA allows for in vivo multichannel recordings of epileptiform activity with a high signalto-noise ratio. The ease of preparation and high flexibility make the µPEA an attractive tool for in vivo spatiotemporal mapping of neural activity.

INTRODUCTION:

Neural electrodes can be used to develop an understanding of brain functions and have become a clinical tool for the diagnosis and treatment of neurological disorders. ^[1–8] In particular, epilepsy is a common neurological disorder that affects about 1% of the general population and 4% of children. ^[9] Clinically, about 30% of patients with epilepsy respond poorly to antiepileptic drugs and have to undergo surgical resection of the epileptic foci. Subdual intraoperative electrocorticography (ECoG) has been routinely applied in patients with intractable epilepsy for both preoperative localization of the epileptogenic focus and assessment of post-surgical outcomes. ^[10–12] ECoG recordings are typically performed with subdural electrode arrays that are placed directly on a cerebral cortex's surface. ^[13] Subdural electrodes are much less invasive than penetrating depth electrodes that cause tissue damage and elicit a pronounced foreign body response. ^[14,15]

The interfaces between electrodes and neural tissues play an essential role in recording neural activity because extracellular signals decay rapidly with distance. ^[16,17] A key challenge for creating tight interfaces between conventional subdural electrodes and neural tissues has been their sizeable mechanical mismatch. ^[18] The poor contacts between conventional rigid electrodes and soft tissues lead to the poor electrical coupling at their interfaces. As a result, neural activity signals can be notably attenuated by the cerebrospinal fluid in the electrode-tissue gaps. ^[19]

Flexible subdural electrodes based on polymer substrates have been developed to improve the contacts between electrodes and neural tissues. ^[20-25] In addition, they were shown to reduce the foreign body response of the brain tissue in chronic applications. ^[26] Nevertheless, the moduli of the polymer substrates are in MPa to GPa range, ^[27] which is still orders of magnitude higher than that of the brain. This can cause shear force and micromotion at the electrode-tissue interfaces, limiting the accuracy and stability of subdural ECoG recordings.

Here, we introduce a flexible subdural micropillar electrode array (μ PEA) that enables the formation of tight neural interfaces and stable neural activity recordings. The recording sites of the μ PEA consist of protruding microscale pillars with nanoscale roughness obtained by replicating the surface of a lotus leaf. The hierarchical surface structure affords lower impedance compared to planar electrodes. In addition, the protruding micropillars create a tight interface and effective electrical coupling between the electrodes and the cerebral cortex of a rat brain. As a result, the μ PEAs have been successfully demonstrated for stable multichannel recordings of epileptiform activity with high SNR of 252 ± 35.

METHODS

The fabrication process of a µPEA is illustrated in Figure 1. PDMS base was mixed with a curing agent and poured onto a lotus leaf and cured at 50 °C (122 °F) for 1 hour. After peeling off the lotus leaf, a PDMS negative template was obtained. The template was treated with oxygen plasma at 100 W for 5 minutes. Then, a polyimide (PI) mask with a 3 \times 3 hole array was transferred onto the PDMS template. The PI mask/PDMS was heated at 140 °C (284 °F) for 30 minutes under a pressure of ≈ 20 kPa to increase their adhesion. A PI precursor solution was then spin-coated onto the PI mask/PDMS. The system was heated at 120 °C (248 °F) for 20 minutes for the removal of the solvent and then 200 °C (392 °F) for 30 minutes in a vacuum for curing. After peeling off the PDMS template, a PI substrate with spatially patterned micro-



Figure 1: i) A flat lotus leaf, inset shows SEM image; (ii) PDMS was poured on the surface of lotus leaf and cured; (iii) PDMS negative template with random distributed microcavities, inset shows SEM image of a PDMS negative template; (iv) PDMS negative template covered with PI mask; (v) PI was spin-coated on the template and cured; (vi) PI substrate with spatially patterned hierarchical micropillars; (vii, viii) µPEA before and after SU-8 passivation. Scale bars: 10 µm.

pillars was obtained. Planar electrode arrays (PEAs) were also fabricated for comparison.

Neural electrode arrays were defined on a patterned PI substrate by thermal deposition of chromium/gold (Cr/Au) (10 nm/200 nm). The recording sites were aligned with the patterned micropillar regions of the PI substrate. Then a SU-8 passivation layer was defined by photolithography to encapsulate the planar interconnect lines. The μ PEA was bonded to a flexible flat cable through anisotropic conductive film.

3D confocal images of the micropillar electrodes were acquired on a laser confocal microscope (Olympus[®] LEXT[™] OLS4000 system). Scanning electron microscopy (SEM) images were collected using a FEI Nova NanoSEM 430 system and Hitachi-SU8220. Cross-sections of the electrodes were obtained by focused ion beam (FIB) etching using a FIB/SEM dual-beam system. Electrochemical impedance spectroscopy (EIS) of the electrodes was measured using an electrochemical workstation (Reference 3000, Gamry Instruments). A Platinum (Pt) rod and an Ag/AgCl electrode (CHI111, CH Instruments) were used as counter and reference electrodes, respectively.

A Sprague-Dawley rat was anesthetized and fixed in a stereotaxic apparatus. Craniotomy was performed, and the left hemisphere



Figure 2: Structure of flexible μ PEA. a) A flexible μ PEA. Scale bar: 5 mm. b) Optical image of the 3 × 3 micropillar electrode array. Scale bar: 500 µm. c) Optical image of the recording site marked with dashed blue box in inset (b). Scale bar: 50 µm. d) SEM image of an electrode (i) before and (ii) after passivation. Scale bars: 50 µm. e) Magnified SEM image of the area marked with dashed red box in insets (d-(i)). Scale bar: 10 µm. f) 3D confocal images of the electrode in inset (d-(i)) before and (d-(ii)) after passivation. Scale bars: 50 µm. g) Cross-sectional SEM image of the interconnect line marked with dashed orange line in inset (d-(ii)). Scale bar: 10 µm.

was exposed, and the dura mater was carefully removed. A flexible µPEA was placed on the exposed subdural surface of the rat cortex. The neural signals were recorded at a sampling rate of 1 kHz.

RESULTS AND DISCUSSION

Figure 2a shows an as-prepared µPEA with a final thickness of 18 µm. The µPEA is highly flexible and can be bent repeatedly without loss of structural integrity. The µPEA consists of nine recording sites arranged in $3 \times$ 3 matrices with 1 mm spacing (Figure 2b). Each recording site has a diameter of 120 µm (Figure 2c). SEM images of a typical electrode before and after SU-8 passivation are shown in Figure 2d. The enlarged SEM images in Figure 2e show that the micropillars contain nanoscale wrinkles. The height of the wrinkles ranges from 100 nm - 200 nm. 3D confocal images show that the µPEA consists of protruding micropillars (Figure 2f). Figure 2g shows a cross-sectional SEM image of a planar interconnects line, which consists of a three-layer sandwich structure of SU-8/Au/PI.

The performance of neural electrodes is mainly limited by the thermal noise that arises from the impedance at the electrode-electrolyte interface. ^[28] The impedance at the electrode-electrolyte interface is inversely proportional to the effective electrode area. We performed electrochemical impedance spectroscopy (EIS) on micropillar and planar electrodes on the same PI substrate for direct comparison. **Figure 3**a shows representative EIS results measured in phosphate-buffered saline (PBS). The impedance of the micropillar electrode is lower than the planar one. The reduced impedance can be attributed to the increased electrode area. **Figure 3**b summarizes the averaged impedance of 6 micropillar electrodes and 27 planar electrodes measured at 1 kHz.

We applied the µPEAs for in vivo subdural recordings of penicillin-induced epileptiform activity in the rat cortex. As an antagonist of the gamma-aminobutyric acid (GABA) receptor, penicillin induces epileptiform activity by preventing GABA-mediated inhibitory control of pyramidal neurons. [29] As shown in Figure 4a, the µPEA conformally covered a large cortical area of the rat brain. Notably, the protruding micropillars at the recording sites were engulfed by the neural tissue, which resulted in significantly improved electrical coupling. Figure 4b shows a representative real-time signal recorded by a micropillar electrode (Ch-9), and Figure 4c is the normalized time-frequency spectral analysis of the time-series data. As shown in Figure 4d, three periods, including the basal period, latent period, and epileptiform activity period, could be identified. The epileptiform activity period began with increasing discharges arising from the hyperexcitability and hypersynchrony of neuronal activity. As shown in Figure 4c, there was an associated increase in the spectral power between 5 Hz – 25 Hz. The amplitude of the discharges reached a maximum of 3.5 mV at 0.5 h after penicillin injection, and the µPEA



Figure 3: a) EIS of micropillar and planar electrodes measured in PBS. b) Averaged impendence of micropillar and planar electrodes

allowed stable recordings over 3 h. The discharge frequency decreased from 0.8 spikes/s in the initial period to 0.2 spikes/s in the late epilepsy period. The high signal amplitude could be attributed to the tight interfaces and efficient electrical coupling between the protruding micropillars and neural tissue. **Figure 4**e,f shows simultaneous multichannel recordings by the µPEA. We applied a thresholding method to detect epileptiform discharges recorded by the nine channels, from which spike times were extracted (**Figure 4**g). Spike-time delays at different channel locations were then calculated relative to the spike-time



Figure 4: In vivo neural activity recordings with µPEA. a-(i) Optical image of a µPEA conformally attached onto the cortical surface of rat brain and a-(ii) schematic illustration of the tight interface between micropillars and brain tissue. Scale bar in (i): 1 mm. b) Representative real-time recording of neural activity by a micropillar electrode (Ch-9). c) Normalized time-frequency spectrum of the time-series data in inset (b). d-(i) Neural signals recorded during the basal period, d-(ii) latent period, and d-(iii) epileptiform activity period, respectively. e) Multichannel recordings of epileptiform activity with the µPEA. f) Array layout of the voltage traces during an epileptiform discharge, as marked with the dashed black box in inset (e). g) Overlaid voltage traces. The colored dots marked the spike-times. h) Spike-time delays of 50 discharges recorded by the nine channels in a 255-s window. i) Array layout of the average spike-time delays determined from inset (h).

of Ch-9. **Figure 4**h summarized the spike-time delays of 50 epileptiform discharges recorded in a 255 s window. The spike-time delays show a clear dependence on the channel locations. This allowed us to construct a pattern map by plotting the average spike-time delays as a function of each channel's location (**Figure 4**i).

CONCLUSIONS

In summary, we demonstrated a facile biotemplate method for the fabrication of flexible µPEAs. The hierarchical surface structure of the µPEAs effectively reduced the impedance of the micropillar electrodes. Moreover, a tight electrode-neural interface was obtained due to the engulfment of the micropillars by neural tissues. As a result, the µPEAs allowed stable subdural recordings of neural activity with high SNR. Multichannel recordings further revealed the propagation characteristics of epileptiform activity across the cerebral cortex. These results show that flexible µPEAs can offer new opportunities to study the tempo-spatial dynamics of neural activities.

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Advanced Optical Metrology

Part III

Roughness

Introduction: Surface Roughness

Lawrence A. Renna

Surface roughness has critical implications for the properties and function of materials including, wettability, friction resistance, optical properties, anti-scaling performance, corrosion resistance, sensor activity, and electronic properties, to name a few. Thus, using surface metrology to characterize surface roughness provides important information in describing material morphology. Scanning electron microscope (SEM) and scanning probe techniques such as profilometry and atomic force microscopy (AFM) are the more traditional methods for investigating surface roughness. Surface roughness analysis by SEM usually requires additional sample preparation (e.g., gold sputtering), and SEM images typically cannot guantify surface texture characteristics or precise morphologies over a large surface area. AFM can measure very small surface roughness features; however, it is often difficult to perform on very soft or sticky surfaces, and cannot characterize surfaces with small and large surface features.^[1] Thus arises optical metrology, specifically laser scanning confocal microscopy (LSCM) to address many of the needs of surface metrology.

LASER SCANNING CONFOCAL MICROSCOPY

LSCM is a topological optical microscopy technique that can create a bright image of the specimen's in-focus region while causing all out-of-focus areas to appear dark. One of the major limitations of traditional optical microscopy is the narrow depth of field. LSCM can take a series of optical sections, at different optical planes, to assemble a "through-focus" image. This feature endows LSCM with a virtually infinite depth of field. ^[2]

Two different modes of LSCM operation are typically used to characterize material structures. They are fluorescence-mode LSCM and reflectance-mode LSCM. Fluorescence-mode uses the excitation of fluorophores to generate image contrast, whereas reflectance-mode is used to characterize the surface texture or roughness of material surfaces. ^[1] In reflectance mode, a 405 nm laser is typically used because it provides the smallest probe size. Moreover, highly tuned optics provides extremely high, sub-micron resolution. ^[3]

In scanning probe techniques, roughness measurements are generally made along a straight line by scanning the sample's surface with a probe. LSCM instruments can perform a line-scan such that the instrument measures the surface features along a defined line in any orientation, providing the same roughness features as scanning probe methods. However, LSCM can also measure the surface features of the entire area of a sample, which provides a more representative view of the overall surface. ^[3]

The quantification of surface features results in surface parameters, and are discussed in the next section. Surface parameters are characterized by profile methods and areal methods. Profile methods were derived for conventional stylus probe measurements, but can be easily calculated from LSCM measurements. Areal methods can characterize the entire surface rather than just a line across the surface and are one of the main benefits of using LSCM. ^[1]

Profile Methods. The primary profile curve is obtained by applying a low-pass filter to the measured primary profile. The surface texture parameter calculated from the primary profile is referred to as the primary profile parameter (P-parameter). The roughness profile can be derived from the primary profile by applying a high-pass filter to remove the long wave components of the profile. The surface texture parameter calculated from the roughness profile is referred to as the roughness profile parameter (R-parameter). Lastly, the waviness profile is derived from the primary profile by applying a larger high-pass filter to remove the long-wave components greater than the waviness components, followed by a cutoff filter to remove



Figure 1: Top, an example of the application of areal filters to a surface obtained by confocal microscopy showing the eliminated and resulting surfaces from the application of the filters. Bottom, conceptual drawing of the areal methods of analysis, displaying filters and their respective nesting indices, and the length-scale information contained within different calculated surfaces. Reproduced with permission from Ref.^[4].

the roughness components from the profile. The surface texture parameter calculated from the waviness profile is referred to as the waviness profile parameter (W-parameter).^[4]

Areal Methods. Filters are also used to calculate new surfaces (called areal filters), which display the features of a surface at different length/height scales. The filters effectively separate the long and/or short wave components contained in the scale-limited surfaces. According to function, three types of filters are defined: the S filter eliminates the small wavelength components, the L filter that eliminates the large wavelength components, and the F operation, which removes specific forms (e.g., spherical or cylindrical features). The value representing the threshold wavelength for areal filters is called the nesting index and is equivalent to cutoff values used in profile methods.^[4] Combinations of filters can be utilized to calculate new surfaces that display features at different length scales. The S-F surface is obtained by applying a Gaussian low-pass S filter to remove noise and keep the primary surface followed by applying an F operator to remove the form. The S-F surface displays the texture of the material's surface. By applying a Gaussian high-pass L filter to the S-F surface, the waviness is filtered out and leaves the S-L surface. The S-L surface displays the surface roughness of the analyzed material. ^[5] An example

application of the S filter, L filter, and F operation, and the resulting surfaces are shown in **Figure 1**. Moreover, **Figure 1** also displays a conceptual drawing of areal methods displaying the filters and their respective nesting indices, and the length-scale information contained within different calculated surfaces.^[4]

SURFACE ROUGHNESS PARAMETERS

Superficial irregularities (roughness and undulation), dents, parallel grooves, and other characteristic surface features are collectively called "surface textures." Converting these surface characteristics into numerical measurements is referred to as surface texture parameters. Surface texture parameters are roughly categorized into the profile methods and the areal methods. ^[4]

A variety of parameters can characterize surface roughness. Areal/field parameters are used to describe the entire measured surface of the sample, whereas feature parameters only consider select points, lines, or areas of the sample. ^[6] Surface roughness parameters provide more information, and their determination is uniquely enabled by confocal microscopy. ISO 25178 categorizes the 3-D

Group Parameters Notes Sa, Sq, Ssk, Amplitude methods, defined for the **Height Parameters** Sku, Sp, Sv, Sz defined area Smr, Smc, Sk, Functional Areal material ratio as a function of the scale-limited stratified functional surface Parameters 1 Spk, Svk Functional Svq, Spq, Smq Areal material probability curve, with Parameters 2 the areal material area ratio expressed as Vm, Vv, Vmp, Vmc, a Gaussian probability **Volume Parameters** Vvc, Vvv Functional Fractal cross-scale descriptive methods Svs, Srel, Svfc, Safc Parameters 3 Hybrid Parameters Sdq, Sdr Surface envelope and gradients **Spatial Parameters** Sal, Str Autocorrelation functions Std Texture direction Other Parameters

Table 1: ISO 25178 roughness parameters. Adapted from Ref. [7].



Figure X: Surface Metrology and Scales – Why and how?



Figure 2: Height distribution obtained from LSCM showing the selected areal height parameters. Reproduced with permission from Ref. ^[4].

surface parameters into six groups as shown in **Table 1**. ^[7] Surface parameters have the symbol S, and volume parameters have the symbol V. The selected area and filtering are not defined by the parameter designation; therefore, the filtering conditions should be stated when reporting a surface parameter. ^[6]

The areal surface height parameters are commonly used to describe the height distribution or the unevenness of a surface, and select parameters are presented in **Table 2**. Height parameters are calculated using the distribution of height information from the measurement. ^[6] Therefore, lateral features are not captured by these parameters, but can be described by other parameters in **Table 1**. ^[8] An example height histogram obtained by confocal microscopy is shown in **Figure 2** and shows the relationship between the selected areal height parameters and the height distribution. ^[4]

Table 2: Selected areal surface unevenness height parameters. Adapted from Ref. ^[8] .	

Parameter	Definition
Sq	Root mean square height is the standard deviation of the height distribution, or RMS surface roughness
Sp	Maximum peak height is the height between the highest peak and the mean plane
Sv	Maximum pit height is the depth between the mean plane and the deepest valley
Sz	Maximum height is the height between the highest peak and the deepest valley
Sa	Arithmetical mean height is the mean surface roughness

FUNCTIONAL ASPECTS OF SURFACE ROUGHNESS

The surface roughness of a material can have a significant functional impact on the material, depending on the surface features, the type of material, and its application. The following will identify some examples of the functional impacts of surface roughness on material properties and functionality.

Wettability. The surface wettability of a material plays a key role in various fields. Thus, controlling the wettability of a surface is desired for a range of applications. Surface can be prepared, which are not easily wet by aqueous media (hydrophobic surfaces), non-polar media (oleophobic surfaces), or both (amphiphobic surfaces). These types of surfaces are often prepared by introducing surface roughness. In one example, films were made with a blend of surface-functionalized poly(methyl methacrylate) and polyvinylidene difluoride (PVDF). [9] The surface showed a rough relief, using an Olympus LEXT confocal microscope using 405 nm laser light, which often occurs in films of polymer blends (Figure 3A). The surface is hydrophobic, demonstrated by the high contact angle of water on the surface. Upon application of an electric field, the piezoelectric response of PVDF causes the film to become smoother (Figure 3B), and the surface is better wet by water, and the wetting contact angle decreased. Thus, the coating displayed a reversibly hydrophobic surface using an electric field as the stimulus.

Additionally, super-hydrophobic and oleophobic surfaces on aluminum alloy substrates were achieved by chemical etching, followed by the deposition of an organosilicate. The surface roughness achieved through chemical etching was optimized to a surface roughness to achieve hydrophobicity, and oleophobicity was achieved due to air entrapment at the oil-surface interface. This topic is presented in detail in the digest article "Super-hydrophobic and Oleophobic Aluminum Alloy Surfaces via Chemical Etching and Functionalization."

Friction Resistance. The surface of a material also has import implications on its ability to resist friction. In terms of dry friction, the beneficial effects of surface structures can be mainly attributed to the storage of wear debris and a reduced contact area. ^[10] Amanov et al. showed a reduction in Cu alloy surfaces' friction coefficient with patterned bulges due to the reduced contact surface area. ^[11] With lubrication, the reduced friction associated with rough and textured surfaces can be attributed to the accumulation of wear particles to create conformal interfaces, ^[12] lubricant reservoirs in the textured surface features, and additional hydrodynamic pressure. ^[10, 13] In the article digest "Effects of Multi-Scale Patterning on the Run-In Behavior of Steel-Alumina Pairings under Lubricated Conditions" Grützmacher et al. showed the effect of largescale micro-coined features and small-scale laser patterning features of steel-alumina pairings under lubricated conditions. ^[10]

Optical Properties. Surface roughness features can be used to tune the optical properties of a surface, such as reducing reflection, or increasing scattering. Surface roughness can be used to achieve better light trap-



Figure 3: Confocal images, using an Olympus LEXT microscope using 405 nm laser, of the PVDF/PMMA surface A) without and B) with the application of external voltage (EF intensity = 1 V μ m–1). The top part of the image gives the schematic representation of the proposed mechanism of surface smoothening. Reproduced with permission from Ref. ^[9].

ping and absorptance in solar cells to improve solar energy conversion efficiency. Light trapping can compensate for short optical path lengths and minority carrier diffusion lengths in thin light absorbers. Light trapping increases the amount of absorbed light in thin absorbers. Randomly textured transparent conductive oxides (TCO) are commonly used in silicon thin-film solar cells as front contacts. The TCOs' surface textures assist in reducing reflection losses and increasing scattering/diffraction of the incident light. ^[14]

Additional optical properties are dependent on material surface roughness and texture, including the gloss reflectance of materials. For example, Vessot et al. showed a strong correlation between surface texture and the gloss reflectance of photographic paper using confocal microscopy. Examples of surface textures of photographic paper obtained using an Olympus LEXT OLS4000 confocal microscope with different objective lenses are shown in **Figure 4**. ^[15]

Anti-scaling Properties. The surface roughness of a material also has an impact on its potential to resist fouling or scaling. In addition to surface roughness, the chemical composition, adsorption characteristics, charge, and nanostructure of the surface can modify the surface energy and, thus, the adhesion between the material and the scaling particles. In scaling, surface nucleation sites on the surface must be present. The presence of free and active nucleation sites depends mostly on the topography and roughness of the material. Thus, it has been demonstrated that the best anti-scaling surfaces have the lowest surface roughness. ^[16]

Corrosion Resistance. The corrosion resistance of metals, such as stainless steel, is correlated with its surface topography, which has important implications for product lifetime. ^[17] For example, Pistorius and Burstein showed that more corrosion pits formed on the rougher surface and concluded that deep depressions on steel surfaces have a lower potential to activate corrosion than surfaces which contain more open pits because of different diffusion rates. ^[18] Interestingly, Li et al. reported that Cu surface roughness resulted in local fluctuations in the electron-work function, which act as surface microelectrodes, resulting in accelerated corrosion. ^[19] Conversely, Hagen et al. found that surface roughness and asperities can be beneficial to corrosion resistance when utilizing a polymer coating. They found that increasing roughness on surfaces with triangular peaks increased the effective contact area and decreased the corrosive delamination. [20]

Sensor Activity. The surface properties of materials also have an impact on their performance in sensor applications. As an example, Yin et al. fabricated ZnO hollow nanospheres under different conditions that vary the surface roughness. The particles were utilized in chemiresistance sensors for alcohol vapors. The authors found that the roughest sample gave the best sensor response toward alcohol vapor. The improved response with the introduction of surface roughness was attributed to factors including the introduction of beneficial atoms in the surface features, improved crystalline quality, and the presence of many surface adsorption sites. ^[21]

Electronic Devices. Surface roughness plays an important role in the properties and function of electronic devices. This is particularly true for thin film electronics, where the size of the surface roughness features approaches the finite film thickness and edge/surface effects contribute more to the bulk material properties. Electron scattering at the boundaries becomes important in thin metallic films and increases with increasing surface roughness resulting in increased resistance. ^[22] For example, Luo et al. showed that the resistivity of silver films, deposited under different conditions to vary the surface roughness. ^[23]

Moreover, the existence of surface roughness on capacitor electrodes can increase the leakage current. This is due to the exponential relationship between leakage current and electric field. Rough features on electrodes result in an inhomogeneous electric field, and high leakage current at points where the local electric field is high. ^[22]

CONCLUSIONS

To conclude, surface roughness is an important material property that significantly impacts material properties and functionality in myriad applications. Although traditional methods of measuring surface roughness have been able to characterize a variety of surface features, LSCM provides the most encompassing solution to surface metrology. LSCM requires minimal sample preparation and can image virtually any material. Also, LSCM is inherently faster than SEM or AFM; it delivers very high-resolution and high-contrast images and has a high angle of detection capabilities to image steep interfaces. Moreover, LSCM uniquely enables the measurement of areal surface parameters. Surface parameters provide more information than profile-based methods and are more representative of the sample. Finally, examples have been provided that show the functional impacts of surface roughness for various applications, including wettability, friction resistance, optical properties, anti-scaling performance, corrosion resistance, sensor activity, and electronic properties.



