

Advanced Optical Metrology

Additive Manufacturing







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Imprint

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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

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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 guality 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-





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

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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, 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 TiO_2 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 $216 \pm 10 W \text{ mm}^{-2}$ (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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