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Published in:
Proceedings of SPIE

Link to article, DOI:
[10.1117/12.2186317](https://doi.org/10.1117/12.2186317)

Publication date:
2015

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):
Argyraki, A., Lu, W., Petersen, P. M., & Ou, H. (2015). Scalable nanostructuring on polymer by a SiC stamp: Optical and wetting effects. In E. M. Campo, E. A. Dobisz, & L. A. Eldada (Eds.), *Proceedings of SPIE* (Vol. 9556). [955607] SPIE - International Society for Optical Engineering. Proceedings of SPIE - The International Society for Optical Engineering <https://doi.org/10.1117/12.2186317>

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Scalable nanostructuring on polymer by a SiC stamp: optical and wetting effects

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ABSTRACT

A method for fabricating scalable antireflective nanostructures on polymer surfaces (polycarbonate) is demonstrated. The transition from small scale fabrication of nanostructures to a scalable replication technique can be quite challenging. In this work, an area per print corresponding to a 2-inch-wafer, is presented. The initial nanopatterning is performed on SiC in a 2-step process. Depending on the nanostructures the transmission of the SiC surface can be increased or suppressed (average height of nanostructures ~300nm and ~600nm, respectively) while the reflectance is decreased, when compared to a bare surface. The reflectance of SiC can be reduced down to 0.5% when the ~600nm nanostructures are applied on the surface (bare surface reflectance 25%). The texture of the green SiC color is changed when the different nanostructures are apparent.

The ~600nm SiC nanostructures are replicated on polymer through a process flow that involved hot embossing and galvanization. The resulted polymer structures have similar average height and exhibit more rounded edges than the initial SiC nanostructures. The polymer surface becomes antireflective and hydrophobic after nanostructuring. The contact angle changes from 68 (bare) to 123 (nanostructured) degrees. The optical effect on the polymer surface can be maximized by applying a thin aluminum (Al) layer coating on the nanostructures (bare polymer reflectance 11%, nanostructured polymer reflectance 5%, Al coated nanostructured polymer reflectance 3%).

The optical measurements were performed with an integrating sphere and a spectrometer. The contact angles were measured with a drop shape analyzer. The nanostructures were characterized with scanning electron microscopy.

Keywords: Scalable polymer nanostructuring, Optical effects, Wetting effects, hot embossing, galvanization, SiC

1. INTRODUCTION

Nanoengineering enables a controllable fabrication of interfaces at the micro/nanoscale level; pushing performance of innumerable devices towards their optimum limits. The applications can be ranging from implants (dental,^{1,2} orthopedic³) to catalysis,⁴ photovoltaics,^{5,6} light emitting diodes,^{7,8} biosensors,⁹ and drug delivery.¹⁰ The unbreakable relationship between nanotopography and mechanical, physical and chemical properties of materials permits the usage of functional micro-nanostructuring. Though, in order for the technology to be adopted the fabrication process should be rapid, low-cost and applicable on wafer-scale high throughput. Nano-pattern definition can be achieved by various techniques like, electron-beam lithography,¹¹ block copolymer micelle nanolithography,¹² nanosphere lithography¹³ and self-assembly of noble metals¹⁴ etc. However, such techniques can rarely accomplish all aforementioned requirements. Moreover, polymer materials are gaining interest both as semiconductors¹⁵ and conductors^{16,17} due to their low cost and flexibility; offering exiting alternatives to traditional materials.

In this work we report a 2-step method to fabricate nanostructures on wafer scale on SiC and their replication on a polymer surface. The resulted polymer structures have similar average height and exhibit more rounded edges than the initial nanostructures. The polymer surface becomes antireflective and hydrophobic after nanostructuring, demonstrating how nanotopography can change physical properties of a surface, namely optical and wetting properties.

2. WAFER-SCALE NANOSTRUCTURING OF SiC STAMP

The fabrication flow for nanopatterning on SiC and optimization details from $1 \times 1 \text{ cm}^2$ areas could be found in.¹⁸ The processing parameters have been slightly modified in order to fit wafer-scale production (2-inch wafers). A thin Al layer (40nm) was deposited on the 2-inch SiC surface. Reactive ion etching (RIE) was performed for 30 minutes with a mixture of CF_4 and O_2 gases (24 sccm and 6 sccm respectively) at 130 Watt RF power and 100mT chamber pressure. The processed 2-inch SiC wafers demonstrate extreme reflection suppression compared to unprocessed wafers (as shown in Fig. 1)

Figure 1. Two 2-inch SiC wafers with (a) and without (b) nanostructures. The nanostructured wafer demonstrates extreme reflection suppression.

Depending on the processing parameters the nanostructure morphology can be changed from low to high nanostructures, average height of nanostructures $\sim 300 \text{ nm}$ and $\sim 600 \text{ nm}$, respectively (Fig. 2). The nanostructure morphology was characterized with scanning electron microscope (SEM, Zeiss Supra VP 40). The morphology of nanostructures affects the color texture and transmission properties of SiC samples; the transmission of the SiC surface can be increased or suppressed (Fig. 3), when compared to a bare surface.