Figure 4: Surface textures cropped to an identical region of photographic paper collected with an using an Olympus LEXT microscope using different objective lenses: (a) 5x, (b) 10x, (c) 20x, and (d) 50x. Reproduced with permission from Ref. ^[15].
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01

Effects of Multi-Scale Patterning on the Run-In Behavior of Steel – Alumina Pairings under Lubricated Conditions

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ABSTRACT

The effect of multi-scale surfaces on frictional and wear performance was performed on a ball-on-disk tribometer under lubricated conditions using additive-free poly-alphaolefine oil. Multi-scale stainless steel samples (AISI 304) were prepared by micro-coining and subsequent, direct laser interference patterning. A comparison of different samples (i.e., polished reference, laser-patterned, micro-coined, and multi-scale) shows a clear influence of the fabrication technique on the tribological properties. For multi-scale structures, the structural depth from the micro-coining plays an important role. Multi-scale samples with lower coining depths (50 μ m) showed an increased coefficient of friction compared to the purely micro-coined surfaces, whereas larger coining depths (95 μ m) result in stable and lower friction values for the multi-scale patterns.

INTRODUCTION

Friction is a multi-scale phenomenon affected by various factors such as adhesion, deformation, fracture, and third-body interactions ranging from nanometer to millimeter scale.^[1] This scale dependency is well known and manifests when measuring the coefficient of friction (COF) at the nano- and macro-scales. ^[2,3] The question that arises is how to overcome this multi-scale phenomenon and manipulate friction on different scales. Nature accomplishes this by creating hierarchical surface patterns. ^[1,4–6] In bio-mimetics, this design idea is used to create well-defined surfaces with specially tailored frictional properties. ^[7]

The tribological effectiveness, under dry and lubricated conditions, of single scale surface features has been demonstrated. ^[8–11] In terms of dry friction, the beneficial effects of surface structures can be mainly traced back to the storage of wear debris and a reduced contact area. ^[12,13] Under lubricated conditions, the improvements can be attributed to the storage of produced wear particles, ^[14] a reservoir effect for lubricants, ^[15] and hydrodynamic pressure build-up. ^[16]

There are various methods to manufacture artificial topographies with variable pattern parameters such as structural depth, pitch, diameter, or area density, including lithographic techniques, ^[17] embossing/coining, ^[18] and laser surface texturing. ^[19] Laser surface texturing and, in particular, direct laser interference patterning (DLIP) is a suitable technique to structure various materials with patterns having mm and even sub-mm features. ^[20] To produce larger feature sizes on metallic substrates, coining/embossing seems to be a viable process route, which also offers mass production capability. ^[21]

Despite the fact that nature demonstrates plenty of beneficial effects for multi-scale surface patterns, those patterns have been rarely investigated in terms of their frictional and wear behavior. Most of the tested patterns are "multi-shape" structures combining at least two pattern geometries with similar dimensions. Therefore, the goal of this research work is to investigate the frictional and wear performance of multi-scale surfaces combining a larger micro-coined surface pattern with a cross-like laser surface pattern (DLIP). The tribological behavior of the produced multiscale surface patterns is compared to single-scale micro-coined and laser patterns.

METHODS

Stainless steel (AISI 304) blanks with a thickness of 1 mm (0.04 in.) and a polished surface (root mean square roughness Rq = 30 nm) were used. The samples were ultrasonically cleaned for 10 min. in cyclohexane, acetone, and then isopropanol.

Micro-coining is a forming process in which a pre-structured tool is used to imprint the tool's pattern into the surface of a workpiece. To coin high strength materials, the workpiece needs to be heated up to reduce the flow stress, decreasing the die load. The current density and heating time were set to 35 A mm⁻² and 5 s, respectively. This leads to a maximum sample temperature of ~1200 °C (2192 °F). First, the sample is heated by conductive heating. Afterward, the sample gets cut and coined in one tool movement at 5 mm s⁻¹. Circular dimples with structural depths of 50 μ m and 95 μ m, diameters of 181 μ m and 212 μ m, as well as a pitch of 558 μ m, were fabricated (called A2 and A3, respectively). Polished reference samples were coined with a flat die keeping all coining parameters constant.

A high-power, solid-state, neodymium-doped (Nd) glass YAG laser with a pulse duration of 10 ns, a wavelength of 355 nm, and a repetition rate of 10 Hz was used for DLIP. The laser fluence was a constant 29 J cm⁻² for all samples. By using two interfering sub-beams, line-like surface topography is induced. Well-defined, cross-like surface topography with a periodicity of 9 μ m and a structural depth of 1 μ m was obtained. To create the cross-like pattern, the samples are structured with two line-like patterns which are rotated by 90° relative to each other. Multiscale samples were first coined and subsequently superimposed by a cross-like laser pattern.

The samples' topography was characterized by laser scanning microscopy (Olympus® LEXT[™] OLS4100 laser scanning confocal microscope) to study the surface roughness and the quality of the patterns. The tribological tests were done using a ball-on-disc tribometer in rotational sliding mode with a constant normal force of 5 N and a track radius of 5 mm (0.2 in.). The tribological counter body was an aluminum oxide (Al₂O₃) ball with a diameter of 6 mm (0.24 in.). The estimated Hertzian contact pressure is ~1.29 GPa. The sample is located in a rotating lubricant containment filled with 7 mL of polyalphaolefine (PAO 40) oil. Linear variable differential transducers measured the friction force. A sliding velocity of 0.01 m^{s-1} was selected for this study.

RESULTS AND DISCUSSION

The coined surfaces are analyzed before and after DLIP using LSM. As shown in **Figure 1**c and **Figure 1**d, the small structures with a depth of ~1 μ m created by DLIP are homogeneously distributed over the entire sample with features on the fillets between the dimples, as well as inside the dimples. The two different coined patterns are produced with the same die but varying coining pressures.



Figure 1: Overview as well as profile information of the coined samples a), c) A2 and c), d) A3, respectively. The top view as well as the profiles are shown before a), b) and after laser patterning c), d). All data are given in μ m.

Figure 2 summarizes the COF's temporal evolution for the polished reference, the purely coined (A2), and laser-patterned samples. The figure shows the frictional behavior of the corresponding multi-scale sample (A2). The polished reference sample starts with a COF of ~0.11 and stays constant over the entire measuring time of 200 sliding cycles. The smooth trend of the COF, without any increase, combined with the fact that no pronounced wear tracks can be observed for the reference (Figure 3) at a sliding velocity of 0.01m s⁻¹ leads to the conclusion that the prevailing lubrication regime can be assigned to elastohydrodynamic lubrication (EHL). This goes hand in hand with the estimated nominal Hertzian contact pressure of 1.29 GPa. This implies that elastic deformation of the rubbing surfaces and a viscosity increase with pressure become relevant. [22]

As can be seen in **Figure 2**, the COF of the laser-patterned sample starts at ~0.20 and

decreases in the first 75 sliding cycles. Afterward, the sample reaches steady-state conditions. The observed effects can be attributed to the wearing-off of the highest surface asperities during the laser pattern's run-in and degradation. ^[10] The increased surface roughness and spiky surface topography increase the contact pressure, which makes a transition from full-film EHL to mixed lubrication. [8] Furthermore, the laser-patterned surface's load-bearing capacity is reduced compared to the plateau-like surface of the reference, which can also lead to more pronounced wear features and an increased wear rate. The laser pattern effects lead to the generation of wear particles and a modified contact area, which results in a higher COF over time. [23, 24]

The COF of A2 starts at ~0.07 and shows a slight increase in the first sliding cycles. This can be explained by an initial high wear rate in which the sharpest asperities are worn off. ^[25] After a decrease of the COF in the subsequent cycles, the COF remains relatively constant at ~0.05. Compared to the polished reference, A2 leads to a friction reduction by a factor of ~2. The significant friction reduction can be explained by a pressure build-up and an additional oil supply from the surface structures. ^[22]

As shown in **Figure 2**, the respective multiscale pattern (coining A2 and DLIP) shows worsened frictional behavior compared to the purely coined sample. The initial COF is ~0.10 and decreases to ~0.08. Compared to the polished reference, the multi-scale surface shows a ~20% decrease in COF. However, compared to the purely micro-coined surface, the COF of the multi-scale pattern is ~60% higher.



Figure 2: Temporal evolution of the COF of the polished reference, the purely coined sample (A2), the purely laser-patterned sample and the multi-scale sample.



Figure 3: Surface of the polished reference after 200 sliding cycles at two different positions imaged by LSM.





To explain the worsened frictional behavior of the multi-scale surface, the wear behavior of those samples needs to be examined. **Figure 5** shows the entire wear track of the multi-scale surface (combining A2 and the laser pattern). The multi-scale surface shows a well-pronounced wear track. As a consequence, it can be assumed that the additional cross-pattern results in an increased contact pressure due to the rougher topography compared to the micro-coined samples. This can lead to undesired edge effects and stress raisers. Further, the alumina ball's deflection from its track is prominent, where it encounters several coined dimples in a row (see blue colored rectangle). The deflection of the ball might occur due to pressure build-up in the structures due to a converging gap that is formed between the ball and the structure.

Figure 6 summarizes the temporal evolution of the COF of the reference, the purely coined (A3), the laser-patterned samples, and the multi-sale sample (A3 combined with laser-patterning). The initial COF of A3 is ~0.17 and then decreases to ~0.11. Com-



pared to A2, the COF of A3 is greater. For the polished reference, the COF of sample A3 is significantly increased in the first 50 sliding cycles. In the following sliding cycles, the COF of the reference and A3 are rather similar. Surface structures with a larger structural depth have a higher probability for cavitation, thus reducing the oil film thickness and load-bearing capacity. ^[22,26]

The initial COF of the multi-scale surface is ~ 0.11 . After a slight decrease in the COF, the COF remains constant at ~ 0.10 . It can be assumed that the cross-pattern helps to reduce pronounced cavitation due to a better lubricant distribution in the contact zone. By reducing cavitation, a larger local oil film thickness can be present, improving the load-bearing capacity and reducing the COF.



Figure 6: Temporal evolution of the COF of the polished reference, the purely coined sample (A3), the purely laser-patterned sample, and the multi-scale sample.



Figure 7 shows the wear behavior of the multi-scale pattern (A3 and laser-pattern) imaged by LSM. The deflection of the alumina ball from its track is prominent at the positions where it encounters several coined dimples in a row. Compared to the purely laser-patterned samples, the multi-scale patterns show a considerably reduced wear with a still intact laser-pattern after 200 sliding cycles. Wear behavior differences can be attributed to different lubrication regimes for the laser-patterned samples (mixed lubrication) and the multi-scale surfaces (mixed EHL).

CONCLUSIONS

To conclude, we found that the coined structures' depth determines whether the multiscale patterns have a beneficial or detrimental frictional effect. The COF of the multiscale pattern is decreased for deep structures (95 µm) and increased for shallower ones (50 µm). Further, laser-patterned samples show an increased COF due to the spiky surface topography, which increases the contact pressure and causes the transition from full-film EHL to mixed lubrication. For the purely microcoined surfaces, lower coining depths lead to the best tribological performance due to a pressure build-up in the lubricant and additional oil supply in the coined pockets. In contrast, the corresponding multi-scale sample shows worsened behavior due to increased surface roughness. The larger coined surfaces are less efficient over the entire measuring time because the deeper dimples are more prone to pronounced cavitation and do not allow for a sufficient pressure build-up. The multiscale surfaces show advantageous effects and are characterized by a stable and relatively low COF. The additional laser patterns help reduce cavitation and therefore contribute to enhanced lubrication in the contact zone.

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02 Super-Hydrophobic and Oleophobic Aluminum Alloy Surfaces via Chemical Etching and Functionalization

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ABSTRACT

Super-hydrophobic and oleophobic surfaces on ASTM 1200 H14 aluminum alloy substrates were achieved by chemical etching followed by the deposition of organically modified silicate coatings. The chemical etching solutions iron(III) chloride + hydrogen chlorine + hydrogen peroxide (FeCl₃ + HCl + H_2O_2) and etching time were varied to increase the surface roughness. The chemical etching produces rough surfaces with superficial square pores and edges about 1 μ m–2 μ m. The chemical modifications modified silicate solutions based on perfluorooctyltriethoxysilane (PFOTES) and hexadecyltrimethoxysilane (HDTMS) sol-gel precursors induced water contact angles about 154° and 150°, respectively. Moreover, the surface modification based on PFOTES demonstrated an oleophobic character with an oil contact angle of 136° due to air entrapment in the surface roughness at the oil-aluminum interface.

INTRODUCTION

In the last decades, the development of super-hydrophobic surfaces has received attention due to their interesting properties and potential applications on the surface of metals, ceramics, and polymers. ^[1–12] Such surfaces exhibit almost no interaction with water, showing contact angles higher than 150°. ^[13] Some benefits of super-hydrophobic surfaces include easy cleaning, anti-adherence, and corrosion resistance. ^[4,13] Thus, the production of surfaces with such properties on aluminum alloys has attracted particular interest due to the many potential applications of such a light metallic substrate, especially to increase corrosion protection. ^[14] Further, the control over the wettability of organic and apolar fluids such as oil, is also sought for many applications. ^[4,15,16] In this context, various studies have

been carried out to create surfaces that are both super-hydrophobic and super-oleophobic. Such surfaces, called super-amphiphobics, can repel both water and oil. ^[17–19] These surfaces are commonly prepared by increasing surface roughness and reducing surface energy. ^[8,20–23]

Several techniques create rough superficial structures on metals, including chemical etching, anodic oxidation, lithography, and deposition of nanoparticles. [18,24,25] Chemical etching, accelerated and controlled corrosion, ^[26] is commonly used because it is an easy and cheap method. ^[18] Aqueous solutions of iron (III) chloride (FeCl₃) have been used in industry as a chemical etching agent ^[27] for metals such as steel, aluminum, and copper alloys. [26] As an example, Liu et al. ^[1] produced superhydrophobic surfaces in AISI 304 stainless steel by creating a micro-/nanostructure, using an etching solution composed of FeCl₃ + HCl + H_2O_2 (FHH), followed by a coating deposition using the dodecyltriethoxysilane precursor. We applied this method to create a rough surface on an aluminum substrate for the first time.

Organically modified silicates (ORMOSIL) are organic-inorganic hybrid materials synthesized by hydrolysis and condensation reactions of organically modified silanes precursors. ^[28] The most straightforward class is formed from precursors with chemical formula as RSi(OCH₃)₃, where R is an organic terminal group that does not create bridges in the three-dimensional gel network. ^[29] In the case of hexadecyltrimethoxysilane (HDTMS) and 1H,1H,2H,2H-perfluorooctyltriethoxysilane (PFOTES) precursors, the R groups are composed of C–H and C–F bonds, respectively; they are responsible for the hydrophobic and oleophobic character of the functionalized materials.

Herein the surface of ASTM 1200 H14 aluminum alloy was chemically and morphologically modified with an etching treatment in the FHH solution ^[1] followed by the deposition of hybrid organic-inorganic coatings based on modified silica materials obtained by sol-gel process. PFOTES and HDTMS were used as alkoxide precursors to obtain the super-hydrophobic surface. The surface morphology was characterized by confocal microscopy, and contact angle measurements with deionized water and mineral oil were carried out to characterize the modified aluminum alloy surfaces' functionality.

METHODS

The ASTM 1200 H14 aluminum alloy sheets with a size of 60 mm × 40 mm × 0.3 mm (2.36 in. × 1.57 in. × 0.01 in.) were cleaned with acetone and deionized water in an ultrasonic bath for 5 minutes each. After cleaning, the samples were immersed in an FHH solution consisting of a mixture of iron (III) chloride aqueous solution with concentrations ranging from 0.05 mol L⁻¹ to 0.50 mol L⁻¹,



Figure 1: Schematic of the etching and ORMOSIL deposition.



Figure 2: Confocal microscopy images and roughness values (Ra) of the (A) as-received aluminum surface, and chemically etched for 5 min in FHH solutions with $FeCl_3$ concentrations of (B) 0.05 mol L⁻¹, (B) 0.1 mol L⁻¹, and (D) 0.25 mol L⁻¹.

37% hydrochloric acid, and 35% hydrogen peroxide with volume proportion of 10:1:1, respectively. ^[1] The immersion times were 5, 7, 10, and 15 minutes. After etching, the samples were cleaned using a soft sponge, rinsed with deionized water, and washed with acetone and deionized water in an ultrasonic bath for 5 minutes. Then, water was removed with a hot air flow followed by drying in an oven for 20 minutes at 60 °C (140 °F).

ORMOSIL sol-gel solutions were prepared by hydrolysis and condensation of the hybrid precursors PFOTES and HDTMS in the presence of ethanol, deionized water, and 37% HCI. The molar ratio Precursor:EtOH:H2O:HCI was kept at 1:856:7.2:0.9. Coatings using TEOS and mixtures of TEOS with PFOTES as sol-gel precursors with the same molar proportions were also performed for comparison. Then, the solgel solutions were vigorously stirred for 2 minutes. The deposition was performed at room temperature using dip-coating. The deposited coatings were then heat-treated in an oven for 30 minutes at 60 °C (140 °F). Then, the oven temperature was raised to 120 °C (248 °F) for another 60 minutes. The chemical etching, followed by the deposition process of the ORMOSIL coating, is schematized in **Figure 1**.

The samples' surface morphology and roughness measurements were evaluated using a confocal microscope (Olympus[®] LEXT™ OLS4100 3D laser confo-





cal microscope). For the roughness measurements, a cut-off value of 80 µm and a Gaussian filter were selected. The chosen analysis parameter to quantify the roughness was the average roughness (Ra) determined from a cross-sectional line of 180 µm in length drawn along the surface samples.

The coating hydrophobicity and oleophobicity were quantified by water and oil contact angle (WCA and OCA) measurements using ~ 10 μ L of deionized water and ~5 μ L mineral oil, respectively. A portable optic tensiometer was used for the measurements.

RESULTS AND DISCUSSION

The FeCl₃ concentration of the FHH etching solution and the time of immersion was varied to optimize the aluminum substrates' roughness. Images obtained by confocal microscopy and the corresponding roughness values of the samples etched for 5 min in FHH solution with FeCl₃ concentrations of 0.05 mol L⁻¹, 0.1 mol L⁻¹, 0.25 mol L⁻¹, and 0.5 mol L⁻¹ are presented in **Figure 2**. The as-received aluminum has a roughness Ra = 0.21 µm. The 0.05 mol L⁻¹ FeCl₃ solution was not sufficient to create a uniformly rough surface, leading to a partial etching and Ra = 0.7 μ m. For FeCl₃ concentrations of 0.1 mol L⁻¹ and 0.25 mol L⁻¹, irregular and porous microstructures were uniformly formed over the entire surface, presenting higher Ra = 1.29 μ m and Ra = 1.27 μ m, respectively. The FeCl₃ concentration of 0.5 mol L⁻¹ was also tested in this work; however, it caused excessive etching of the aluminum substrate.

Figure 3 shows the WCA as a function of $FeCI_3$ concentration in the FHH solution, followed by ORMOSIL coating from the PFO-TES precursor. Non-etched (NE) and chemically etched samples with a $FeCI_3$ concentration of 0.05 mol L⁻¹ showed similar average WCA values around 120°. The etched samples with a concentration of 0.1 mol L⁻¹ and 0.25 mol L⁻¹ showed relatively high WCAs, but not enough to reach for super-hydrophobicity (WCA > 150°). These results demonstrate that roughness really acts as a wettability amplifier, turning the hydrophobic character of the PFOTES ORMOSIL coating more hydrophobic.

The confocal microscopy images of the aluminum surfaces etched with a FeCl₃ concentration of 0.1 mol L^{-1} with immersion times of 5, 7, 10, and 15 minutes, and the corresponding Ra values are presented in



Figure 4: Confocal microscopy images and roughness values (Ra) of the chemically etched aluminum surfaces in the FHH solution with a FeC_{I3} concentration of 0.1 mol L⁻¹ with etching times of (A) 5 min, (B) 7 min, (C) 10 min, and (D) 15 mi.

Figure 4. The images show that the morphologies are similar. However, the roughness slightly increases, followed by a gradual decrease as a function of the immersion time. For times greater than 7 minutes, the rough microstructure was slowly destroyed, decreasing the roughness until complete embrittlement.

In **Figure 5** are presented the WCA as a function of the etching time after PFOTES ORMOSIL deposition. It can be observed that all chemical etching with an immersion time of at least 5 minutes increased the hydrophobicity of the coated surface. However, only the time of 7 minutes provided the roughness necessary to obtain super-hydrophobicity, (WCA = 154.1°).

Figure 6 shows the WCA obtained for the uncoated samples and coated ones with the different ORMOSIL coatings and not-etched (NE) aluminum substrates. WCA measurements were also made on substrates coated with ORMOSIL based on TEOS precursor, which do not have hydrophobic groups, for comparison.

As-received and chemically etched substrates without ORMOSIL coating are hydrophilic (WCA < 90°). Non-etched aluminum substrates coated with ORMOSIL coating based on PFOTES and HDTMS became hydrophobic, with their contact angle increased to 120° and 110°, respectively. For etched and coated samples, the WCAs reached values above 150°. Such evidence demonstrates that the



Figure 5: Water contact angle as a function of the chemical etching immersion time in the FHH solution with a FeCl_3 concentration of 0.1 mol L⁻¹ and for non-etched samples after PFOTES ORMOSIL deposition.

rough surface enhanced the surface's intrinsic property, hydrophilic surfaces become more hydrophilic, and the hydrophobic surface becomes more hydrophobic, which is in agreement with the Wenzel model. ^[30] The high surface area of the rough surface (Wenzel model) or air trapped between the droplets and the rough hierarchical structure of the coated surface (Cassie-Baxter model) increased the hydrophobic property of the coating to reach a super-hydrophobic behavior. ^[30] Moreover, this behavior is also observed for the TEOS-coated samples, where the hydrophobicity increased for etched surfaces.

Figure 7 shows the mineral OCA measured with NE and etched aluminum substrates, uncoated (UC), and coated with ORMOSIL based on PFOTES and HDTMS. Compared with water wettability results, the values obtained are lower, suggesting a higher affinity of the surfaces with oil. This characteristic is justified considering the lower surface tension of mineral oil (30 mJ m⁻²) than the water one (72 mJ m⁻²). ^[57] The coated sample with PFOTES without etching exhibited oleophilic behavior (OCA <90°), which can be attributed to the van der Waals forces between the apolar alkyl chains and the mineral oil. The OCA of the same film deposited on an etched surface greatly increased to 137°. This result is in opposition

to the Wenzel model that can only amplify the surface's intrinsic behavior, as mentioned previously. However, this behavior can be explained by the Cassie-Baxter model, where the air is entrapped in the material roughness, and the oil drop is deposited on a composite surface with oleophobic behavior. [30] The HDTMScoated surfaces appeared to be oleophilic, both etched and NE substrates. The long apolar alkyl chains with only carbon and hydrogen atoms of HDTMS are responsible for the good spreading of oil. Moreover, the etching treatment of the aluminum surface-enhanced classically oleophilic property following the Wenzel model. In this case, we can infer that the surface is not oleophilic enough to let air pockets in the rough structure to repeal the oil spreading. On the contrary, due to a smaller dispersive component of its surface energy and high roughness, the PFOTES-coated sample succeeds to be super-hydrophobic and oleophobic. In this sense, the influence of the roughness shows again to be fundamental.

The TEOS ORMOSIL coating shows that the OCA values obtained on NE samples were about 30°. The smaller OCA measured for this sample, compared with the HDTMS and PFO-TES coated ones, corroborate results discussed in previous work showing that the dispersive component of the surface energy, responsible





for the oil spreading, is higher for the surface with few alkyl chains than for the one with more of such groups. ^[31] Finally, as expected for such oleophilicity, the etching process increased the oil spreading on TEOS-coated surface, in agreement to the Wenzel model.

CONCLUSIONS

To conclude, super-hydrophobic and oleophobic coatings were fabricated on the surface of 1200 H14 aluminum alloy. The aluminum surface roughness was optimized via an etching treatment using an FHH solution. A FeCl₃ concentration of 0.1 mol L⁻¹ and an immersion time of 7 min were determined to be optimal to enhance the surface roughness and the hydrophobicity after the deposition of ORMOSIL coatings using HDTMS and PFOTES sol-gel precursors. The etching treatment leads to a homogeneously rough surface with square pores with edges about 1 µm-2 µm. WCA measurements indicated that all etched surfaces functionalized with ORMOSIL showed super-hydrophobic properties. Finally, OCA showed that etched surfaces coated with s so-gel solution using PFOTES were oleophobic due to air entrapment at the oil-surface interface.

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Figure 7:. Oil contact angles for uncoated (UC) and coated substrate with ORMOSIL coatings on (///) non-etched and (\\\) etched aluminum substrates.

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03

Assessment of Possibilities of Ceramic Biomaterial Fracture Surface Reconstruction Using Laser Confocal Microscopy and Long Working Distance Objective Lenses

Sebastian Stach, Wiktoria Sapota, Zygmunt Wróbel et al.

ABSTRACT

A numerical description of fracture is an essential step in searching for the correlations between specific micromechanisms of decohesion and material characteristics designated with the use of fracture mechanics methods. This issue is critical to search for fundamental relationships between chemical composition, technology, structure, and properties of materials. It often happens that fracture surfaces are well developed, which can significantly hinder or even prevent the measurement and reconstruction of the tested material surface geometry. Herein, comparative measurements of a biomaterial surface were performed using laser confocal microscopy.

INTRODUCTION

Qualitative fractography often provides enough knowledge about material fracture mechanisms and fracture morphology but does not give any information useful for designing of new materials. These deficiencies are compensated by quantitative fractography, which enables the presentation of fractographic analysis quantitatively. Measurement of characteristics on a fracture surface and the use of stereological parameters allow a more thorough assessment of the fracture process. The combination of fractographic observation techniques and geometric parameters obtained with quantitative fractography methods gives a comprehensive picture of the fracture process. ^[1–3]

A numerical description of fracture is important in the search for the correlation between specific micromechanisms of decohesion and material characteristics designated with the use of fracture mechanics methods. ^[4–6] In this article, comparative measurements of a biomaterial surface were performed using laser confocal microscopy. To this end, short working distance lenses designed to be used with a focused UV laser beam and long working distance objective lenses were used.

Confocal laser scanning microscopy (CLSM) is an imaging method for material surfaces at the nanometer scale. ^[7–9] The basic premise of CLSM is to obtain a high-resolution, sharp image of the sample, which is mainly achieved by eliminating images outside the lens's focal plane. ^[7,10] In a confocal microscope, the signal used for image formation reaches the sample area where it is then reflected. The reflected beam must have a small diameter and a large angle of divergence to get a very high resolution. Owing to this, the signal is focused on the detector aperture in a plane common with the lens focal plane. The signal only reaches the focal plane, and the

result is an image of the sample in its cross sections. Then, the images can be saved and combined, giving a three-dimensional image of the entire surface with an increased depth of focus (all image elements are sharp and clear).

Optical microscopy methods are used for surfaces where contact with the surface is unacceptable due to the material sensitivity and specificity. There is characteristic variation in the quality and accuracy of the analysis of surfaces obtained using a laser confocal microscope compared to the analysis obtained using a profilometer due to the nature of the respective probes used in each. ^[11,12] In profilometry, the large surface area needle makes it impossible to measure the asperities smaller than the probe (**Figure 1**). The laser confocal microscope does not have this deficiency— it can measure an area's roughness at much higher resolution (**Figure 2**).



Figure 1: Course of the analysis performed with the contact method.



Figure 2: Analysis performed using the CLSM.

METHODS

The study of ceramic surface morphology was performed using the Olympus[®] LEXTTM OLS4000 laser confocal microscope. The lenses used in the microscope are designed for microscopic tests involving an observation technique in a bright field of view. This technique involves illuminating the sample with a light beam in the form of a cone (previously formed by a condenser) so that all the light covered by the lens apparatus falls on the sample. The obtained contrast results from the differences in light absorption and scattering by different areas of the sample surface. ^[13]

The Olympus LEXT OLS4000 microscope has a motorized revolving nosepiece that enables an automatic change of the lens during testing. The system automatically adjusts the image sharpness and the light intensity, which allows an easy and quick change of magnification. The lenses mounted in the nosepiece were either semi-apochromatic or apochromatic ^[14] and ranged from 2.5× to 100×. LEXT dedicated lenses have reduced aberration, which

is influenced by a higher numerical aperture and an enhanced optical system, giving a high performance for a 405 nm laser beam. However, they also have a small working distance (1 mm to 0.35 mm); thus, alternative long working distance lenses were also available for surfaces with a high degree of development.

To assess the suitability of long-distance lenses for reconstructing of the geometry of a surface with a relatively high degree of development, it is necessary to carry out comparative studies of short- and long-distance lenses. The test surface cannot be too developed to enable analysis with the lens having the shortest working distance. For comparative studies, an aluminum oxide (Al₂O₃) sample with a relatively flat surface was deposited electrolytically on an aluminum alloy.

RESULTS AND DISCUSSION

To compare the results of analyses obtained using two types of lenses mounted on two different revolving nosepieces, it was neces-



Figure 3: Nine coordinates of the table position defined on the observed surface.



Figure 4: Screenshot of the observed surface for the 50× lens.



Figure 5: Surface images obtained with 20× lenses. **a:** Short distance. b: Long distance. The first image in the lines was obtained in 2D mode (white light), and the other one in 3D mode (laser light).



Figure 6: Surface images obtained with 50× lenses. a: Short distance. b: Long distance. The first image in the lines was obtained in 2D mode (white light), and the other one in 3D mode (laser light).

> sary to develop a system of analysis, which would enable us to observe precisely the same areas after replacing the revolving nosepieces. For this purpose, the option of stage coordinates available in the microscope software was used, and nine coordinates of the table's position with the sample were defined (**Figure 3**). The observed surface was centered relative to the characteristic place in the observed image, and, additionally, screenshots of the observed area were performed (**Figure 4**).

First, the ceramic coating sample was analyzed in the nine different locations, using the 20× and 50× LEXT lenses with short working distances. The sample was preset using the table coordinates, and then its position was corrected manually by observing the sample with the 50× lens and using previously captured screenshots. This procedure ensured that the observed area was the one that was previously measured.

Second, the sample was observed using 20× and 50× lenses with a larger working

distance. It was necessary to calculate the table settings by adjusting the previously set coordinates to repeat the centering of the observed surface using the previously captured screenshots. The results of observation with short-distance and long-distance lenses are given in **Figure 5** and **Figure 6**.

20× lenses enabled observation of the surface sized 639 μ m 3 639 μ m with a sampling step of 625 nm in the X and Y axes, and 485 pm in the Z-axis. 50× lenses enabled observation of the surface sized 256 μ m × 256 μ m with a sampling step of 250 nm in the X and Y axes, and 208 pm in the Z-axis. The surface observation was carried out in 2D (white light) and 3D fine (laser light) modes, and the obtained images had a resolution of 1,024 points by 1,024 lines.

For all measurement data, an analysis of the surface morphology was performed (**Figure 7**) using the height parameters, [^{15]} namely Sq, Sp, Sv, Sz, and Sa, where:

		Short distance						Long distance					
Lens	Area	Sq (µm)	Sp (µm)	Sv (µm)	Sz (µm)	Sa (µm)	_	Sq (µm)	Sp (µm)	Sv (µm)	Sz (µm)	Sa (µm)	
	1	1.12	8.44	12.72	21.16	0.78		1.41	10.76	13.18	23.94	1.07	
	2	1.16	9.09	11.65	20.74	0.81		1.47	10.74	11.08	21.81	1.12	
	3	1.17	9.92	12.09	22.01	0.82		1.47	11.82	12.73	24.56	1.13	
	4	1.16	8.38	11.84	20.22	0.81		1.49	7.78	14.16	21.94	1.14	
20×	5	1.08	9.02	11.43	20.45	0.75		1.37	7.51	11.47	18.98	1.05	
	6	1.26	10.88	11.5	22.38	0.89		1.53	10.28	12.23	22.51	1.17	
	7	1.22	10.11	11.98	22.09	0.87		1.54	7.5	12.12	19.62	1.18	
	8	1.11	11.23	11.81	23.04	0.78		1.45	9.99	12.12	22.12	1.12	
	9	1.23	8.83	11.7	20.53	0.87		1.47	8.98	13.36	22.34	1.13	
50×	1	1.03	4.46	9.95	14.42	0.69		1.18	6.11	10.26	16.37	0.85	
	2	1.08	4.53	6.98	11.51	0.74		1.27	4.88	10.14	15.03	0.92	
	3	1.11	3.66	9.57	13.23	0.77		1.47	12.66	9.14	21.8	1.01	
	4	1.13	3.62	6.86	10.48	0.84		1.32	3.89	10.32	14.2	1.02	
	5	0.91	3.49	7.31	10.8	0.63		1.09	5.03	8.41	13.44	0.82	
	6	1.17	4.17	10.34	14.5	0.82		1.37	3.97	10.31	14.28	1.02	
	7	1.19	5.03	8.63	13.66	0.81		1.36	5.05	11.21	16.26	0.99	
	8	1.03	2.75	8.66	11.4	0.74		1.23	3.64	8.02	11.65	0.94	
	9	1.04	4.74	9.6	14.35	0.7		1.22	5.98	9.6	15.58	0.9	

Table 1: Results of the surface morphology analysis

Sq—Root mean square height is the standard deviation of the height distribution or RMS surface roughness. Sp—Maximum peak height is the height between the highest peak and the mean plane. Sv—Maximum pit height is the depth between the mean plane and the deepest valley. Sz—Maximum height is the height between the highest peak and the deepest valley. Sa—Arithmetical mean height is the mean surface roughness.

These parameters belong to the height parameters included in ISO 25178-2. ^[15] Height parameters are a class of surface finish parameters that quantify the Z-axis perpendicular to the surface. The results of the surface morphology analysis are given in **Table 1**.

When analyzing the images (**Figure 5** and **Figure 6**), it can be noticed that the long-distance lenses give a better quality of an image observed in white light than the short-distance dedicated LEXT lenses. The opposite is the case when dimensional images obtained under

the illumination of the surface with a focused laser beam are compared. A comparison of the surface morphology analysis (**Table 1**) for 20× lenses shows that relatively higher height parameters were obtained for the long-distance lenses compared with the short-distance ones. The situation is similar when comparing 50× lenses. However, the differences are much smaller than in the case of 20× lenses.

Synak et al. successfully used the Sq parameter to compare roughness measurement results obtained with different methods. Given the large difference in the measurement principle and the large difference in the size of the measured surface areas, which exist in both methods used, ^[16] the authors concluded that results' compatibility is high. Greater divergence of results occurred in the case of surfaces with Sq less than 2 nm. A large change of this parameter depending on the test area was found when examining such surfaces, which indicates that the heterogeneity of the height of surface roughness may be the leading cause for the measurement differences.



Figure 7: Stereometric view of the sample surface obtained with 50× lenses. **a**: Short distance. **b**: Long distance.

	Sq (μm) 20×	Sq (µm) 50×
1	1.04	0.6
2	1.05	0.63
3	1.06	0.94
4	1.06	0.63
5	1.04	0.59
6	1.08	0.62
7	1.07	0.63
8	1.07	0.61
9	1.1	0.61

Table 2: RMS calculated for the difference

of subtracted surfaces

Thus, to emphasize the differences between the surfaces, subtraction of surfaces obtained for both types of lenses was performed. The value of the RMS parameter (Sq, root mean square deviation) of the resulting surface allows verifying the quality of the subtraction. ^[15] Sq values are given in **Table 2**. The values of RMS are satisfactory and prove that the observed surfaces are very similar.

CONCLUSIONS

To conclude, it was found that an indisputable advantage of confocal microscopes is that they provide images of very high quality and resolution compared to conventional optical microscopy. The sharpness is not only limited to an area or point but the entire image. Bright and clear images result from using a confocal aperture and advanced lenses arranged in front of the detector. Detector signal selection, specialized shapes, and the lenses inside the objective give clear, colorful, and sharp images, which enable the imaging of individual elements of the sample surface. Two-dimensional observations allow the testing and analysis of individual surface layers, whereas three-dimensional observations enable the observation of diverse surface shapes and assess the quality of materials. Lastly, long-distance lenses made it possible to reconstruct the material surface geometry and the description of its morphology.

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Advanced Optical Metrology

Part IV

Electronics

Introduction: Electronic Materials for Sustainable Energy Conversion and Storage

Markus Fabich

Given the present environmental crises there is a pressing need for sustainable methods to convert and store energy. Consequently, strenuous efforts are made to develop high-performance materials for photovoltaics, batteries, gas reservoirs, just to name a few. This chapter outlines the research that is done in Dr Manuela Schiek's group in Oldenburg, Germany, on sustainable manufacture of photovoltaics. The group has discovered how the latest technology in confocal laser scanning microscopy is enhancing both accuracy and efficiency of their research into organic semiconductors and transparent electrodes. Following this, you can find current studies on the fabrication of environmentally friendly supercapacitors (pp. 8-13), the metallization of silicon heterojunction solar cells by electroplating of copper onto a multifunctional patterned metal layer stack (pp. 14-18), and the manufacturing of spray-coated polymer solar cells based on low-band-gap donors (pp. 19-23).

Harvesting energy directly from the sun in order to generate electricity, solar cells appear to represent the epitome of green energy. Unfortunately, the manufacturing process of common starting materials, like crystalline silicon as the main component of conventional solar cells, requires a huge amount of energy. Firstly, transforming silica ore into its crystallized form requires temperatures of above 2,000°C. Not only is this an incredibly energy-hungry process in itself, but obtaining ultra-pure silicon also involves several hazardous chemicals and a potent greenhouse gas. Other main offenders in the modern manufacture of many inorganic thin-film solar cells include components comprising finite resources such as indium, or the toxic elements selenium and cadmium.

With the increasing strain on the global power grid and the drive towards sustainable energy production, we must therefore ensure that methods of manufacturing green-energy devices are equally sustainable – and this is the goal of Dr Manuela Schiek's research group at the University of Oldenburg, Germany. Their research focuses on alternative materials for solar cell manufacture that are both non-hazardous and readily available. This includes the use of organic semiconductors within the energy-capturing active layer, and a transparent electrode system formed from a silver nanowire mesh embedded in an organic polymer matrix (see text box "organic solar cell architecture").

With its complex multi-layered structure, surface analysis techniques provide vital insights into the workings of a solar cell. While tactile profilometry and Atomic Force Microscopy (AFM) have been the mainstays of surface metrology for a number of years, 3D confocal laser scanning microscopy (CLSM) is becoming an ever more popular tool.

Combining the ability to generate detailed, true-color optical images with the non-contact capabilities of laser scanning technology, the confocal laser scanning microscope really comes into its own as an optical profilometer. Faster and more efficient than stylus-based techniques, 3D CLSM is able to measure soft or adhesive surfaces and offers a resolution of 0.2 µm.

ORGANIC SOLAR CELL ARCHITECTURE

The most popular organic solar cell architecture is based on a photon-harvesting active layer, sandwiched between two electrodes – one of which must be transparent in order to allow light to penetrate (Figure 1).



Fig. 1: Schematic view of the most popular organic solar cell architecture.

Photons hitting the organic semiconductor generate the charge-carrying excitons, which by the use of two materials – an electron donor and an electron acceptor – are then separated into their separate electron and holes. Driven by an electrical field, the electrons and holes travel toward their respective electrodes, creating the charge separation necessary to form an electrical circuit.

Dr Schiek's research looks at using a transparent silver nanowire (AgNW) mesh electrode to replace the brittle and rare ITO, in addition to forming the active layer from organic materials as an alternative to environmentally damaging chemicals – creating flexible, sustainable and affordable thin-film solar cells for consumer applications.

ORGANIC MATERIALS IN THE ACTIVE LAYER

The active layer is where energy is captured from photons, and within organic solar cells this is often formed from a discontinuous blend of two materials – a polymer and a fullerene. With the polymer acting as an electron donor and the fullerene as an electron acceptor, this bulk heterojunction structure leads to enhanced charge separation of electrons and holes, and hence improved solar cell function. But polymers are often roughly defined mixtures of material with differing chain lengths, and with properties that are highly batch-specific. Molecular semiconductors, on the other hand, are defined building blocks with properties that can be adjusted by small changes to their structure, which can therefore be optimized for improved solar cell function. An interesting class of such molecules are the squaraine dyes (Figure 2), whose structure gives a broad absorption in the red region of the light spectrum. Dr Schiek's research is investigating a bulk heterojunction active layer formed from squaraines mixed with a fullerene acceptor (for more information, see reference 1). The thickness of the active layer is crucial for this application: too thin and the mobility of charge carriers is restricted, but too thick and both light absorbance and flexibility are significantly reduced.

Accurate measurement of layer thickness is therefore equally important. Within Dr Schiek's laboratory, once a scratch is made through the active layer surface with a fine needle, the step edges of this 'valley' are subsequently mea-



Fig. 2A: single crystals exhibit a golden metallic luster.



Fig. 2B: a spincoated layer of neat squaraine, with spherulite aggregates forming through crystallization upon thermal annealing

sured using profilometry. Tactile profilometry was previously relied upon, but the softness of the organic material hampered accurate measurement. In fact, a height discrepancy of around 20 nm was frequently observed between the two step edges, which is significant considering the average thickness of the active layer is 100 nm. As the needle steps up from the valley, it scratches into the surface and results in the false lower height reading.

With 3D confocal laser scanning microscopy, it is the laser that scans the surface, and such a

Fig. 3A: Non-contact profilometry.

non-contact approach achieves far greater accuracy of surface profilometry (Figure 3). Moreover, providing a visual image of the sample is more intuitive, and with the LEXT OLS4100 this information is easily compiled into a report, presenting the image in support of numerical data (Figure 2B).

SQUARAINES UNDER POLARIZED LIGHT

These molecular dyes present a sustainable alternative for the active layer, here visualized between crossed polars.

Accurate metrology of soft material

Formed from soft organic material, the active layer is typically 100 nm thick and easily damaged by contact.

Transparent electrodes

Combining optical transparency with conduction, transparent electrodes form the anode of the solar cell while also allowing light to pass through to the active layer. The rapidly diminishing resource of ITO is currently the industrial standard for transparent electrodes. Moreover, ITO is a brittle material, restricting its use in mechanically flexible devices, and the hunt is on for a lightweight, cheap, flexible alternative that is also compatible with large-scale processing. Graphene presents a potential alterna-

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Fig. 3B: Data compiled into a report.



Fig. 4: A flake of multilayer graphene coated with a light emitting organic semiconductor.

tive, for example (Figure 3), but the flakes are quite small, which limits its use for larger areas.

One promising alternative is a mesh of silver nanowires (AgNWs) embedded in a polymer matrix, and a second project within Dr Schiek's laboratory focuses on the production of the AgNWs, the subsequent pro-

cessing to form the electrodes and ultimately the integration into organic solar cells.

For optimum conductivity, a uniform connection must exist between the active later and electrode, demanding a homogenous AgNW mesh. Since the diameter of AgNWs at 100 nm is equivalent to the thickness of the active layer, it is also important to avoid these regions of aggregation and to prevent puncturing the active layer. However, in practice this is challenging to achieve across the whole solar cell using current spin-coating production techniques, and surface roughness evaluation plays a central role in optimizing the synthesis protocol.

AFM has been the main technique employed for the surface roughness evaluation of the AgNW mesh, but CLSM (using the LEXT OLS4100) has vastly improved the efficiency of this. Firstly, Dr Schiek found that expanding the field of view using the image stitching function allowed her to view a more representative sample of the electrode surface. The AgNW mesh may appear regular on a smaller scale, but by creating high-resolution images of one mm² (ten times greater than possible with AFM), regions of aggregation are easily identified that would otherwise have been missed (Figure 4 A,B). As can be seen in Figure 4C, the software also allows the height profile to be visualized in 3D, useful for both analysis and documentation. Moreover, the ability to increase the low-pass filter from a height of 80 µm to 800 µm allows more insightful analysis of the elevated regions of the silver nanowires.

It is also the case that AFM is time consuming. Not only does the scan itself take up to an hour, after setting up the instrument and adjusting for tip-related artefacts, it can often take a whole day to acquire a single useful image. With 3D CLSM, image acquisition is rapid and also highly intuitive owing to the dedicated software, even for students lacking microscopy experience. In terms of performance, the researchers found that AFM and CLSM produced comparable results, and have benefited from the improved efficiency of surface roughness evaluation of transparent electrodes.

Another interesting aspect of this project is the far-reaching potential of transparent electrodes throughout opto-electronic applications, including LEDs and touch screens, where developing alternatives to ITO is also a focus of intense investigation. In the



Fig. 5A: facilitating analysis of nanowire distribution on a larger scale in brightfield.



Fig. 5B: Height colour plot.



future, opto-electronic interfaces might even enable sight restoration, with retinal implants using light to generate electrical output and stimulating neuronal activity.

This structure is currently under investigation for organic light emitting diodes, while graphene also has potential for use as a transparent electrode – although flakes are too small for larger photovoltaic surfaces. Visualized with crossed.

Surface roughness evaluation of silver nanowire mesh electrodes

Image stitching function expands the field of view, Low-pass cut-off filter set to 800 $\mu m.$

SUMMARY

Feeding the global power grid in a sustainable fashion remains one of the biggest challenges faced by the modern world, and it's an exciting time for research into innovative solutions. The use of widely available materials holds future promise in providing a green alternative to conventional solar cell manufacture, with such investigations driven by the latest technological developments.

From enabling accurate step measurements of the active layer with non-contact profilometry, to improving the efficiency of analysis with speed and advanced software functions, the 3C confocal laser scanning microscope has provided Dr Manuela Schiek's research group with many advantages over stylus-based methods. As alternative energy becomes a greater focus in the coming years, the evolving light microscope technologies are likely to play a central role in the solar revolution.

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01 Nanodiamond-Based Separators for Supercapacitors Realized on Paper Substrates

Giuseppina Polino, Alessandro Scaramella, Valerio Manca et al.

ABSTRACT

Significant interest is focused on developing environmentally friendly supercapacitors. In this context, cellulose-based substrates for energy storage devices can be well-engineered, lightweight, safe, thin, and flexible. Herein, a scalable, low-cost, and easy-to-process approach for the preparation of supercapacitors using large area techniques like spray and blade coating is presented. Symmetric supercapacitors using common copy paper and electronic paper as the substrate and poly(3,4-ethylenedioxythiophene)- poly(styrenesulfonate) (PEDOT:PSS) as electrodes are realized and investigated. This work uses composites based on detonation nanodiamonds (DNDs) and hydroxypropyl cellulose (HPC) as solid-state electrolyte and separator, achieving performance comparable to when in the presence of a liquid electrolyte.

INTRODUCTION

Cellulose-based substrates are considered among the most appealing solutions for green recyclable flexible electronics due to their compatibility with large-scale printing techniques. In that context, cellulose nanofibrils networks ensure a high surface area and a large amount of hydroxyl groups that can be functionalized, tuned, and are compatible with hydrophilic environment.^[1]

In the current work, a route for the realization and characterization of a biocompatible paper-based symmetric supercapacitor using electronic paper and common copy paper as substrates and poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) spray-coated electrodes is proposed. Moreover, we proposed a composite material based on hydroxypropyl cellulose (HPC) and detonation nanodiamond (DND) as separator and as solid electrolyte. DNDs are obtained by the purification of the soot generated through the detonation of explosives and present outstanding properties, such as thermal conductivity, thermal and chemical stability, low electrical conductivity, and mechanical properties (abrasiveness and hardness).^[2] Of particular interest, it has been shown that porous aggregates of DND and of DND dispersed in a polyelectrolyte (Nafion) are capable of increasing the ionic conductivity in the electrochemical system.^[3, 4]

We also compared the performance of devices based on solid electrolyte (HPC + DNDs) and liquid solution electrolyte (HPC + ND + Na₂SO₄) realized on both substrates (copy and electronic paper) using PEDOT:PSS spray-coated electrodes. The performances obtained are comparable with those found in the literature for devices realized on polyethylene terephthalate substrate using spray-coated PEDOT:PSS electrodes.^[5]

METHODS

To investigate the effects of different paper morphologies on the supercapacitor, we used a common acid-free copy paper with alkaline reserve (copy paper) and an electronic ultra-smooth paper designed for high-definition patterning and electroplating (electronic paper). The negative electrode was deposited on paper substrates by spray-coating. A thickness of 400 nm of PEDOT:PSS was obtained. After the deposition of the separator and the solid electrolyte, the positive electrode was spray-coated. The thickness of 300 nm of PEDOT:PSS for the positive electrode was chosen to avoid the melting of the separator, but still maintaining a sheet resistance comparable with the negative electrode. The deposition of the separator and the solid electrolyte was conducted by an automatized blade/ slot-die coater with drying step (hot air).

Morphology characterization of the devices' layers was performed using an Olympus[®] LEXT[™] OLS4000 laser microscope and a field emission SEM. The thickness of the layers was evaluated using a feeler gauge (digital thickness gauge).

Electrical and electrochemical characterizations were made using a four-probe setup connected to a source meter (Keithley 2420), and a potentiostat PGSTAT302N (EcoChemie Autolab B.V.).

RESULTS AND DISCUSSION

The steps of fabrication and the final layout of the device can be seen in Figure 1.

Figure 2 shows the morphology of the spraycoated PEDOT:PSS negative electrode deposited on electronic and copy paper. Here, it is possible to observe that the porous and



Figure 1: Process steps of fabrication; a) final layout (dry device); and b) immersion in liquid electrolyte (wet device).

(а) PEDOT:PSS ON E-PAPER (b) PEDOT:PSS ON COPY PAPER <u>160 µm</u> (c) HPC+ ND ON PEDOT:PSS (E-PAPER) <u>160 µm</u> <u>160 µm</u>

Figure 2: Microscope images of morphology: a) spray-coated PEDOT:PSS electrode on electronic paper substrate; b) spraycoated PEDOT:PSS electrode common copy paper substrate; c) HPC + ND separator on PE-DOT:PSS electrode deposited on electronic paper substrate; and d) HPC + ND separator on PE-DOT:PSS electrode deposited on copy paper substrate.



Figure 3: Layer-by-layer SEM images of the device on copy paper. a) Morphology of spray-coated PEDOT:PSS (negative electrode); b) morphology of the negative electrode blade coated with HPC; c) morphology of the negative electrode blade coated with HPC + DND; d) morphology of spray-coated PE-DOT:PSS (positive electrode) (on HPC layer); and e) morphology of spray-coated PEDOT:PSS positive electrode (on HPC + DND layer). rough nature of the copy paper substrate affects the deposition of the PEDOT:PSS electrode. Comparing the morphology of the HPC + DND separator deposited on the PEDOT:PSS electrodes, it can be noted that a smoother surface can be obtained on electronic paper, whereas for copy paper, the roughness of the starting PEDOT:PSS electrodes affects the separator morphology.

Figures 3 and 4 show layer-by-layer scanning electron microscopy (SEM) images, from the negative electrode to the subsequent upper layers of the final wet device on copy and electronic paper, respectively. On copy paper, the presence of DND seems to strongly affect the substrate roughness, filling the concavities and voids in the paper structure (Figure 3c), thus allowing a better deposition of the positive electrode (Figure 3e), which results in a more continuous and homogenous appearance with respect to the device prepared without DND (Figure 3d). On the contrary, as expected, on electronic paper, a smoother surface is always observed. PEDOT:PSS deposition results a high amount of homogeneity for both electrodes (Figure 4a,d). Conversely to what we observed with copy paper, the presence of DND leads to a rougher surface (Figure 4c,e), without, however, affecting the homogeneity of the deposition. A few Na_2SO_4 electrolyte crystals were observed, especially in the case of electronic paper, where the presence of DND seems to increase the quantity of the electrolyte retained in the separator.

Electrochemical tests of the assembled devices with both the typologies of electrolyte and electrode substrate show only an electric double-layer capacitor (EDLC) behavior. A stronger resistive behavior is produced for solution electrolyte and was observed in charge-discharge tests. We also identified a better charge propagation at lower scan rates. In fact, we observed an increasing shape deviation with an increase in the scan rate, probably due to higher internal resistance. In all the cases, we did not record rectangular-shaped cyclic voltammograms due to the use of PEDOT as electrode material.^[6]



Figure 4: Layer-by-layer SEM images of the device on electronic paper. a) Morphology of spray-coated PEDOT:PSS (negative electrode); b) morphology of the negative electrode blade coated with HPC; c) morphology of the negative electrode blade coated with HPC + DND; d) morphology of spray coated PE-DOT:PSS (positive electrode) (on HPC layer); e) morphology of spray coated PEDOT:PSS positive electrode (on HPC + DND layer).

	C [μF cm ⁻²]	C_{sp} [F g ⁻¹]	Q [μC cm ⁻²]	Ε [μWh cm ⁻²]	Ρ [μW cm ⁻²]
HPC + ND 1% solid electrolyte					
Copy paper	319.14	0.13	255.31	0.056	22.69
E-paper	1248.09	0.52	998.47	0.221	19.48
HPC + ND 1% + Na_2SO_4					
Copy paper	907.37	0.38	725.89	0.161	24.19
E-paper	1957.29	0.82	1565.83	0.347	22.77

Table 1: Electrochemical parameters extracted from charge-discharge cycles.

Supercapacitor parameters were calculated from charge–discharge cycles, are shown in Table 1, and are graphically represented in Figure 5. It is possible to observe that the devices produced with electronic paper show higher values of specific capacitance for both solid and solution electrolytes. Conversely, comparable power densities were achieved for both papers in dry and wet supercapacitors.

Although still an object of study, it is reasonable to assume that the hygroscopic environment guaranteed by the cellulose derivative-based separator allows the deprotonation/protonation of carboxylates and amphoteric functional groups present on the DND surface. As hypothesized by Postnov et al. (2017) and Gareeva et al. (2014),^[3, 4] the presence of DND could also ensure a structural arrangement of ionic channels and pores of DND aggregates and HPC chains organization crucial to charge transfers.

In Figure 8, the normalized capacitance values decay obtained from several charge-discharge cycles for both solid (Figure 8a) and solution electrolytes (Figure 8b) are reported. Devices on electronic paper present much higher capacitance values, and the capacitors realized with a solid electrolyte exhibit higher capaci-



Figure 5: Radar plot comparison of the performance of all the devices realized.

Figure 8: Capacitance evaluated over time obtained for: a) devices on copy paper and electronic paper with solid electrolyte; b) devices on copy paper and electronic paper with solution electrolyte.



tance retention. From this experimental data, we assume that in absence of DND, it is not possible to have significant measures due to observed short circuit of the device. This is ascribable to the deterioration (due to hydrolysis processes) of the thin separator layer, mainly caused by the high acidity of PEDOT electrodes above and below it. The better performance of the device with the solid electrolyte (DND + HPC) if compared with the one with solution electrolyte (DND + HPC + Na_2SO_4) could also be related to the deterioration of the HPC layer that occurs when the device is immersed in the electrolyte solution. Therefore, it is clear that DND manages to preserve the integrity of the separator; however, a significant drop in potential was still observed in the chargedischarge tests of the wet device if compared with the solid-state electrolyte curves.

CONCLUSION

We fabricated symmetric supercapacitors using upscalable techniques and green materials. Our devices are based on conducting PEDOT:PSS polymer electrode sprayed on two different types of papers (i.e., copy paper and electronic paper). Moreover, a new nanocomposite material based on HPC charged with DNDs was used as both separator and solid electrolyte and compared with the same composite wet with a Na₂SO₄ solution electrolyte. This work confirmed DND electrolytic properties due to both its special surface chemistry and its capability to modify and organize the structure of the matrix in which it is dispersed. Moreover, DND has once again proven to be an efficient consolidating material for cellulose derivatives, as we demonstrated that the device does not work in its absence due to the chemical nature of the separator.

The performance of our devices has been evaluated, and maximum power densities of ~24 μ W cm⁻² and specific capacitance of ~0.8 F g⁻¹ were achieved. Our results demonstrate that it is possible to obtain comparable performances on paper substrates with respect to analogous super-capacitors fabricated on plastic substrates with spray-coated PEDOT:PSS electrodes.

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ORIGINAL PUBLICATION

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02 Native Oxide Barrier Layer for Selective Electroplated Metallization of Silicon Heterojunction Solar Cells

Thibaud Hatt, Sven Kluska, Mananchaya Yamin et al.

ABSTRACT

The metallization of silicon heterojunction (SHJ) solar cells by electroplating of highly conductive copper onto a multifunctional patterned metal layer stack is demonstrated. The approach features several advantages: low temperature processing, high metal conductivity of plated copper, no organic making, and low material costs (almost silver-free). A PVD layer stack of copper and aluminum is deposited onto the cell subsequently to TCO deposition. The aluminum layer is patterned with a printed etchant, and its native oxide on the remaining areas inhibits plating. During electroplating, the full-area aluminum layer supports plating current distribution and allows homogeneous plating height distribution over the cell. The NOBLE (native oxide barrier layer for selective electroplating) approach allows reaching a first encouraging SHJ solar cell efficiency of 20.2% with low contact resistivity.

INTRODUCTION

Electroplated copper contacts are particularly attractive for crystalline silicon heterojunction (SHJ) solar cells, which require a low-temperature metallization. Current trends in the silicon photovoltaic field point toward passivated contact architectures for high-efficiency solar cells.^[1, 2]

The symmetrical SHJ solar cell architecture is created by first depositing a thin intrin-

sic amorphous hydrogenated silicon layer – i.e., a-Si:H(i) onto the cleaned and textured c-Si wafer, followed by the doped a-Si:H (n or p), which act as carrier-selective junction. Both ultra-thin a-Si layers are quite sensitive to process temperatures above 200 °C (392 °F).^[3] Typically, a transparent conductive oxide (TCO) is sputtered onto the a-Si:H layers to contact the silicon, promote the lateral conductivity in the solar cell, and to serve as an antireflective coating. The cell architectures then need to be contacted by metalli-



Figure 1: Overview of the low-temperature routes to metallize bifacial SHJ solar cells covered by TCOs.



Figure 2: Sequence and tools used for the low-temperature NOBLE metallization on TCO for bifacial silicon heterojunction solar cells.

zation approaches, where metal paste printing is the most common and metal plating offers promising alternatives. Figure 1 presents an overview of the low-temperature routes to metallize SHJ solar cells covered by TCO.

Our work demonstrates an alternative plating approach containing one step less than the "Resist Masking route" and uses very low amount of silver (Ag). Our novel native oxide barrier layer for selective electroplating ("NOBLE route") aims at improving the process flow with fewer steps and by avoiding the use of any costly organic masks. In this concept, the native oxide of a thin aluminum (Al) layer enables performing selective copper (Cu) plating onto a patterned metal seed. An etchant is inkjet-printed to structure the contact positions in the Al layer. This grid-patterning method is even cheaper than the deposition of a reactive silver ink onto the aluminum.^[4, 5]

The NOBLE metallization route depicted in Figure 2 allows fast and homogeneous electrodeposition of copper onto a multifunctional patterned metal layer.

After vacuum deposition of the PVD layer stack (Figure 2(1)), the grid patterning is achieved by printing a low concentrated alkaline ink or paste to etch the aluminum-aluminium oxide (Al-Al₂O₃) selectively (Figure 2(2)). In the present work, inkjet printing was employed. This selective etching removes the Al layer only in grid positions and does not impact the underlying metal-seed (on top of the TCO). This patterning step allows plating Cu selectively onto the metal seed (Figure 2(3)). At this state, the less noble metal Al and the Al₂O₃ are acting as barrier to inhibit Cu plating in the non-grid positions as described by Hatt et al.^[5] A thin silver capping (≈200 nm) follows to protect the Cu-contacts against oxidation. The remaining PVD layers (Al and metal seed) in nongrid positions are then etched-back by chemical processing without damaging the underlying TCO (Figure 2(4)). On the contact flank, only a few nanometers of Cu are not protected by Ag in comparison to the "Resist route," which leaves several micrometers un-capped.

METHODS

Investigations on metal etching were realized on planar glass (soda-lime glass) with different sputtered metals (Al, Cu, Ag, NiV (93:7), and Ti) Electron-gun evaporation was also used to deposit Al onto glass to observe the impact of the PVD technique on the etching rate for this metal. The metal thicknesses were measured before and after etching using an Olympus[®] LEXT[™] OLS4000 confocal microscope, a profilometer (Dektak - STYLUS PROFILER), or an X-ray fluorescence tool.

After sputtering the metallic layers onto the SHJ solar cells, a PIXDRO LP50 printer from Meyer Burger Technology AG was used to print the grid positions with NaOH_{aq}, thus completely etching the Al. A complete description of the cell fabrication process can be found in the original work. The contact metallization was characterized by the Olympus LEXT OLS4000 confocal microscope after each processing step.

RESULTS AND DISCUSSIONS

The etching selectivity of different metals was studied to enable the selective etching steps mentioned above. There are many solutions that may etch metals deposited by PVD. The investigation was focused on PVD AI, Ti, NiV, Cu, and Ag, which are promising for either low-contact resistance or plating selectivity. The etch rates in nm s⁻¹ are presented in Figure 3 for metals sputtered on planar

glass. Although etching rates might be different on different surfaces, general trends were confirmed to be similar on TCOs and on the textured surface of the SHJ solar cells.

In summary, it was observed that Al can be selectively removed versus Cu or Ag with dilute alkaline solutions and at high etching rates. On the other hand, Cu can be etched with $FeCI_3$ or $(NH_4)_2S_2O_8$, while Ag and Al will remain unaffected.

For the NOBLE processing, both sides of the textured SHJ precursor with ITO are entirely covered by thin layer stacks of either PVD-Cu/ Al (50/100 nm) or Ag/Al (20/100 nm). The selective etching of Al against the metals below (Cu or Ag) enables easy patterning of the grid positions. In the present work, inkjet-printing of NaOH_{aq} was employed to structure lines in the Al-Al₂O₃ layer. Narrow lines in the PVD Al of around 25 μ m wide without spreading or interruption were created. The underlying PVD Cu-seed can be observed in line positions as demonstrated in Figure 4a.

The selective Cu electrodeposition is then performed onto the Cu-seed as observed in Figure 4b. The native oxide, covering the Al surface, acts as inhibitor for Cu deposition out-

Figure 3: Etching rates of thin ($\leq 1\mu$ m) sputtered metal layers removed from planar glass at room temperature in different solutions (*lower NH₃/H₂O₂ concentration)





Figure 4: Microscopic pictures of a finger on the ITO from a SHJ solar cells along the NOBLE metallization after: a) inkjet-printing of NaOH_{aq}, b) Cu-Ag plating, and c) etching-back PVD layers in non-contacted positions.



Figure 5: SEM pictures in the cross-section of the SHJ solar cell covered by ITO after NOBLE metallization: a) finger plated on Cu-seed, b) area on a pyramid flank in non-finger position, and c) finger plated on Ag-seed.

side of the designated contact area. The Cu grows isotropically onto the metal seed, which widens the contact a bit. The Cu deposition is fine-granular, which gives high contact conductivity near the value of the Cu-bulk. A thin silver capping is also deposited to prevent Cu from any oxidation, as seen on the inset.

After plating, the PVD layers are selectively etched back (Figure 4c) in non-grid positions with a solution of H_3PO_4/HNO_3 . SEM images of the fingers' cross-sections (Figure 5) confirms that ITO was not significantly damaged through the etch-back step, and the layers presented good adhesion even with non-optimized conditions. No voids or uncontacted area could be detected, which would increase the resistivity at the interface. Good adhesion was also confirmed by tape testing.

Sheet resistances (R_{sh}) of ITO and contact resistivities (ρ_c) measured on both sides of different stacks after NOBLE metallization are summarized in Table 1. The measured ρ_c shows little difference between PVD metal seed composed by Cu or Ag, which means the use of Cu-seeds can be an efficient way of cost reduction, getting closer to Ag-free metallization. Moreover, our contact stack after NOBLE metallization present similar results to the one used by CSEM to reach a very high efficiency up to 24.1% on a bifacial plated SHJ solar cell.^[6]

SHJ solar cell made with NOBLE metallization presented efficiency (η) of 20.2% and an encouraging fill-factor (FF) of 78.0% was obtained. This is despite the fact that the pseudo fill factor (pFF) of this cell is already limited to only 80.5%, due to the small cell size. Table 2 presents the SHJ solar cell properties under 1-sun illumination.

The open-circuit voltage V_{oc} and pseudo fill-factor pFF limitations result from the non-optimized metal sputtering process on ITO and from the small cell size. The fill factor is impacted by the non-optimal grid design. The short-circuit current J_{sc} might be reduced by the lab-scale etch-back procedure of the PVD layers. Optimizations of the process might exploit further the full potential of the solar cell in combination with the apparently well performing metallization. **Table 1:** Sheet resistances (R_{sh}) of ITO and contact resistivities (ρ_c) of different stacks measured by TLM after NOBLE metallization on commercial SHJ solar cells.

Metal stack	Rsh [Ω sq ⁻¹]	ρ _{contact}	[mΩ cm²]
c-Si (n)/a-Si:H(i/n)/ITO/Cu _{PVD} /Cu-Ag _{plated}	82.7 ± 0.2	4.0 ± 0.4	
c-Si (n)/a-Si:H(i/n)/ITO/Ag _{PVD} /Cu-Ag _{plated}	80.6 ± 0.2	3.5 ± 0.8	
c-Si (n)/a-Si:H(i/p)/ITO/Cu _{PVD} /Cu-Ag _{plated}	169.7 ± 0.5	2.8 ± 0.5	Not influenced
c-Si (n)/a-Si:H(i/p)/ITO/Ag _{PVD} /Cu-Ag _{plated}	120.3 ± 0.4	1.8 ± 0.3	by the bulk

Table 2: SHJ solar cell properties after NOBLE metallization.

Area [cm ²]	V _{oc} [mV]	pFF [%]	FF [%]	J _{sc} [mA cm ⁻²]	η [%]
6.25	718	80.5	78.0	36.1	20.2

CONCLUSION

An alternative approach for low-temperature metallization of solar cells with TCO layer (e.g., SHJ solar cells), which is currently in the early development stage, was demonstrated. It takes advantage of the selectivity of etchants and plating processes toward different metals.

A thin stack of two PVD metal layers were sputtered onto the cell right after the TCO in the same tool without breaking the vacuum. Thus, sputtering costs are kept low, especially for these thin layers and materials such as Al and Cu. These metal layers allow plating the patterned contacts on both sides of the cell at the same time quickly and homogeneously. The selective etching of metals was investigated in a study of etching rates for Al, Cu, Ag, Ti, and Ni in different acidic and alkaline solutions. This selectivity enabled grid patterning of a thin PVD-Al layer by inkjet printing of an alkaline solution. Copper could then be plated in the printed areas, without parasitic deposition, onto the underlying PVD metal-seed due to the presence of native oxide on the Al surface. After electroplating, the thin PVD layers were removed by etching in non-grid positions selectively. Contact resistivity below 3 mΩcm² were achieved on stack systems of ITO-Cu_{PVD}-Cu_{plated}-Ag_{plated}, and the improvement of the sputtering might allow reaching 0.4mΩcm², as reported in the literature. A promising efficiency of 20.2% with a FF of 78.0% was presented on a commercial SHJ solar cell precursor. This approach saves processing steps and consumables as compared to the electroplating into openings in an organic mask.

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O3 Spray-Coated Polymer Solar Cells Based on Low-Band-Gap Donors Processed with *ortho*-Xylene

Luca La Notte, Giuseppina Polino, Claudio Ciceroni et al.

ABSTRACT

Low-band-gap polymer donors in the field of polymer solar cells (PSCs) allow high conversion efficiencies to be achieved. Unfortunately, optimal performance is strongly correlated to the use of chlorinated solvents, known to be toxic in working conditions. For this reason, high-performing PSCs have been only deposited via small-area techniques. We report the use of a PBDTTTC-T:PC₇₀BM blend dissolved in the non-chlorinated solvent *ortho*-xylene for the deposition of spin-coated and spray-coated active layers in direct PSCs. The results in this work open the way to the use of low-band-gap materials in spray-coating, a nonwasteful technique compatible with coating large areas.

INTRODUCTION

Polymer solar cells (PSCs) have attracted the attention of the scientific community because they offer the possibility to fabricate photovoltaic devices by solution processing, enabling a reduction in cost and increase in their potential for application in fields such as consumer electronics and building-integrated photovoltaics (BIPVs).^[1, 2] In recent years, marked improvement was made possible by the use of photoactive layers based on low-bandgap polymers, which allow better harvesting of solar energy compared to the conventionally used material poly(3-hexyl-thiophene) (P3HT). In particular, poly{[4,8-bis-(2-ethyl-hexyl-thiophene-5-yl)-benzo[1,2-b:4,5-b']dithiophene-2,6-diyl]-alt-[2-(20-ethyl-hexanoyl)-

thieno[3,4-b]thiophen-4,6-diyl]} (PBDTTT-C-T) in combination with $PC_{70}BM$ is an effective blend system that reaches high efficiency.^[3-5]

In spite of this remarkable progress, a strong limitation that hinders the scaling-up of PSC fabrication is the use of chlorinated solvents (toxic toward human health and the environment), which serve to effectively dissolve the polymer/fullerene blend to obtain a suitable morphology. Hence, blends dissolved in more eco-friendly solvents have attracted significant interest.

We report on the use of a PBDTTT-C-T: PC₇₀BM composite dissolved in *ortho*-xylene, and deposited both via spin-coating and spray deposition, in direct PSCs. A record conversion efficiency of 8% is achieved by devices with the spin-coated blend, whereas the devices with the spray-coated blend reach an efficiency of 4.4% after proper optimization of the spray parameters.

METHODS

The photovoltaic devices were fabricated on ITO-coated glass substrates. The electron transport layer was PEDOT:PSS VPAI 4083. The PBDTTT-C-T and PC₇₀BM blend (1:1.5) were dissolved in *ortho*-xylene. Undiluted and diluted blends with and without di-iodooctane (DIO) were prepared before deposition.

Glass/ITO substrates were patterned by wet etching. PEDOT:PSS was spin-coated in a glove box and then dried by thermal annealing at 150 °C (302 °F) for 10 minutes in a nitrogen atmosphere. PBDTTT-CT:PC₇₀BM was either spin-coated or sprayed by using a dual-action commercial airbrush supplied by compressed air. After drying, the samples were completed by thermal evaporation of 10 nm of calcium and 100 nm of aluminum in high vacuum.

Optical images of the deposited photoactive layers were acquired by using an Olympus[®] LEXT[™] OLS4000 microscope. The thicknesses of the as-deposited films were measured with a profilometer (Dektak 150). The surface topography was monitored using an A.P.E. Research AFM. Absorption curves were obtained by a UV-VIS-NIR spectrophotometer (Shimadzu UV2550). A custom-made tool comprising a sourcemeter (Keithley, mod.2612) and a monochromator (Newport, Mod.74000) was used to measure the external quantum efficiency (EQE) values of the photovoltaic cells. J–V curves of the devices were evaluated by using a class A solar simulator (ABET Technologies, Sun2000). Before each measurement, the irradiation level at the height and position of the solar cell was verified by a means of a calibrated pyranometer (SkyeSKS1110).

RESULTS AND DISCUSSION

A preliminary investigation was carried out to choose the different solution formulations for spin and spray deposition in order to obtain suitable layers of the PBDTTT-C-T:PC₇₀BM blend dissolved in *ortho*-xylene. We found that the solution used for spin-coating was also applicable for the spray technique; in fact, the pure solution was not viscous and easy to spray. However, we also investigated a diluted solution (1:4) to determine the effect of dilution on film-forming properties of the spray-coated samples. Blend deposition was performed by using blends both with and without di-iodooc-



Figure 1: Optical images of the active layers obtained with various blend formulations and deposition techniques.

Active Layer	Deposition Technique	Thickness [nm]	RMS [nm]
PBDTTT-C-T:PC ₇₀ BM	spin	100	1.52
PBDTTT-C-T:PC ₇₀ BM + DIO	spin	130	3.85
PBDTTT-C-T:PC ₇₀ BM + DIO	spray	122	2.90
PBDTTT-C-T:PC ₇₀ BM (1:4 dilution)	spray	126	1.76
PBDTTT-C-T:PC ₇₀ BM + DIO (1:4 dilution)	spray	120	18.8

 Table 1: Thickness and root-mean-square (RMS) roughness of the active layers with various blend formulations and deposition techniques.

tane (DIO) in order to understand the influence of the additive on the morphology of PBDTTT-CT:PC₇₀BM dissolved in *ortho*-xylene.

Figure 1 shows an optical analysis of the active layers. The DIO additive evidently enhances the surface morphology of the photoactive layer, which should result in a better performance compared to the cases without DIO. In fact, when DIO is not added, large agglomerates of non-dissolved fullerene are visible in the spincoated films, whereas in the spray-coated ones, there is no coalescence among the droplets, with most of them surrounded by coffee rings. Focusing on the diluted blend, DIO improves the appearance of the surface morphology of



Figure 2: UV/Vis absorption spectra of the active layers obtained with various blend formulations and deposition techniques.

the film but coalescence is not at an advanced stage, leading to the deposition of visible droplets that are homogenous in composition but still different in size. Some uncovered areas are noticeable in the layer obtained using the undiluted blend with DIO, suggesting that it is difficult to obtain perfectly uniform coverage by spraying the blend for a few seconds.

A deeper investigation of the surface topography was performed by atomic force microscopy (AFM). The corresponding root-meansquare (RMS) roughness values and layer thicknesses were measured by profilometry and are reported in Table 1. Topographies of spin- and spray-coated active layers without DIO are similar and present low roughness. The addition of DIO increases the RMS roughness of both spin and spray-coated films; in particular, for sprayed layers, the diluted blend with DIO exhibits larger, differently sized domains, showing higher roughness than the diluted blend without DIO. Notably, the RMS roughness is very low in spray-coated PBDTTT-C-T:PC₇₀BM (1:4 dilutions) because the AFM measurement covers only a small area within the large (tens of micrometers) droplets shown in Figure 1 and does not consider the overall topography, which includes the solid content of droplet boundaries, and thereby underestimates the measurement. Regarding thickness, spin-coated active thickness increased with addition of DIO, which can be attributed to the higher viscosity of the modified solution.^[6] Meanwhile, the spray-coated blends with and without DIO have similar thicknesses.

Absorbance spectra (Figure 2) show a greater absorption when DIO is added to the solutions; also, the spectra for the undiluted solutions with DIO used both for spin- and spray-coating match very closely. Regions of lower absorption are apparent in the 1:4

Active Layer	Deposition Technique	Voc [V]	Jsc [mA cm ⁻²]	FF	PCE [%]
PBDTTT-C-T:PC ₇₀ BM	spin	0.57 (0.49±0.14)	5.6 (5.03±0.05)	0.35 (0.33±0.02)	1.1 (0.84±0.33)
PBDTTT-C-T:PC ₇₀ BM	spin	0.78	16.2	0.65	8.0
+ DIO		(0.77±0.005)	(15.1±0.05)	(0.63±0.01)	(7.39±0.34)
PBDTTT-C-T:PC ₇₀ BM	spray	0.72	12.2	0.50	4.4
+ DIO		(0.71±0.02)	(11.1±0.11)	(0.48±0.01)	(3.8±0.55)
PBDTTT-C-T:PC ₇₀ BM	spray	0.39	4.8	0.32	0.5
(1:4 dilution)		(0.34±0.04)	(4.6±0.02)	(0.31±0.005)	(0.48±0.04)
PBDTTT-C-T:PC ₇₀ BM +	spray	0.7	9.6	0.44	2.7
DIO (1:4 dilution)		(0.65±0.03)	(8.1±0.1)	(0.38±0.03)	(2.03±0.47)

Table 2: Electrical performance of the best fabricated devices from various blend formulations and deposition techniques. Average values and standard deviations over eight devices are reported in parentheses.

diluted solution with DIO. Because the thicknesses are approximately the same as in the undiluted spray-coated layer, this decrease may be due to the use of a non-optimized DIO concentration. The lower intensities of the sprayed diluted active layer without DIO suggest a poor morphology of the phase-separated bulk heterojunction (BHJ) materials.

In Table 2 we summarize the photovoltaic performance of the described blend formulations and deposition techniques in terms of short-circuit current density (J_{SC}), open-circuit voltage (V_{OC}), fill factor (FF), and power conversion efficiency (PCE). The film-forming properties of the various solutions deposited by spin and spray-coating, with and without DIO, are clearly correlated to the observed photovoltage in the finished cells. Voc is high only in the presence of DIO, revealing that such an additive is essential in achieving a favorable morphology and proper coverage of the surface, in agreement with the optical analysis in Figure 1. An abrupt decrease of fill factor occurred in the case of spin and spray-coated active layers without DIO, and this may be caused by the poor bulk nanometer-scale morphology. In addition, in the spray-coated layer the droplet boundaries (as evident in Figure 1) hinder charge transport, leading to a high series resistance that heavily affects the J_{SC} and the FF values.

Comparing the performance obtained using the additive in PBDTTT-C-T:PC₇₀BM both for spin and spray-coating, an enhancement of the photo-generated current is observed. This enhancement can be ascribed to improved charge transport at the interface, corresponding to a larger surface roughness (as shown by the RMS values in Table 1) that implies a more uniform distribution of the domains on the active layer's surface.^[6] The different values of J_{SC} observed in the diluted and undiluted cases suggest that the dilution does not achieve the same uniformity in the thickness of the active film, as confirmed by the very large value of roughness in the diluted film. Moreover, the photocurrent is affected by resistive losses (high series resistance).

Remarkable electrical performance is obtained from the device based on the undiluted blend deposited by spray-coating, but it is lower than those from a device using the same blend applied by spin-coating. We ascribe this difference to the spray environment (air) and to non-optimal coverage due to short spraying time. Focusing on the data in the Table 2, a satisfactory reproducibility is observed both for spin- and spray-coating in the case of the undiluted blend, and for spray-coating in the case of the diluted blend. This demonstrates the good control over the process and the ability to generate good coverage by using solutions with different formulations in two different techniques (see Figure 1), providing reliable electrical results.

Figure 3 shows the external quantum efficiency (EQE) spectra of the best-performing devices fabricated with the spin- and spray-coated active layers. Although the solution used to deposited both the layers is the same (PBDTTT-C-T:PC₇₀BM + DIO), the EQE for the spray-coated layer is lower than that

of the spin-coated layer, explaining the lower J_{SC} values; moreover, at short wavelengths the peak associated to $PC_{70}BM$ absorption is not so distinct and at longer wavelengths the profile is decreased, probably due to the lack of a uniform coverage which influences the blend/evaporated contact interface.

The difference between the devices with spin-coated and spray-coated layers is still large, but this work opens the way to the use of low-band-gap materials in spray-coating, a non-wasteful technique that is compatible with large areas and potentially effective for the fabrication of organic photovoltaic devices.

CONCLUSION

We report the results of a study on the behavior of spin- and spray-coated PBCDTTT-C-T:PC₇₀BM active layers, both pristine and with an amount of additive (DIO), to fabricate bulk heterojunction polymer solar cells. This work highlights the critical issues of the spray-coating technique in relation to the use of a low-band-gap polymer. However, we achieve promisingly high efficiencies of 8% for a spin-coated PBCDTTT-C-T:PC₇₀BM layer and 4.4% for a spray deposited layer, both processed in a non-chlorinated solvent in ambient atmosphere. We also demonstrate the importance of the solution used in the improvement of the film quality and the compatibility with large-area processes. Those results are promising to produce organic solar cells with non-chlorinated solvents at low temperatures and low costs.

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© 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim **Figure 3:** EQE spectra of the best performing devices with spin- and spray-coated active layers (undiluted PBDTTT-C-T:PC₇₀BM with DIO).

Advanced Optical Metrology

Part V

Composites

Introduction: Composites

The concept of combining two or more materials to produce an end material with improved and unique properties dates back to 3400 B.C. when Mesopotamians glued wood strips at different angles to create plywood for structural applications. Later, in the 12th century, the Mongols created the first composite bow made of a combination of wood, bamboo, bone, cattle tendons, horn, silk, and pine resin. The modern era of composites began with the development of plastics in the early 1900s ^[1]. Since then, manufacturers, engineers, and researchers have continued to develop composites made using a wide variety of materials for a broad spectrum of applications.

The two constituents of a composite are the matrix and reinforcement, whereby the matrix surrounds and binds the reinforcement. Composites combine the best properties of the constituent materials, which remain separate and distinct within the final composite structure as they do not blend or dissolve each other ^[2]. Composite materials are often preferred to conventional materials, such as metals and ceramics, due to their high specific strength, light weight, ease of fabrication, design flexibility, resistance to fatigue and corrosion, and low cost ^[3–7]. Today, composites are commonly applied in the aerospace, military, automotive, and construction industries, where they have largely replaced conventional materials.

As with all materials used to create objects, defects and damage can occur during manufacture or in service. In service, composites are subjected to static, fatigue, impact loads, and extreme conditions (e.g., high temperatures and moisture), affecting their performance ^[8]. Therefore, it is important to ensure composites' structural integrity, strength, and performance throughout their service life using robust and reliable inspection techniques, especially in safety-critical industries like aerospace. However, compared with conventional materials, which comprise only one type of uniform, isotropic material with known and predictable properties, composite materials are inhomogeneous and anisotropic with varying and less predictable properties ^[9]. Thus, several nondestructive testing techniques have been developed for composite inspection purposes. This introduction briefly describes some composite types discussed in the following digest articles and the most important techniques to inspect and monitor composite materials.

1. COMPOSITE TYPES

Particulate-reinforced metal matrix composites (PRMMCs): PRMMCs consist of a metal matrix reinforced by ceramic or organic particles and exhibit better mechanical properties (e.g., higher stiffness and strength) than the corresponding unreinforced matrix ^[10]. PRMMCs are most commonly manufactured by powder metallurgical and casting processes, with the latter being performed in the liquid or liquid-solid state [11,12]. Their mechanical properties depend mainly on the load-carrying capacity and morphology of the ceramic reinforcement particles. Aluminum has a low density, high ductility, and good corrosion resistance; therefore, it is widely used in PRMMCs. Particle-reinforced aluminum composites are popular because many inexpensive reinforcements and working processes to shape aluminum are available [13]. Moreover, aluminum-based composites are in great demand in the aerospace and automotive industry because of their high strength-to-weight ratio [14]. In the digest article "Wettability of Low Weight Borides by Commercial Aluminum Alloys—A Basis for Metal Matrix Composite Fabrication," the wetting behavior of different boron compounds by aluminum alloys was investigated to identify promising boride reinforcements for the fabrication of aluminum-based composites.

Piezoelectric composites: Piezoelectric materials are commonly used as actuator and sensor materials because of their ability to translate a mechanical impulse into an electric response ^{[15–}

^{17]}. Ceramic/polymer composites in which a ferromagnetic ceramic filler is embedded in a polymer matrix combine the piezoelectric properties of the filler with the flexibility of the matrix. The properties of a composite depend on the number of phases, the volumetric fraction of each phase, the properties of each phase, and the connectivity of the phases [18]. The connectivity describes the configuration; that is, how the phases are interconnected in the composite. Each phase can connect up to three directions, whereby the first configuration number indicates the connectivity of the dispersed filler and the second one that of the matrix. The connectivity of the filler controls the electric flow distribution in the composite ^[19]. Composites with 0-3 connectivity consist of homogeneously dispersed particles in the matrix and are most commonly produced because of their simple fabrication. However, composites with 1-3 connectivity exhibit higher piezoelectric activity because their particles align along the preferred direction in the composite [20, 21]. Piezoelectric composite-based sensors have various applications, especially in the automotive industry, where they are used to assess the acceleration and damping force in semi-active suspension [22, 23]. The digest article "Micro-Structuration of Piezoelectric Composites Using Dielectrophoresis: Toward Application in Condition Monitoring of Bearings" describes the fabrication of a piezoelectric composite-based sensor in 1-3 configuration, consisting of a lead zirconate titanate filler and polydimethylsiloxane matrix, for the condition monitoring of aircraft ball bearings.

Hybrid composites: Hybrid composites comprise two or more types of reinforcements in the same matrix. They are fabricated with the aim to synergize the properties of the reinforcements, leading to materials with superior properties to those of conventional and (non-hybrid) single composites. The overall properties of hybrid composites are considered a weighted sum of the individual constituents in which the inherent advantages and disadvantages are balanced [24]. Thus, the advantageous property of one reinforcement can counterbalance the disadvantageous property of another reinforcement. Accordingly, cost-effective hybrid composites with desired properties can be produced by proper material choice. The mechanical properties of a hybrid composite strongly depend on fiber orientation, fiber length, fiber content, fiber/ matrix adhesion, and failure strain of individual fibers ^[25]. A positive hybrid effect is obtained when the mechanical properties of the hybrid exceed those of the corresponding non-hybrid composites. The properties of a hybrid system consisting of two components can be determined by the rule of mixtures ^[24]: $P_{H} =$ $P_1V_1 + P_2V_2$, where P_H is the mechanical property of the hybrid, P_1 and P_2 the properties of the first and second system, respectively, and V_1 and V_2 the corresponding volume fractions of the systems. Hybrid composites are used in many engineering applications because of their light weight, high strength, and ease of fabrication. In particular, the automotive industry applies hybrid composites for various applications ^[26]. In the digest article "Mechanical Properties and Slurry Rrosion Resistance of a Hybrid Composite SiC Foam/SiC Particles/ EP," a novel hybrid composite is presented consisting of an E-51 epoxy resin (EP) as the matrix and SiC foam/SiC particles as reinforcements. The hybrid composite outperformed the non-hybrid composite SiC_{foam}/EP in terms of mechanical and anti-erosive properties.

2. COMPOSITE INSPECTION SOLUTIONS

Conventional ultrasound testing: Ultrasound testing is the most commonly used nondestructive inspection method for composite materials ^[27]. In ultrasound testing, a transducer generates high-frequency waves that propagate through the material before being received by the same or a second transducer. As the motion of any wave is affected by the medium (e.g., composites) through which it propagates, one or more of the following parameters associated with high-frequency waves are changed: scattering, frequency, transit time, and attenuation^[27]. The changes in these parameters provide valuable information on the properties of materials, such as hardness, elastic modulus, density, and grain structure. Therefore, ultrasonic testing can evaluate composites and detect flaws, such as hidden cracks, voids, and porosity. However, conventional ultrasound testing is often unsuitable for composite inspection because of their inhomogeneous and anisotropic nature ^[28]. Ultrasound wave propagation in anisotropic composites is intricate and accompanied by random scattering and high attenuation of ultrasound waves, impeding defect detection ^[27, 29].

Phased array ultrasound testing: Phased array ultrasound testing can overcome the limitations of conventional ultrasound testing by steering ultrasound waves to create constructive interference of the wavefronts, focusing the energy ^[30]. In contrast to conventional ultrasound testing where a single-element transducer generates ultrasound waves, phased array ultrasound testing systems use multi-element transducers that can be separately pulsed in a programmed manner. Each transducer emits a spherical wave at a specific time so that the superimposed wavefront steers and shapes the final beam. In this way, a vast number of ultrasound beam profiles can be generated from a single probe, enabling electronic scanning. These capabilities make phased array ultrasound testing a powerful, nondestructive composite inspection solution that is rapidly becoming more popular in the composite industry.

Confocal laser scanning microscopy (CLSM): CLSM is an optical imaging technique that combines high-resolution optical imaging with depth selectivity, allowing the collection of two-dimensional images at different depths (optical slicing) and, consequently, the construction of three-dimensionally resolved images of the investigated sample. CLS microscopes comprise a confocal optical system with a spatial pinhole positioned in front of the detector that eliminates out-of-focus light, leading to micrographs of high optical resolution with excellent contrast. In detail, when a laser illuminates the pinhole, the light emitted from the pinhole passes through a beam splitter and is focused by an objective lens to a spot on the sample, which is placed at the focal plane [31]. Light reflected from this spot on the sample's surface travels back to the beam splitter, where it is converged on the pinhole and directed toward the detector. Light reflected from parts of the sample outside the focal plane is not detected.

Although the confocal microscope was invented in 1953 by Minky [32], his invention remained largely unused until the development of lasers, providing the system with a light source of sufficient brightness and stability. Since then, CLSM has been widely used to study and inspect composites. CLSM has some key advantages over conventional widefield microscopy in the field of material science ^[33]. For example, three-dimensional imaging by CLSM allows detailed analysis of the (micro-) structure of composites without the need for thin material sections. Furthermore, the horizontal and vertical resolution of CLSM is higher than that of conventional light microscopy. Thus, CLSM represents an excellent composite inspection solution. Three of the following digest articles demonstrate the application of CLSM to analyze the surface morphology of different composite materials.

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Wettability of Low Weight Borides by Commercial Aluminum Alloys — A Basis for Metal Matrix Composite Fabrication

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ABSTRACT

Boron compounds are promising candidates for reinforcing metals because of their high strength and stiffness at low specific weights. For composite fabrication, wetting behavior is important. Isothermal wetting of B_4C , AlB_2 , CaB_6 , MgB_2 , and TiB_2 by liquid pure aluminum (99.5%) and the alloy AlSi10MgMn was studied at 700 °C (1292 °F) for 15 minutes in a vacuum using the dispensed drop method. No wetting occurred for all substrates during testing. The contact angles remained constant for CaB_6 , MgB_2 , and TiB_2 , while those for AlB_2 and B_4C decreased continuously with time.

INTRODUCTION

Particulate-reinforced aluminum metal matrix composites (MMCs) combine the beneficial properties of aluminum (low density and high ductility) and ceramic reinforcement materials (high strength and modulus), making them attractive engineering materials for the aerospace and automotive industries [1, 2]. The most commonly used manufacturing processes for particulate-reinforced MMCs are powder metallurgical and casting processes ^[2,3]. Aluminum casting is typically performed at approximately 700 °C (1292 °F); thus, the particulate reinforcements should be stable under these conditions. To obtain stiff and lightweight MMC parts, the reinforcement particles should increase the mechanical properties and decrease the density of the composite. Depending on the loading geometry, the effect of density may be

more important than the mechanical properties, which is why low weight metal borides are attractive reinforcement materials.

Various metal borides are available; some of them are summarized in **Table 1**. In this study, we focused on stiffness, whereby particles with high Young's modulus and low density provide the greatest enhancement in composite stiffness. TiB₂ promises the most efficient enhancement in Young's modulus; however, taking the density into account, the highest specific stiffness can be achieved by adding CaB₆ and B₄C (**Figure 1**).

Many attempts have been made to disperse ceramic particles in liquid aluminum alloys, but the poor wettability of most ceramic particles with liquid aluminum promotes the agglomeration of particles in the melt and hinders homogenous particle distribution.

Properties	AlB_2^{a}	$B_4 C^{a)}$	$CaB_6^{a)}$	$MgB_2^{a)}$	TiB ₂ ^{b)}
Purity [%] Theoretical density [kg m ⁻³] Young's modulus [GPa] Bulk density [kg m ⁻³] Pycnometer density [kg m ⁻³] Total porosity [%] Open porosity [%] Roughness Ra [μm]	$\begin{array}{c} 99.5\\ 3.19^{[23]}\\ 244-269^{[25,26]}\\ 2.43\\ 2.68\\ 23.82\\ 9.03\\ 1.84\end{array}$	$\begin{array}{c} 99.5\\ 2.52^{[24]}\\ 441-472^{[25-31]}\\ 2.51\\ 2.52\\ 0.40\\ 0.63\\ 0.30\end{array}$	99.5 $2.45^{[23]}$ $451^{[23]}$ 1.78 2.46 27.35 27.50 2.98	$\begin{array}{c} 99.5\\ 2.57^{[23]}\\ 278-299^{[25,32,33]}\\ 1.90\\ 2.57\\ 26.07\\ 25.50\\ 1.31\end{array}$	$\begin{array}{r} 99.9\\ 4.52^{[23]}\\ 500-581^{[23,25,34-36]}\\ 3.74\\ 4.28\\ 17.26\\ 12.67\\ 1.99\end{array}$

Table 1: Properties of the ceramic substrates used for the wettability studies and calculation of the composite stiffness. a) produced by Metallic Flex GmbH (Habichtswald, Germany); b) produced by Mateck GmbH (Juelich, Germany).

> There are different testing procedures to measure the contact angle and thus the wetting behavior of aluminum in contact with ceramic substrates. In the classical sessile drop procedure, the ceramic substrate and aluminum sample are jointly heated from room temperature (contact heating), whereas in the dispensed drop procedure, the aluminum sample is heated separately and squeezed onto the substrate from above (non-contact heating). In the dispensed drop procedure, the liquid aluminum drop is free of oxides; that is, the result is supposed to be free from artifacts, at least at the beginning of the test ^[4].

While there are studies on the wetting properties of TiB_2 and B_4C with pure aluminum, no data on the wetting properties of AlB_2 , CaB_6 , and MgB_2 with liquid aluminum and its alloys have been published so far.

Therefore, in this study, the wetting behavior of the aluminum alloys Al99.5 and AlSi10MgMn with the substrates AlB₂, B_4C , CaB_6 , MgB_2 , and TiB_2 was investigated at a moderate temperature (700 °C, 1292 °F) and time (15 minutes) using the dispensed drop method.

METHODS

The boride substrates for the wetting investigations were produced via hot pressing, and their densities were measured using a helium pycnometer and compared with the theoretical and bulk densities to quantify the amount of porosity. After grinding and polishing, the surface roughness of the substrates was measured using an Olympus[®] LEXT[™] OLS4000 laser scanning microscope. The properties of the ceramic substrates are listed in **Table 1**.

The wetting kinetic tests were performed at the Foundry Research Institute (Cracow, Poland).

A detailed description of the experimental procedure can be found in Eustathopoulos et al. ^[4] and Sobczak et al. ^[5]. The dispensed drop method was applied in all tests to produce oxide-free droplets ^[4]. For this purpose, the aluminum sample was placed in an alumina capillary located above the substrate inside a molybdenum furnace and then (non-contact) heated to 700 °C (1292 °F) within 60 minutes in vacuum (<10⁻⁵ mbar). When the testing temperature was reached, the melt was pushed and dropped onto the substrate. Images of drop/substrate couples at 700 °C were recorded for 15 minutes using a high-resolution CCD camera, and contact angles were calculated.

RESULTS AND DISCUSSION

Depending on the initial powder size and hot-pressing parameters of the ceramic substrates, the density and corresponding porosity varied over a wide range (**Table 1**). For



Figure 1: Stiffness index $E^{1/3}/\rho$ as a function of the reinforcement content.

AlB₂, the bulk and pycnometer densities differed significantly from the theoretical density. This could be due to an incomplete reaction between the aluminum and boron powder during hot pressing, resulting in a mixture of boron, aluminum, and AlB₂ phases. The amount of total porosity (i.e., the difference between the theoretical and bulk density) can be divided into the closed and open porosity; the latter influences the surface roughness and wetting properties of the material. Although all substrates were polished in the same way, their surface roughness varied from 0.3 to 2.98 μ m due to differences in their open porosity. Rough surfaces can affect the spreading of the liquid drop, leading to apparent contact angles ^[4, 6]. Although MgB₂ exhibited a large amount of open porosity, its roughness was lower than that of TiB₂, AlB₂, and CaB₆ because of differences in the hot-pressing process and initial powder size. Moreover, polishing can clog the pores of the



Figure 2: Isothermal wetting kinetics of the dispensed drops at 700 °C with the changes in drop diameter and height for Al99.5 and AlSi10MgMn on (a) CaB₆, (b) MgB₂, (c) TiB₂, (d) B₄C, and (e) AlB₂.

surface, and, as a result, lower surface roughness is measured by laser scanning microscopy while still a large amount of open porosity can occur as the helium pycnometer measurement is not affected by surface clogging.

Figure 2 illustrates the time-dependent wetting behavior of the investigated ceramic substrates with Al99.5 and the AlSi10MgMn alloy at 700 °C (1292 °F) for 15 minutes. No wetting (contact angle θ >90°) occurred for all examined couples. The contact angles for Al99.5 were higher than those for AlSi10MgMn, except for the MgB₂ substrate in which case the contact angle for Al99.5 was slightly lower (~4°). The reason for the lower contact angles for the AlSi10MgMn alloy is that most alloying elements, especially the combined addition of silicon and magnesium, reduce the surface tension ^[7].

Furthermore, different drop spreading characteristics were identified. A non-wetting behavior with no spreading was observed for CaB₆, MgB₂, and TiB₂. The contact angles remained almost constant for 15 minutes for both the pure aluminum and alloy. Consequently, the height and diameter of the liquid drop also remained constant (Figure 2). The initial contact angles measured immediately after drop dispensing were approximately 126°–127° for AlSi10MgMn on CaB₆, MgB₂, and TiB₂ and 134°–136° for Al99.5 on CaB₆ and TiB₂. After 15 minutes, the contact angle for Al99.5 on TiB₂ decreased by $3^{\circ}-4^{\circ}$, and the drop diameter increased slightly by 5%. However, these changes were too small to assume a reactive wetting behavior. Even the large amount of open porosity did not lead to the infiltration of liquid aluminum.

A different wetting behavior was observed for AIB_2 and B_4C for which drop spreading occurred with time. Liquid aluminum reportedly reacts with B_4C by forming intermetallic phases; however, the wettability is poor at temperatures below 900 °C (1292 °F) ^[8, 9]. The initial contact angles were 118° and 126° for AlSi10MgMn and Al99.5 on B_4C , respectively. A decrease in the contact angle by 11°–13° and slow spreading were observed along the B_4C surface as the drop diameter increased, and the drop height decreased during testing.

Both Al99.5 and AlSi10MgMn penetrated the AlB₂ substrate during testing, leading to decreased drop heights but constant drop diameters. The initial contact angles after drop deposition were 119° and 129° for AlSi10MgMn and Al99.5, respectively, which after 15 minutes decreased to 107° and 120°, respectively. The AlB₂ substrate was probably a mixture of boron, aluminum, and AlB₂ phases, significantly influencing its wetting behavior. In the absence of disturbing oxide layers, liquid metals wet metal surfaces. Therefore, aluminum impurities present in the substrate could exhibit strong adhesive interactions with the liquid aluminum drop, forcing the spreading of the drop. However, due to the open porosity and surface roughness of the substrate, the liquid aluminum drop preferred to infiltrate the AlB₂ substrate.

CONCLUSION

The wetting behavior of the liquid aluminum alloys Al99.5 and AlSi10MgMn on B_4C , AlB_2 , CaB_6 , MgB₂, and TiB₂ was investigated at 700 °C (1292 °F) for 15 minutes via the dispensed drop technique. No wetting occurred within 15 minutes for all substrates and alloys. The contact angles of both aluminum alloys remained almost constant on CaB₆, MgB₂, and TiB₂ during testing. However, for B₄C and AlB₂, changes in the drop shape were observed, indicating reactive wetting. In addition, alloying elements reduced the contact angles of AlSi10MgMn, which were lower than those of Al99.5 on most substrates.

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02 Micro-Structuration of Piezoelectric Composites Using Dielectrophoresis: Toward Application in Condition Monitoring of Bearings

G. D'Ambrogio, O. Zahhaf, Y. Hebrard et al.

ABSTRACT

A piezoelectric material based on inorganic/organic composites suitable for aerospace and aeronautical monitoring sensors was fabricated. The designed piezoelectric composite was made of a lead zirconate titanate (PZT) filler embedded in a polydimethylsiloxane (PDMS) matrix. To improve the piezoelectric properties of the film, we increased the connectivity of the ceramic filler via electric field-assisted structuration, leading to a columnar arrangement of the filler across the thickness. This structure (1-3)showed higher piezoelectricity than one with a randomly dispersed filler (0–3). Piezoelectric and dielectric activities of PZT/PDMS in 0–3 and 1–3 configurations were compared at different volume fractions. The 1–3 connectivity led to superior piezoelectric behavior. Thermal stability and high-temperature X-ray diffraction analyses indicated that the composites were stable and maintained a good piezoelectric response even at 200 °C (392 °F). Following process optimization, the piezoelectric behavior of this new class of composites approached that of fluorinated ferroelectric polymers, with the advantage that the stability of the piezoelectric properties was preserved at a higher temperature and lower poling electric field. In conclusion, there is potential for integrating the designed sensor in aircraft ball bearings for condition monitoring.

INTRODUCTION

In aeronautics and aerospace, there is a growing need for new sensor materials suitable for direct health condition monitoring of complex structures. The main requirements when designing such sensors are sensibility, frequency bandwidth, and temperature drift ^[1, 2]. For simple system integration, these sensors must also be light and non-intrusive for the system with high mechanical resistance and easy processability.

Due to their ability to translate a mechanical impulse into an electric response, piezoelectric materials are commonly used as sensors in vibration monitoring, impact detection, and ultrasonic receiving sensors ^[2–5]. Different classes of piezoelectric materials exist, such as ferroelectric ceramics, piezoelectric polymers, and piezoelectric composites made of a ferroelectric ceramic filler embedded in a polymer matrix. Piezoelectric composites are most suitable for the above applications as they combine the piezoelectric properties of the filler with the flexibility of the matrix ^[5]. Furthermore, they are characterized by a low poling electric field and high Curie temperature, making them more suitable than ferroelectric polymers ^[6]. Being well workable, piezoelectric composites can be simply integrated into complex designs ^[5].

Phase arrangement is a key factor influencing the piezoelectric properties of a composite. Composites with 0–3 connectivity are most commonly produced because of their simple fabrication. However, they exhibit low piezoelectric sensibility until they reach large volumetric filler contents, which in turn deteriorate the mechanical properties ^[7]. A solution to this problem is to align the fillers in columns within the matrix. In such anisotropic structures, called 1–3, the particles are closely aligned along the preferred direction, enhancing the piezoelectric properties of the whole material ^[4, 5].

In this study, dielectrophoresis was used to develop a piezoelectric sensor coating consisting of a polydimethylsiloxane (PDMS) matrix filled with lead zirconate titanate (PZT) particles. The effect of the particles' alignment on the piezoelectric and dielectric properties was investigated using 0–3 and 1–3 PZT/PDMS composites with particle volume contents ranging from 3.2% to 24%. The thermal stability and influence of the poling electric field amplitude on the piezoelectric properties of the composites were also investigated. Furthermore, the dielectrophoresis process was examined for its dependence on the electric field frequency. Finally, as piezoelectric composites are widely exploited in the health monitoring system of structural components ^[4, 5], a potential application is described, indicating that the proposed 1–3 material sensor is suitable for condition monitoring in aircraft bearings.

METHODS

For sample fabrication, linear vinyl terminated PDMS consisting of a base and a crosslinker was selected as the matrix and PZT as the piezoelectric phase. PZT powder and silicone base were mixed by ultrasonication, and the cross-linker was added at a ratio of 1:10 (curing agent/base). The 0–3 composites were prepared by casting the dried mixture as a film on a glass substrate. The casting film was cured for 30 min at 120 °C (248 °F). Finally, the fabricated films were cut into circular shapes, and gold electrodes were sputtered onto both sides of the composites. The 1–3 composites were prepared by pouring the dried mixture into a mold positioned between two aluminum plates. The aluminum plates acted as electrodes for the structuring field. The mold was first incubated for 15 minutes at 25 °C (77 °F) and then for 1 hour at 120 °C (248 °F). During incubation, an AC electric field (amplitude, 2 V µm⁻¹) was applied, leading to aligned particle chains along the poling direction. Samples in both 0-3 and 1-3 configurations were prepared with different PTZ volume contents (3.2%, 12%, and 24%).

The dielectric permittivity of the 0-3 and 1–3 PZT/PDMS composites was determined by dynamic dielectric spectroscopy. To assess the piezoelectric behavior of the composites as a function of particle volume fraction (ϕ), all samples were poled at 100 °C for 30 min under an applied DC electric field (amplitude, $20V \mu m^{-1}$). Composites with the same filler content (24 $\%_{vol}$) were poled under different electric fields (5, 10, 20, and $30 V \mu m^{-1}$) to evaluate the dependence of the piezoelectric behavior on the poling electric field. In addition, the piezoelectric charge coefficient (d_{33}) of all samples was determined and evaluated as a function of the volume fraction and the poling electric field.

To investigate the thermal stability of the piezoelectric composites, we used samples with the same particle content $(24\%_{vol})$. After poling, the composites were annealed for 10 min-



Figure 1: Microscope images of (a) 0–3 PZT/PDMS with 3.2% vol, (b) 1–3 PZT/PDMS with 3.2% vol, and (c) 1–3 PZT/PDMS with 12% vol.

utes in a short circuit at various temperatures (25 °C, 50 °C, 100 °C, 150 °C, and 200 °C (77 °F, 122 °F, 212 °F, 302 °F, and 392 °F)). The samples were then cooled to 25 °C (77 °F), and the d_{33} response was recorded. The morphology and structure of the composites were investigated by X-ray diffraction (XRD) at 25 °C (77 °F), 150 °C (302 °F), and 200 °C (392 °F).

For the dielectrophoresis process, two parallel strips of conductive tape (electrodes) spaced 1 mm apart were placed on a glass microscope slide. A $3.2\%_{vol}$ PZT/PDMS solution was placed on the slide. After applying an electric field between the two stripes, the dependence of the particle's alignment on the electric field frequency was studied at 2 Hz and 2 kHz (constant amplitude, $2V\mu m^{-1}$). The microstructures of the particle chains were observed with an Olympus[®] BH microscope.

The full article of this digest includes a detailed description of 0–3 and 1–3 connectivity models.

RESULTS AND DISCUSSION

The dielectric permittivity of the structured sample (1–3) was significantly greater than that of the randomly dispersed sample (0–3). Compared with the 0–3 composites, the 1–3 composites filled with $12\%_{vol}$ and $24\%_{vol}$ PZT showed an approximate three- and two-fold increase in permittivity, respectively. In 1–3 composites, the dielectric particles are closely packed in the alignment direction and less shielded by the polymer matrix, causing a higher permittivity in the column direction. This is the first proof that dielectric poperties of composites. The dielectric permittivity

ity of the 1–3 composites was comparable to that of fluorinated ferroelectric polymers ^[8].

The 1–3 composites also exhibited markedly enhanced d_{33} values, regardless of their volume content. This can be explained by the more favorable distribution of the electric field in structured composites, allowing greater polarization. Plotting the d_{33} values of the 1–3 composite (24%_{vol} PZT) against increasing poling field amplitudes revealed a saturation of the poling level at 20 V µm⁻¹ above which all the dipoles in the particles were oriented. Higher electric fields did not further increase the piezoelectric response. Even at this low poling field, the d_{33} value of the 1–3 composite was similar to that of classical ferroelectric polymers, which usually require an electric field of >100 V µm⁻¹.

The piezoelectric activity of the composites was also analyzed at high temperatures to investigate their thermal stability. Both 0-3 and 1–3 PZT/PDMS (24%vol PZT) composites maintained their piezoelectric activity up to a temperature of 100°C (212 °F), above which d_{33} started to decrease gradually. Between 150 °C and 200 °C (302 °F and 392 °F), d₃₃ decreased by 20%-30% due to some temperature-induced structural changes in the crystalline cells. Beyond 350 °C (662 °F), which is the Curie temperature of PZT, the PZT particles exhibit a morphotropic phase boundary (MPB) perovskite structure, whereas, above the Curie temperature, the cell structure is cubic ^[9]. The MPB cell is formed by the coexistence of rhombohedral and tetragonal ferroelectric phases, whereas the cubic cell is symmetrical and paraelectric ^[9]. In the high-temperature XRD analysis, the rhombohedral phase peak of the 0-3 and 1-3 samples decreased with increasing temperature, leading to an increase in the tetragonal phase. At 200 °C





Volume fraction [%vol]	d₃₃ 0–3 [pC N ⁻¹]	d₃₃ 1–3 [pC N ⁻¹]
0	0	0
3.2%	0.07	2
12%	0.1	5.2
24%	5.4	12.45

Table 1: Piezoelectric charge coefficient, crystalline volume fraction, poling electric field, and FoM of the present composites compared with those of conventional piezo-electric composites and polymers.

(392 °F), the symmetry was only tetragonal. This was more noticeable in 0–3 than in 1–3 composites, indicating that the lattice stability of the structured composites was higher. These results indicate that the present composites, regardless of their structure (random or aligned), can withstand temperatures up to 200 °C (392 °F) without significantly changing their piezoelectric behavior. This makes them more suitable for high-temperature applications than classical ferroelectric polymers, which are more temperature-sensitive.

Electrically induced structures in 0-3 and 1-3 PZT/PDMS composites with volume fractions of $3.2\%_{vol}$ and $12\%_{vol}$ were visu-

ally observed. In the 0–3 sample $(3.2\%_{vol})$, the particles dispersed randomly (**Figure 1a**), whereas, in the 1–3 sample $(3.2\%_{vol})$, they exhibited a chain-like structure (**Figure 1b**). In the 1–3 PZT/PDMS composite with $12\%_{vol}$ PZT, the filler arranged in a columnar disposition with denser columns due to the increased volume fraction (**Figure 1c**).

The dependence of the dielectrophoresis process on electric field frequency was analyzed. **Figure 2** shows the isotropic structure of the 0–3 composite before the process and the aligned inorganic particles within the polymer matrix after applying an electric field at different frequencies (2 Hz and 2 kHz). Structuring was more effective at 2 Hz as the particle columns were more defined and continuous than those obtained at 2 kHz. The average thickness of the columns was 23.9 µm at 2 kHz and 48.6 µm at 2 Hz. Moreover, the d_{33} value of the 1–3 composite (24%_{vol}) processed at 2 Hz was 28% higher than that of the composite processed at 2 kHz.

The present composites were then compared with other piezoelectric composites and polymers in terms of d_{33} , poling electric field (E_{Pol}) , and volumetric fraction of the crystalline phase (φ_{Cr}) . On the basis of these parameters, a figure of merit [FoM = $d_{33}/(E_{Pol} \times \varphi_{Cr})$] was calculated, indicating the profitability of the materials (**Table 1**). According to this

FoM, the 1–3 PZT/PDMS composite is superior to other reported materials $^{[10-17]}$.

Rolling-element bearings are an important part of jet engines, and condition monitoring can help detect bearing faults and predict bearing life. However, the development of smart bearing coatings is complex because of the extreme bearing environment (e.g., high shaft rotational speed, vibration, and temperature). Piezoelectric coatings are promising candidates for developing smart bearings as they are thermally stable and easy to process. **Figure 3** shows the implementation of the present piezoelectric layer on a bearing.

The sensing response of the piezoelectric coating was compared with that of a classical accelerometer. Regarding the temporal response, the signals of both sensors had a similar appearance of vibrations; that is, the amplitude was relatively small and steady before rotation but varied and increased significantly during rotation (Figure 4a). This observation indicates that piezoelectric materials can provide information on the vibration. To further analyze these responses, we performed a fast Fourier transform (FFT)-based frequency method. Figure 4b shows the frequency content of the sensing signal of the piezoelectric coating and the classical accelerometer, which is a simple way to locate frequencies characteristic of faults [18]. The frequency spectra of both sensors differed as they represented different physical quantities. The piezoelectric coating reflected bearing deformations, the frequency harmonics of which (multiples of 12 Hz) were

lower than those produced by the accelerometer (50 Hz), which, in contrast, were related to bearing rotation. Based on the frequency-time analysis shown in **Figure 4b**, variations in rotational speed could be identified.

CONCLUSION

This work highlights the effects of dielectrophoresis on piezoelectric composites made of a silicone matrix doped with PZT particles. The columnar arrangement of particles along the field direction led to significantly improved dielectric and piezoelectric performances. The d_{33} values of 1–3 composites were markedly higher than those of 0-3 composites, regardless of their PZT concentration. The achieved properties make 1-3 composites an excellent alternative to classical ferroelectric polymers as they exhibit similar piezoelectric properties but at a lower poling electric field. The piezoelectric activities of the 0-3 and 1-3 composites were thermally stable up to 200 °C (392 °F). XRD analysis confirmed the structural stability of the composites at different temperatures. These results indicate that the present composites are more suitable for high-temperature environments than ferroelectric polymers. Furthermore, the 1–3 composite was superior to other piezoelectric composites and organic ferroelectric polymers in terms of piezoelectric activity, filler volume content, and poling field. Therefore, the 1-3 piezoelectric material is an excellent candidate for various applications in multifunctional sensing devices, particularly for condition



Electronic interface

Figure 3: Illustration of the piezoelectric coating for bearing condition monitoring.



Figure 4: Responses of a piezoelectric coating mounted on a bearing (red curve) and a classical accelerometer (blue curve). (a) Temporal response and (b) frequency response obtained via FFT and frequency-time analysis (blue background).

monitoring of ball bearings in the aeronautic area. By depositing the piezoelectric element on a bearing ring, we could detect local vibrations indicative of imminent bearing failure. Thus, the piezoelectric material represents a cheap alternative to common accelerometers.

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03 In Situ Integration of SERS Sensors for On-Chip Catalytic Reactions

B. Han, Y.-Y. Gao, L. Zhu et al.

ABSTRACT

The rapid progress of microfluidics has contributed to modern analytical methodology. However, in situ integration of chemical/biological sensors for on-chip reaction monitoring remains a big challenge. Here, a graphenebased catalytic chip with surface-enhanced Raman scattering (SERS) sensors was fabricated by laser scribing of a graphene oxide (GO)-silver nanoparticle (AgNP) composite (AgNPs@GO). The surface plasmonic effect of AgNPs promoted the photoreduction of GO (RGO), inducing a highly porous nanostructure. By combining the AgNPs@RGO composite patterns with polydimethylsiloxane microfluidic channels, a bifunctional microfluidic chip was fabricated capable of on-chip catalysis and SERS detection. As a proof-of-concept demonstration, onchip AgNP-catalyzed 4-nitrophenol reduction was performed while the reaction process was monitored by the in situ SERS sensor. The integration of SERS sensors with functional microfluidic devices holds great promise for developing advanced Lab-on-a-Chip systems.

INTRODUCTION

Lab-on-a-Chip (LoC) systems are highly integrated devices allowing multiple experimental procedures, including sample injection, reaction handling, product separation, and component analysis, on a single chip ^[1]. The ultralow consumption of fluids makes LoC favorable in medical diagnostics, environmental monitoring, and chemical analysis ^[2–4]. To further extend the functionalities of LoC devices, various functional components have been successfully integrated with microfluidic chips, which significantly facilitated automatic analysis ^[5]. Nevertheless, most of these proof-of-concept devices cannot be applied in real production as the fabrication of these multifunctional LoCs generally involves complex manufacturing procedures ^[6]. The channel networks need to be specially designed, and the on-chip fabrication techniques are usually highly precise 3D nanotechnologies that are not yet fully developed for market-oriented commercialization. Therefore, realizing multi-functionalization on a single chip remains a big challenge.

Laser scribing technology that converts near-infrared light (NIR, \approx 780 nm) inside a digital versatile disc (DVD) drive into localized heat is a cost-effective and simple tool for flexible patterning of graphene and many composite materials ^[7]. Laser-scribed graphene oxide (GO) has been widely used to produce electronic devices because of its good mechanical properties, high electrical conductivity, and high surface area ^[8]. Thus, laser scribing of GO is promising for fabricating graphene-based chemical sensors, actuators, and various electronics, which may contribute to the development of microfluidics. However, laser scribing of GO has not been fully applied to LoC functionalization.

In this study, a surface-enhanced Raman scattering (SERS)-active catalytic chip was fabricated by laser scribing of GO/silver nanoparticle composites (AgNPs@GO). The surface plasmonic effect of AgNPs promoted the photoreduction of GO, leading to a highly porous nanostructure. The well-exfoliated graphene served as an excellent catalytic scaffold for AgNPs. The dense distribution of AgNPs on the laser-scribed graphene led to a plasmonic structure, making the microfluidic chip SERS-active. Combining a catalyst bed with the SERS substrate enabled on-chip catalysis and in situ SERS monitoring of 4-nitrophenol (4-NP) reduction. Thus, integrating SERS sensors with functional microfluidic devices holds great promise for developing advanced LoC systems in the future.

METHODS

The composites AgNPs@GO-1–3 were prepared by UV photoreduction. Briefly, GO (10 mL, 4 mg mL⁻¹) was mixed with different amounts (5, 10, and 15 mL) of Ag(NH₃)₂OH, and the resulting solution was irradiated under UV-light (500 W) for 10 minutes. The final composites were obtained after washing with deionized water.

Each AgNPs@GO composite (20 mL) was cast onto a LightScribe-enabled disc to obtain a homogenous film. The disc was then inserted into a laser-scribe-enabled DVD drive equipped with an NIR laser (780 nm), and predesigned patterns of channel networks were directly "written" onto the composite film. Each AgNPs@GO composite was reduced to AgNPs@ RGO (RGO, reduced GO) during laser scribing. Laser-scribed AgNPs@RGO was selectively transferred to a polydimethylsiloxane (PDMS) substrate by simple stamping. A PDMS microfluidic layer with conformal channel networks was then combined with the SERS-active PDMS substrate, and the two PDMS layers were sealed together to create an SERS-active catalytic chip.

For SERS detection, the laser power on the samples was adjusted to \approx 30 µW, and the average spot size was 1 µm in diameter using a long-working distance 50 × objective. SERS spectra were recorded on an instrument equipped with a liquid-nitrogen-cooled argon-ion laser at 532 nm using an exposure time of 5 seconds and three accumulations.

The composites were characterized by scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), and X-ray photoelectron spectroscopy (XPS). Confocal laser scanning microscopy (CLSM) images were obtained with an Olympus[®] LEXT^M OLS4100 3D measuring laser microscope.

RESULTS AND DISCUSSION

Figure 1a shows the fabrication procedure of the catalytic chip and in situ integration of the SERS sensors. Due to the photothermal effect of GO and the plasmonic effect of AgNPs, GO was effectively reduced (AgNPs@RGO) by laser irradiation. Various complex channels were patterned on the composite (Figure 1b). After laser irradiation, the compact AgNPs@GO film was exfoliated into a highly porous structure so that the resulting patterned AgNPs@ RGO could be easily transferred onto a PDMS substrate by simple stamping. The PDMS substrate was then combined with another conformal channel layer, and a flexible catalytic chip with in situ SERS sensors was fabricated (Figure 1c). The chip was integrated with a catalyst bed capable of SERS monitoring.

The morphology of the AgNPs@GO film was investigated before and after laser scribing (**Figure 2a**). The original AgNPs@GO film was compact and had a smooth surface, whereas laser-scribed AgNPs@RGO was expanded and exfoliated, providing many active sites for the subsequent catalytic reaction and SERS detection. SEM of the AgNPs@RGO material indicated that AgNPs were uniformly distributed on the wrinkled RGO sheet (**Figure 2b**). The average size of AgNPs was ≈10 nm, and the gap between particles was ≈2 nm. AgNPs with



Figure 1: *In situ* integration of SERS sensors on a catalytic chip. (a) Fabrication scheme of a catalytic chip by laser scribing. (b) Various computer-designed patterns written on an AgNPs@GO-coated disc. (c) Photograph of the catalytic chip.



Figure 2: Surface morphologies of AgNPs@RGO films. (a) SEM image of a laser-scribed AgNPs@GO film. (b) High-resolution SEM image of an AgNPs@RGO layer. (c,d) SEM and CLSM images of AgNPs@RGO (c) before and (d) after PDMS stamping. Scale bar: 20 µm. (e) The cross-section height of the AgNPs@RGO film before and after PDMS stamping.

diameters smaller than 20 nm are considered attractive catalysts because of their negative redox potential and high surface-to-volume ratio ^[9, 10]. Agglomeration hampers their practical application, but in this study, the exfoliated RGO acted as a scaffold, preventing AgNP aggregation and thus allowing long-term usage of the catalytic chip and SERS sensors.

SEM and CLSM confirmed the expanded structure of AgNPs@RGO (**Figure 2c**). As the lasertreated region could be easily stamped onto the PDMS substrate, any designed pattern was selectively integrated into the microfluidic channels. **Figure 2d** shows the hierarchical structure of the transferred AgNPs@RGO substrate, which retained a loose and exfoliated morphology. A large amount of AgNPs was exposed to the environment, facilitating catalytic reactions and SERS detection. The surface morphology of AgNPs@RGO before and after PDMs stamping was comparable, with an expanded height of ~10 µm (**Figure 2e**).

To investigate the influence of AgNPs during laser reduction, we varied the AgNPs/GO ratio in the AgNPs@GO composite (AgNPs@ GO-1–3). TEM images showed that AgNPs dispersed uniformly on the GO sheets, whereby the distribution density of AgNPs correlated positively with the silver ion concentration. No aggregation was found as the GO scaffold impeded the merging of AgNPs.

Laser-scribing of GO is a photothermal reduction process ^[11], and the addition of AgNPs greatly facilitates GO reduction because of the synergistic effect of the high photothermal conversion efficiency of GO and the remarkable plasmonic effect of AgNPs ^[12]. Pure GO and AgNPs@GO-1-3 were scribed under the same conditions and characterized by SEM. The laser paths were recognizable due to the expanded cracking edge of the graphene layer. The degree of expansion increased with increasing AgNPs/GO ratio, thus, exposing more active sites. AgNPs remained highly dispersed on the RGO scaffold in laser-scribed AgNPs@ RGO-1 and -2. In AgNPs@GO-3, however, the excessive amount of AgNPs, which packed closely on the GO sheet, led to laser-induced coalescence and poor uniformity of AgNPs.

Laser scribing induces not only hierarchical structures but also removes oxygen-containing groups (OCGs) on the GO layer. XPS spectra of C 1s peaks were collected to compare the amount of OCGs before and after laser-scribing. The spectra resolved into three peaks corresponding to C–C, C–O, and C=O. The C–O and C=O peaks of the composites decreased dramatically after laser scribing compared with those of pure GO. The C–O and C=O peaks also decreased with increasing AgNP content in the composites, indicating that AgNPs play a role in the photoreduction of GO. The laser intensity could also control the morphology of the laser-scribed composites. Thus, simple laser scribing can regulate the OCG content and achieve a porous structure of AgNPs@RGO, which are crucial for performing catalytic reactions and SERS detection.

A functional microfluidic chip was formed (Figure 1a), and the closely packed AgNPs endowed the chip with catalytic capability. RGO and AgNPs@RGO-1-3 were transferred into different channels of the chip (Figure 3a). The reduction of 4-NP by sodium borohydride (NaBH₄) was chosen as a classic reaction to evaluate the catalytic activity of AgNPs@ RGO $^{[13]}$. 4-NP (6 mM) and NaBH₄ (20 M) were injected into different inlets of the Y-shaped channels. RGO-based materials can trap 4-NP molecules via noncovalent π - π stacking interaction ^[14]. Reduction of 4-NP occurred only at the AgNPs@RGO region, whereby the fluid changed its color from light yellow to colorless. UV-vis spectroscopy was used to assess the reduction efficiency of the chip as 4-NP and its reduction product 4-aminophenol (4-AP) produce characteristic absorption peaks at 400 and 295 nm, respectively. The conversion of 4-NP to 4-AP depended on the fluid velocity on the chip (Figure 3b,c). In the channel containing AgNPs@RGO-1, 4-NP was completely reduced at a liquid flow velocity of <1 mL h⁻¹. This critical flow rate was defined as the threshold velocity (v_{th}). In the channel containing AgNPs@RGO-2, complete conversion of 4-NP occurred at a much higher v_{th} (5 mL h^{-1}). The difference in catalytic activity between AgNPs@RGO-1 and -2 was due to the different contents of AgNPs and exposed active sites.

We used a pseudo-first-order kinetic model to investigate the catalytic performance on different substrates quantitatively ^[15]:

 $\ln(C/C0) = \ln(A/A_0) = -k_{app}t$

where C and C_0 are the real-time and initial concentration of 4-NP, respectively, A and A_0 the corresponding absorbance intensities, and k_{app} the apparent first-order reaction rate constant. Accordingly, k_{app} was determined to be 0.0054, 0.0207, and 0.0109 s⁻¹ for AgNPs@RGO-1, -2, and -3, respectively, indi-

cating that AgNPs@RGO-2 exhibited the highest catalytic activity (**Figure 3d**). This result implies that laser scribing can improve the catalytic capability of AgNPs@RGO. However, the excessive amount of AgNPs in AgNPs@ RGO-3 led to the coalescence of AgNPs during laser scribing and thus to a dramatically reduced reaction rate. Therefore, microfluidic channels containing AgNPs@RGO-2 were selected to produce practical chips.

The closely packed AgNPs on the RGO scaffold can also be used as efficient SERS sensors ^[16], enabling on-chip, in situ SERS detection to directly monitor the catalytic reaction. We compared the SERS spectra of 4-NP on different substrates. As the SERS signals are attributed to "hot spots" at the nanogaps between neighboring nanoparticles, the electric field and Raman signals were significantly enhanced on the AgNPs@RGO-1 and -2 substrates. The signal from the AgNPs@RGO-2 substrate exhibited the greatest enhancement owing to the plasmonic effect of AgNPs and the effective interaction between 4-NP and RGO.

In practice, complete conversion of the reactant is desired; therefore, we acquired the real-time SERS signals at the end of the channel to determine whether 4-NP has been completely reduced. At a flow rate lower than v_{th} , 4-NP was almost completely converted to 4-AP. However, at a velocity higher than v_{th} , the product was a mixture of 4-NP, 4-AP, and NaBH₄. These results indicate that catalytic chips with *in situ* SERS sensors can effectively avoid the intricate collection of the products and subsequent UV-vis measurements.

To evaluate the reproducibility of the SERS device, we collected SERS spectra of rhodamine 6G (R6G, 10⁻⁷ M) at nine randomly selected positions on the SERS sensor. Consistent signal intensities were obtained, indicating excellent reproducibility. Moreover, the SERS intensities at 1509 cm⁻¹ were compared, and the relative standard deviation (RSD) was ≈2.3%. To test the error of concentration detection, we measured the SERS signals of R6G at different concentrations $(10^{-5}-10^{-10} \text{ M})$; the SERS intensity increased evidently with concentration. The SERS chip is also reusable. After the first SERS detection of R6G, the SERS device was regenerated with water and reused for three further detection and regeneration cycles. The signal intensity at 773 cm⁻¹ was measured after each cycle, and the RSD was ≈6.5%, demonstrating good reusability. Furthermore, the SERS signals of devices stored for 15, 30, 45, and 60



Figure 3: (a) Schematic illustration of the catalytic chip. (b,c) UV-vis absorption spectra of products obtained at various flow rates from (b) AgNPs@RGO-1 and (c) -2. (d) Real-time changes in $\ln(C/C_0)$ for the reduction reaction on different substrates.

days were measured and compared to study the shelf life of the sensor. The SERS intensity of the device stored for 60 days decreased only by 10% compared with that of a fresh device, indicating a shelf life of at least 60 days.

CONCLUSION

In summary, a catalytic chip with in situ SERS sensors was prepared by simple laser scribing. By adjusting the AgNPs/GO ratio, AgNPs@ RGO substrates with designable structures and optimized performance were obtained. The hierarchical structures of the composites exposed numerous active sites to the environment, which contributed to the reduction of 4-NP. Due to the excellent adsorption properties of RGO and the remarkable plasmonic effect of AqNPs, the microfluidic substrates exhibit SERS sensor capability. Thus, the catalytic products could be monitored by in situ SERS detection. This cost-effective strategy for fabricating catalytic optofluidic chips is favorable for future practical applications.

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04 Mechanical Properties and Slurry Erosion Resistance of a Hybrid Composite SiC Foam/SiC Particles/EP

Z. H. Ren, Y. G. Zheng, C. H. Jiang et al.

ABSTRACT

The novel hybrid composite SiC foam/SiC particles/EP (SiCfoam/SiC_p/EP) was prepared, consisting of an E-51 epoxy resin (EP) as the matrix and SiC foam/SiC particles as the reinforcements. The slurry erosion properties of the SiCfoam/SiC_p/EP and SiC_{foam}/EP (SiC_{foam}/epoxy resin) composites were investigated using a rotating disc rig. SiC_{foam}/SiC_p/EP exhibited better mechanical and anti-erosive performances than SiC_{foam}/EP. The SiC particle size had a great impact on the mechanical and anti-erosive properties of the hybrid composites. Smaller SiC particles improved the mechanical strength but tended to decrease the anti-erosive performance of the composite. The hybrid composite SiC_{foam}/ SiC_p/EP can be applied under solid particle erosion conditions because of its excellent anti-erosive properties.

INTRODUCTION

Solid particle erosion, a typical dynamic wear mode, results from the repeated impact of small, solid particles ^[1]. It occurs in various engineering fields, such as automotive, aerospace, marine, and energetics. Polymers and polymer composites are widely used in engineering fields because of their high specific strength and stiffness ^[2, 3]. The erosive resistance of various polymer composites has extensively been investigated, including fiber-reinforced or particle-reinforced composites and hybrid polymer composites. Fiber/matrix adhesion and fiber orientation strongly affect the erosive resistance of fiber-reinforced composites, which show a semi-ductile erosion behavior ^[4, 5]. In particle-reinforced composites, the particle fillers have a significant effect on the erosive performance of the composite ^[6, 7]. The incorporation of particle fillers into fiber-reinforced polymer composites improves the material's erosive resistance. However, the erosive performance of ceramic foam-reinforced polymer composites is poorly studied even though ceramic foams have attracted much interest in the past decade. Ceramic foams, with their unique 3D network architecture and outstanding mechanical and anti-erosive properties, are excellent reinforcements in composite materials [8-11]. The interpenetrating 3D structure of the ceramic foam reinforcement greatly enhances the mechanical and physical performance of composites. For example, the incorporation of SiC foam into SiC particle-reinforced aluminum composites markedly decreased the composite's thermal expansion because of the interpenetrating structure of the SiC foam [8]. Furthermore, co-continuous ceramic foam/aluminum composites were up to twice as wear-resistant as metal-matrix composites made of ceramic powder/fibers, indicating that ceramic foams are more efficient than ceramic powder/fibers as reinforcements in aluminum alloys^[9]. We previously showed that a SiC foam/epoxy co-continuous phase composite (SiC_{foam}/EP) exhibits better slurry erosion resistance than the epoxy matrix alone and the widely used pipeline steel, indicating that SiC_{foam}/EP composites can be applied under solid particle erosion conditions ^[11]. The reinforcing effect of SiC foam on the composite's slurry erosion resistance is greater than that of dispersed SiC particles. However, erosion of the epoxy matrix to a certain degree is inevitable, and increasing the volume fraction of SiC foams to enhance the erosive resistance is an inefficient approach because the preparation of SiC foams at high volume fractions is difficult. Therefore, a hybrid composite in which the reinforcing effects of two reinforcements synergize each other is a good choice for improving the erosive resistance.

This article proposes a hybrid SiC foam/SiC particles/epoxy (SiC_{foam}/SiC_p/EP) composite that can be applied under solid particle erosion conditions. SiC_{foam}/SiC_p/EP exhibited not only improved mechanical properties but also desirable slurry erosion resistance. The mechanical properties and slurry erosion resistance of the SiC_{foam}/EP composite and hybrid composites containing SiC particles of different sizes were systematically compared. The slurry erosion mechanism of the SiC_{foam}/SiC_p/EP composite different sizes was also investigated.

METHODS

The SiC_{foam}/SiC_p/EP composite was prepared by a modified procedure previously reported ^[11]. The SiC foam volume fraction was 60%. The SiC foam had a cell size of ~1.5 mm, and the SiC particles had grain sizes of 0.74, 0.41, and 0.1 mm in SiC_p I, SiC_p II, and SiC_p III, respectively. SiC foam, consisting of α -SiC, β -SiC, and Si, was produced by a solid-state sintering process. SiC particles were treated with the silane-coupling agent KH-550 to modify the adhesion between the epoxy matrix and SiC particles. The SiC particles were then dispersed into SiC foam cells to obtain SiC_{foam}/SiC_p. The SiC_p volume fraction in the three hybrid composites was ~25%. The epoxy resin was then squeezed into SiC_{foam}/SiC_p by vacuum infiltration and compression molding. The uncured sample was kept in a vulcanization machine at 100 °C (212 °F) and 10 MPa for 4 hours to obtain a completely cured epoxy matrix.

For the compression and three-point bend experiments, the samples were tested at a constant displacement rate of 0.5 mm/min with a load capacity of 100 kN. The impact tests were conducted in a pendulum impact-testing machine with a load capacity of 0.5 J.

Slurry erosion experiments were performed in a rotating disc rig. The slurry consisted of water and erodent quartz sand with a grain size of 70–150 mesh. The sand content was 10 kg/m³, and the flow velocity was kept at 10 m/s. The sample surfaces were ground with a 1000-grit abrasive paper and then cleaned in deionized water and dried before the tests. The slurry erosion of each sample was characterized by the erosion rate (*E*): $E = (m_0 - m)/A$ /*t*, where m_0 , *m*, *A*, and *t* represent the initial mass, the mass after the test, the surface area of the sample, and test duration, respectively.

The structures of the SiC_{foam}/SiC_p/EP composites were analyzed using an Olympus[®] SZX16 stereoscopic microscope. The fracture morphologies and microstructures of the composites after the mechanical and slurry erosion tests, respectively, were observed with a scanning electron microscope (SEM) and an Olympus LEXT[™] OLS4000 confocal laser scanning microscope (CLSM).

RESULTS AND DISCUSSION

The cured SiC_{foam}/SiC_p/EP hybrid composites showed no voids and piles, and the epoxy matrix/SiC particles and SiC foam interpenetrated mutually. The SiC particles and epoxy matrix were trapped within the SiC foam cells of the interpenetrating composite structures.

The SiC_{foam}/SiC_p/EP composites exhibited better mechanical properties (i.e., compressive strength, flexural strength, and impact tough-



Figure 1: Flexural fracture morphologies of the four composites. (a) SiC_{foam}/EP, (b) SiC_{foam}/SiC_p //EP, (c) SiC_{foam}/SiC_p II/EP, (d) SiC_{foam}/SiC_p II/EP).

ness) than the ${\rm SiC}_{\rm foam}/{\rm EP}$ composite. Among the SiC_{foam}/SiC_p/EP composites, SiC_{foam}/SiC_p III/ EP performed best as the mechanical properties of the hybrid composites increased with decreasing SiC particle size. Therefore, the grain size of the SiC particles plays a pronounced role in the mechanical properties of the SiC_{foam}/SiC_p/EP composites. Reinforcing the epoxy resin by SiC particles improves its mechanical properties and poor resistance to crack growth ^[12, 13]. Therefore, the SiC_{foam}/ SiC_p/EP composites exhibited better mechanical properties than the SiC_{foam}/EP composite. Figure 1 shows the flexural fracture morphologies of the four composites. The failure mechanism of the hybrid composites included the fracture and detachment of SiC particles. Cracks propagated more tortuously in the hybrid composites than in the ${\rm SiC}_{\rm foam}\!/{\rm EP}$ composite, and the grain size of the SiC particles affected the morphologies markedly. CLSM images of the flexural fractures in SiC foam cells show that the fracture surface of the SiC_{foam}/EP composite was smoother than that of the SiC_{foam}/SiC_p/EP composites (Figure 2). These observations indicate

that more fracture energy is absorbed during $SiC_{foam}/SiC_p/EP$ fracture than during SiC_{foam}/EP fracture. The roughness of the fracture surface and fracture energy increased gradually with decreasing SiC particle size. Smaller particles have a larger total surface, and the strength of particle-reinforced composites increases with the particle surface area ^[14]. Therefore, the mechanical properties of the hybrid composites increased with decreasing grain size.

The SiC_{foam}/SiC/EP composites showed lower erosion rates than the SiC_{foam}/EP composite. The slurry erosion resistance of SiC_{foam}/ SiC_p I/EP, SiC_{foam}/SiC_p II/EP, and SiC_{foam}/SiC_p III/ EP increased by 190%, 94%, and 2%, respectively, compared with that of SiC_{foam}/EP. SEM images of the eroded surfaces of all composites were taken to investigate the erosion mechanism. Severe breaking of SiC_p II particles was observed in SiC_{foam}/SiC_p II/EP, and plenty of SiC_p III particles were detached from the epoxy matrix in SiC_{foam}/SiC_p III/EP (**Figure 3**). Nevertheless, the SiC particles in the hybrid composites were less seriously dam-



Figure 2: CLSM images of the flexural fractures in the SiC foam cells of the four composites. (a) SiC_{foam}/EP, (b) SiC_{foam}/SiC_p I/EP, (c) SiC_{foam}/SiC_p II/EP, (d) SiC_{foam}/SiC_p III/EP).



Figure 3: SEM images of eroded composites. (a) SiC_{foam}/EP , (b) SiC_{foam}/SiC_p I/EP, (c) SiC_{foam}/SiC_p II/EP, (d) SiC_{foam}/SiC_p III/EP).

aged than those in SiC_p/EP, which can be attributed to the shadowing effect of the SiC foams. The shadowing effect decreases the impact energy of quartz sand on SiC particles. Quartz sand with small grain sizes selectively scoops out the epoxy matrix in particle-reinforced, epoxy-based composites ^[15]. However, no scooping of the epoxy resin was observed in the hybrid composites because of the synergistic effect of the SiC foam and SiC particles. Therefore, the hybrid composites eroded to a lesser extent than SiC_{foam}/EP. The SiC foam and SiC particles greatly improved the anti-erosive properties of the epoxy matrix, indicating that SiC_{foam}/SiC_p/EP composites behave completely different from traditional particle-/fiber-reinforced polymer composites under solid particle erosion conditions.

Figure 4 shows sketches of the slurry erosion mechanism for the four composites. During slurry erosion, local removal of EP from the impacted surface of the sample results in the exposure and extrusion of the SiC foam and SiC particles. After 24 hours, the angle (α) between the damaged and initial surface of the SiC_{foam}/EP composite approximately reflects the impact angle of quartz sand (Figure 4a). Less EP is eroded and complex surface morphologies are formed during the slurry erosion of hybrid composites because of the synergistic effect of the SiC foam and SiC particles. The severe breaking of SiC_p II and detachment of SiC_p III occur with successive impact of quartz sand, which inevitably leads to further erosion of the EP after the removal of SiC particles (Figure 4b). The erosion of a material depends on the energy exchange between the erodent particle and the impacted material surface. When the particles striking against the target are softer than the target material, fractures (due to individual impacts) and plastic indentation may not occur ^[9]. Since quartz sand is softer than SiC, the plastic deformation of SiC is negligible during the collision of quartz sand with the sample surface. This means that most of the kinetic energy is transformed into rebounding energy while the rest dissipates through stress wave propagation.

Because of its unique structure, SiC foam dissipates the impact energy of moving quartz sand, whereas SiC particles absorb and dissipate the kinetic energy to the surrounding epoxy resin. Therefore, quartz sand with enough impact energy will inevitably break SiC particles (**Figure 3c**). The contact area and consequently adhesion between SiC particles and EP increase with SiC particle size.





Therefore, SiC_{foam}/SiC_p I/EP exhibited the best anti-erosive properties, without detachment of SiC_p I particles. In contrast, because of the weak adhesion in SiC_{foam}/SiC_p III/EP, the impact energy of moving quartz sand was high enough to detach SiC_p III particles from the composite. Consequently, SiC_{foam}/SiC_p III/EP showed weaker erosion resistance than the other two hybrid composites.

CONCLUSION

A novel hybrid composite, $SiC_{foam}/SiC_p/EP$, was successfully prepared. The four composites SiC-foam/EP, SiC_{foam}/SiC_p I/EP, SiC_{foam}/SiC_p I/EP, and

 ${\rm SiC}_{\rm foam}/{\rm SiC}_{\rm p}$ III/EP exhibited better mechanical properties than the SiC_{foam}/EP composite because of the reinforcement of the epoxy resin with SiC particles. The grain size of SiC particles had a marked effect on the mechanical properties of the SiC_{foam}/SiC_p/EP composites, which increased with decreasing particle size. The SiC_{foam}/SiC_p/EP composites also had better anti-erosive properties than the SiC_{foam}/EP composite. Among the tested hybrid composites, SiC_{foam}/SiC_p III/EP exhibited the highest erosion rate, leading to the detachment of SiC_p III particles from the epoxy resin. The SiC_{foam}/SiC_p/EP hybrid composite can be applied under solid particle erosion conditions because of its excellent mechanical and anti-erosive properties.

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Confocal Laser Scanning Microscopy for Materials Inspection

As demonstrated in this eBook, new fine functional materials have been developed for the application in industrial fields including the automobile, aviation, metal, and chemical industries. As a result, higher accuracy and resolving power are required for minute threedimensional measurement of these components and materials. Although a variety of devices are available to satisfy these requirements, the confocal microscope is gathering attention as the device of choice for easy threedimensional surface profile measuring in air, without touching the sample.

OLYMPUS LEXT™ OLS5100 LASER MICROSCOPE

Laser microscopes are essential equipment in manufacturing R&D and quality assurance due to their powerful capabilities submicron 3D measurements with no sample preparation, noncontact areal roughness analysis and speed. However, some tasks, such as creating and managing an experiment plan and choosing the right objective lens, are time consuming and sources of potential error. The OLS5100 microscope's smart features address these challenges.

The microscope's Smart Experiment Manager helps users manage the planning, acquisition and analysis phases of their experiments. The microscope scans samples according to a customized experiment plan generated by the software, helping to keep users from missing data or redoing work. During analysis, the software's trend visualization tools make it easier for users to spot problems.



The OLS5100 microscope's Smart Lens Advisor takes the guesswork out of selecting the right objective lens when measuring surface roughness. In three simple steps, the Advisor rates the objective lens based on the application, so users know they are using the right objective.

Some laser microscopes are complicated, but the OLS5100 microscope makes data acquisition simple—just place a sample on the stage and press the start button. The microscope will make all necessary setting adjustments and acquire the data.

With outstanding accuracy and optical performance combined with smart tools that make system easy to use, the OLS5100 laser microscope simplifies experiment workflows and delivers high-quality data users can rely on.

ABOUT OLYMPUS

Olympus is a global technology leader, crafting innovative optical and digital solutions in medical technologies, life sciences, industrial solutions, cameras and audio products. Throughout our 100-year history, Olympus has focused on being true to society and making people's lives healthier, safer and more fulfilling.

Our Industrial Solutions Business is committed to the safety and betterment of society through the pioneering, development and manufacture of world-leading test and measurement solutions. These solutions are used in industrial and research applications ranging from aerospace, power generation, petrochemical, civil infrastructure, automotive and consumer products. For more information on Olympus' laser microscopes and other scientific solutions, visit Olympus-IMS.com

OLYMPUS

Scientific Publishing

WHY IS A COVER LETTER to the editor so important? Which information should be included into the title and abstract? These and more questions will be answered in this section. Beginning with the infographic "5 tips for writing better science papers", we will provide you with valuable advice on how to present your research results in the best way throughout the next months.

5 tips for writing better science papers

Don't underestimate the importance of your cover letter

A good cover letter explains to the editor the critical question your research addresses, how you have answered this question, and why it is of significance to the wider community.



Keep the title simple: be consistent, not too technical, and concise

It's important to grab the attention of your editor/reviewer/reader right away and give them an idea of why your paper is a scientific breakthrough. The title also plays into search engine optimization for your article, so think of which search terms you would use when searching for your paper, and try to incorporate those keywords into your title.

Introduce your research with its importance

The reader needs to know the background to your research and, most importantly, why your research is important in this context. What critical questions does your research address? Why should the reader be interested?

Don't cram the abstract with details

What you want is to grab the reader's attention with the first statement, add a few of the most important details, then leave them with the overall message of the manuscript in the last sentence.

You might be tempted to share all your war stories... but don't

When reporting results, keep your focus and make your R&D concise but informative.

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Getting Started

THE START of a new research project or a thesis can be an exciting experience, with all the ideas to be realized ahead. It is tempting to just begin with the practical work and think about how to publish it later; however, there are good reasons (outlined below) to plan the publication of your manuscript at the very beginning of your project:

1. You will save time

Before and during the experimental work, a thorough literature research is essential. Identify the most relevant publications for your own projects from the beginning on to use them for the introduction of your article or communication.

2. You will stay focused

If you use the method described below, you will be able to use your project's outline as orientation to maintain emphasis on the key questions you meant to target.

3. You will read research articles with different eyes

In composing a research project, other scientific articles can have two uses: as well as their content it is useful to focus on their structure, the use of language and relevant keywords. What makes a good scientific text? You will be more aware of all that when keeping your own manuscript in mind.

You will avoid the "fear of the blank page"

The beginning of the writing process is probably the hardest part. If you already prepared the structure of your manuscript, collected ideas and references for the introduction, phrased the key finding of your study and wrote the experimental section while conducting the research, you will have a much easier start.

WHEN IS THE BEST MOMENT TO START THE WRITING PROCESS?

According to the essay "Whitesides' Group: Writing a Paper'", by Prof. George M. Whitesides, it is useful to work with an outline to plan and conduct both your research and the corresponding paper from the project's beginning. To fulfill this function, an outline is structured like a research article - with an introduction, the results and discussion, and conclusions - and will be updated throughout the course of the project. As it contains the main questions you want to answer throughout your research, you will be able to use the outline as a tool to continuously analyze the progress and the focus of your work. In a "brainstorming" session, you can create an outline by writing down all your ideas, questions and hypotheses in any order on an empty piece of paper. Afterwards, you transfer all to another piece of paper using the structure described below.

STRUCTURE AND CONTENTS OF AN OUTLINE

"If you clearly understand the purpose and form of a paper, it can be immensely useful to you in organizing and conducting your research." For Whiteside, the purpose of a paper is not only to serve as an archive, but also as a tool for planning and conducting research. Thus, he recommends creating an outline that is already structured like a scientific article:

• Title

At the beginning this will necessarily be a working title; you should try to formulate the key goal of your research here (we will provide you with tips for creating an article's title in a later edition).

• Abstract

You will leave this section empty at the beginning; you will learn more about writing an abstract later.

Introduction

At the beginning, you use this part of the outline to define the objective of your work and why it is important; based on the literature research you conducted beforehand, you formulate the background and fundamentals of your research; whenever you find a relevant study, you should add it and its key findings to this section.

Results and Discussion

In here, you should add the major points you plan to target in your project. This could look as follows:

Synthesis of the monomers Polymerization reactions Characterization methods Applications

In the course of conducting your research, you add all your results into the respective parts of this section. You will most likely find out that some of the original plans need to be adapted due to unexpected findings; use the results and discussions section as a tool to constantly summarize, analyze and, if necessary, update your key goals of your project.

Conclusions

For the outline, you can condense your conclusions to short phrases; compare them to the key objectives you framed in the introduction – do they match or need reformulation?

Experimental

You will save a lot of time at the end of your thesis or project if you ensure you write down all experimental findings from the beginning on.

Herein, we outlined one of many ways to successfully conduct your research and the writing process. In the next editions of our "Tips on Scientific Publishing", we will give a more detailed look at the different sections of a scientific article.

We highly recommend reading the short essay by Prof. Whiteside (freely available):

Whitesides, G. (2004), Whitesides' Group: Writing a Paper. Adv. Mater., 16: 1375-1377. doi:10.1002/adma.200400767

Title and Abstract

P. Trevorrow, G. E. Martin

This article is a short version of the comprehensive and freely available tutorial "How to write a research article for MRC", written by Paul Trevorrow and Gary E. Martin.

ARTICLE TITLE

When choosing a title for an article, it is advisable to choose a title that best describes the work, is succinct, and free from excessive jargon. The title should entice the reader and authors should keep in mind that the first impression counts! A strong title will likely convince an editor (or reviewer) that the paper is important to the journal's readership. Titles should generally be short, not more than 15 words, and be informative; they need to convey the main message and/ or finding of the paper. Try to be precise without using vague language. It is recommended that authors of research articles and reviews avoid titles such as the following:

- "Studies on ...".
- "Characterization of ...".
- "Optimization of ...".
- "Investigations on ...".
- "Review of ...".
- "... in review".

In some publications, references to "new" or "novel" appear frequently in article titles. Such phrases should be avoided where possible. The point of the academic journal is to publish new research so stating new or novel in the title can appear somewhat redundant.

THE ABSTRACT

Your abstract is one of the most important elements of your article. Firstly, editors may not have time to read your entire manuscript when making initial screening decisions. If you can sell them on the importance of your research in the abstract, they will be able to make a decision on whether the article is acceptably within the scope of the journal quickly and easily. Secondly, when asked to review an article, referees are presented with the abstract in the initial invitation. A poorly structured abstract with unclear motivation is less likely to be accepted for review by an already fatigued referee. Finally, due to abstracting and indexing agencies, such as Web of Science, SciFinder, PubMed, ResearchGate (the list goes on), more people are going to view your abstract than will ever read your paper. If you can make it clear why your article is important, it is more likely to be discovered by the correct audience.

The abstract should be viewed as a self-contained component and should not include references to external sources or supporting information. The abstract should also be concise so that editors, reviewers, or the eventual readers can quickly make an assessment on whether they want to read the full paper.

One should think of an abstract in sections, firstly state the problem, the reason for the research, and why it is important. Remember that your abstract is the biggest advert for your paper, so it is important to put the research in a broad context stating why the research is important to a broad public audience and not only your specialist NMR community. Secondly, introduce the procedure simply, describing the investigative technique and the samples involved. Thirdly, offer a brief and succinct account of the result followed by the final portion, the conclusion. The conclusion should convey the take-home message of the research. In general, an optimal abstract should follow the following structure, which will ensure that all of the important points are covered and expressed logically:

- **Rationale:** state the problem, the reason for the research and why it is important to broad non-specialist audience.
- Method: what procedure/analysis has been undertaken?

- **Result:** what was the outcome of the experiment?
- **Conclusion:** what are the key takehome messages of the research?

EXAMPLE

All articles in this eBook give examples of well-structured abstracts. For example, the abstract of "Flexible Micropillar Electrode Arrays for In Vivo Neural Activity Recordings" (pp. 25-31) mimics the above mentioned, recommended structure:

Rationale

"Flexible electronics that can form tight interfaces with neural tissues hold great promise for improving the diagnosis and treatment of neurological disorders and advancing brain/machine interfaces."

Method

"Here, the facile fabrication of a novel flexible micropillar electrode array (µPEA) is described based on a biotemplate method."

Result

"The flexible and compliant μ PEA can readily integrate with the soft surface of a rat cerebral cortex. Moreover, the recording sites of the μ PEA consist of protruding micropillars with a nanoscale surface roughness that ensures tight interfacing and efficient electrical coupling with the nervous system. As a result, the flexible μ PEA allows for in vivo multichannel recordings of epileptiform activity with a high signal-to-noise ratio."

Conclusion

The ease of preparation and high flexibility make the μ PEA an attractive tool for in vivo spatiotemporal mapping of neural activity."

When reading an article, the abstract appears as the first element; however, it may be prudent to compose this last when writing up the manuscript. This will enable one to keep consistent with the findings of the research and prevent rewriting as the investigative components of the article develop.

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The Introduction

P. Trevorrow, G. E. Martin

This article is a short version of the comprehensive and freely available tutorial "How to write a research article for MRC", written by Paul Trevorrow and Gary E. Martin.

IMPORTANT FIRST IMPRESSIONS AFTER THE TITLE AND ABSTRACT

The Introduction should discuss why you did the research and why it is valuable or necessary. This should be complemented by an expert understanding of prior work in this field, typically via a literature review highlighting the significance of your research in the context of the scientific record. The introduction should cover what is known, what is unknown, and the objective of the current study. A useful guide on how to structure one's introduction is offered by Boyd [R. K. Boyd, *Rapid Commun. Mass Spectrom.* 2012, 26, 1725]. While this guidance is offered in respect to the mass spectrometry discipline, it offers an extremely useful system for the structuring of an introduction. In the Boydian method, the introduction should be considered in four parts or subsections. The first three of which provide a "drill-down" from the general to the specific, topped off with a final subsection discussing the objective of the work as a segue into the Experimental section.

Broken down, these sections can be viewed as follows:

Subsection 1

Broad context behind the experiment—include citations of the broader relevant literature here.

Subsection 2

Narrowing down to the specific problem addressed by the research. Subsection 3

Zeroes in the specific problem, more detailed review of the literature specific to the investigation, with an expert theoretical and experimental critique. Be cautious in this section to keep the literature review relevant, focus on research that is directly relevant to the topic at hand.

Subsection 4

Objective of the present work—this section should simply reflect the main objective of the research as described in the rationale section of the abstract.

THE ANATOMY OF A RESEARCH ARTICLE

Research articles generally follow two standard formats, depending on the nature of the investigation. Although the headings in these structures may be named differently from journal to journal, these formats are commonly referred to as IMRaD and IRDaM. Each of these assemblies consist of an Introduction, Methods, Results, and Discussion although the order and structure of these components differ in each variant.

IMRAD

The IMRaD structure is the most common structure used in scientific writing. This structure is as follows:

- Introduction
- Methods
- Results and Discussion

IRDAM

The IRDaM structure is typically used when a hypothesis is tested without having the experiments planned in advance, a progressive investigative trajectory where the results of one experiment inform which experiment should be undertaken next. These are otherwise known as sequential results. The IRDaM structure is composed as follows:

- Introduction
- Results and Discussion
- Methods

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The Core of Your Research Article

P. Trevorrow, G. E. Martin

This article is a short version of the comprehensive and freely available tutorial "How to write a research article for MRC", written by Paul Trevorrow and Gary E. Martin.

After we have discussed how you can attract the editor's and reader's attention by concise title and abstract of your paper, we now come to the main body of a research article: its structure, the results and discussion section, and the conclusion.

IMRAD OR IRDAM? THE ANATOMY OF A RESEARCH ARTICLE

Research articles generally follow two standard formats, depending on the nature of the investigation. Although the headings in these structures may be named differently from journal to journal, these formats are commonly referred to as IMRaD and IRDaM. Each of these assemblies consist of an Introduction, Methods, Results, and Discussion although the order and structure of these components differ in each variant.

IMRaD

The IMRaD structure is the most common structure used in scientific writing. All articles in this e-Book follow this format. This structure is as follows:

- Introduction
- Methods
- Results and Discussion

IRDaM

The IRDaM structure is typically used when a hypothesis is tested without having the experiments planned in advance, a progressive investigative trajectory where the results of one experiment inform which experiment should be undertaken next. These are otherwise known as sequential results. The IRDaM structure is composed as follows:

- Introduction
- Results and Discussion
- Methods

RESULTS AND DISCUSSION

The Results and Discussion section generally constitutes the largest portion of the manuscript and is arguably the most difficult component of the paper to compose. There are many configurations of Results and Discussion sections preferred by authors and journals; possibilities include separating the two elements where the results and the discussion are reported in isolation or in combination where both the results are critiqued in a format that is logical and digestible for readers.

The Results and Discussion section provides the results for procedures set out in the Experimental section. Each experimental method must have a result, and conversely, each reported result must have a corresponding method reported in the experimental. Each result discussion section should end with a summarizing sentence for clarity; this will direct the reader through the narrative of the research.

Typically, the Results and Discussion section will explore some or all of the following criteria:

- How the results answer the research question set in the Introduction;
- How the results relate to other studies in the field;

- Why the result may differ from the authors' expectations;
- Any limitations of the study;
- How the research is a novel contribution relative to previous research.
- Was the tested hypothesis true?
- What was the result?
- What does the result mean?
- Why it makes a difference?
- Where do the results lead? Do the results obtained open other avenues for enquiry?
- What might the answer imply and why does it matter? What are the perspectives and implications for further research?

CONCLUSION

The conclusion is an opportunity to offer a concise take-home message from the research, and for this reason, much like abstracts, they can be particularly useful for readers, editors, and reviewers who wish to underscore the salient information from a manuscript expediently.

In terms of structure, the conclusion is short and should be no more than a couple of paragraphs. The aim here is for precision, stating the main points of the research concisely.

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