Figure 2. Oblique-view scanning electron microscope (SEM) images of a SiC samples with low nanostructures $\sim 300 \text{ nm}$ (a) and high nanostructures $\sim 600 \text{ nm}$ (b).

Figure 3. Photos of bare and nanostructured SiC. a) SiC with low nanostructures on the surface. b) Bare SiC. c) SiC with high nanostructures. Color texture and transmission properties of SiC samples (smaller than $1 \times 1 \text{ cm}^2$) depend on the nanostructures applied. The clarity of the text under the samples is maximum for sample a.

Optical measurements were performed with an integrating sphere (8/8deg incident angle) and a spectrometer (QE 65000, Ocean Optics) to confirm the results of the altered optical properties due to nanostructuring; a halogen lamp was used as light source. Reflection and transmission spectra are presented in Fig. 4. The average reflectance (integration over visible wavelengths) was suppressed from 25% (bare surface) to 5% and 0.5% respectively when low nanostructures and high nanostructures were applied. The average transmittance was increased from 33% (bare surface) to 37% after low nanostructures were applied. To the contrary, when high nanostructures were applied the average transmittance was reduced to 13%. The wetting properties of the SiC surface are changed after nanostructuring from hydrophilic to hydrophobic¹⁸.

Figure 4. (a): Reflectance spectra from bare and nanostructured SiC surfaces. The reflection of nanostructured samples is suppressed compared to the bare surface. (b): Transmission spectra from bare and nanostructured SiC surfaces. Transmission can be increased or suppressed, depending on the type of nanostructures applied.

3. REPLICATION OF NANOSTRUCTURES ON A POLYMER SURFACE

The nanostructures that resulted in the most effective antireflective surface ($\sim 600\text{nm}$) were replicated on polymer through a process flow that involved hot embossing and galvanization (Fig. 5). The resulted polymer structures have similar average height and exhibit more rounded edges than the initial SiC nanostructures (Fig. 6 right). When a thin aluminum (Al) layer ($\sim 40\text{nm}$) was deposited on the nanostructured surface, the Al film followed the morphology of the underlying surface (Fig. 6 left).

Figure 5. Schematic illustration of the polymer nanostructured surface process flow.

Figure 6. (a): SEM image of nanostructured polymer surface. (b): SEM image of Al coated nanostructured polymer surface ($\sim 40\text{nm}$). The Al layer follows the morphology of the underlying surface. The replicated nanostructures exhibit more rounded edges.

The color texture of the polymer surface changes significantly when nanostructures are applied (Fig. 7); from mirror like (Al coated bare surface, Fig. 7a) to grey-black (Al coated nanostructured surface, Fig. 7b), and foggy-white (nanostructured surface, Fig. 7c) to transparent see-through (bare surface, Fig. 7d). The transparency of the polymer surface is also affected as illustrated in Fig. 7 (right).

Figure 7 Photos of Al coated (a), nanostructured and Al coated (b) nanostructured (c) and bare (d) polymer surface. Left: The color texture of the polymer surface changes significantly after nanostructuring (foggy-white, c); and nanostructuring and thin film coating (black, b). Right: The transparency of the polymer surface is affected by the presence of the nanostructures and the Al coating. At the border between the Al coated (b) and not Al coated region (c) one can observe that transparency gradually increases, probably due to that the Al thickness gradual decrease.

The optical properties of the nanostructured polymer surface and nanostructured and Al coated polymer surface were measured as described in section 2. Their reflection and transmission spectra are presented respectively in Fig. 8 (a) and (b). The average reflectance of the polymer surface was reduced from 11% (bare) to 5% when the nanostructures were applied. A further reduction to 3% was achieved after the thin Al layer was deposited on the surface. The average transmittance of the polymer surface was changed from 88% (bare) to 85% when nanostructures were applied and drastically reduced to 33% after the Al coating. Moreover, the wetting properties of the various surfaces namely bare surface, nanostructured surface, Al coated bare and Al coated nanostructured surface were measured with a drop shape analyzer (Krüss DSA 100S). The surfaces were transformed from hydrophilic (68/75 degrees water contact angle) to hydrophobic (123/132 degrees water contact angle) after the nanostructures were applied (respectively for polymer and Al coated). The water contact angle measurements are shown in Fig. 9.

4. CONCLUSIONS

We have demonstrated scalable (2 inch area) nanostructuring on a polymer surface by a SiC stamp and studied the optical and wetting properties of the related surfaces before and after nanostructuring. It was shown that the color texture of the surfaces (SiC and polymer surface) is affected significantly by the presence of nanostructures. Moreover, it was demonstrated that when a thin Al coating is applied on the nanostructured polymer surface the reflectance and

transmittance can be even further reduced. Finally, we have shown that the presence of the fabricated nanostructures on a surface can transform it from hydrophilic to hydrophobic.

Figure 8. (a): Reflectance spectra from bare, nanostructured and nanostructured and Al coated polymer surfaces. The reflection of nanostructured and Al coated samples is suppressed compared to the nanostructured and bare surface. (b): Transmission spectra from bare and nanostructured and nanostructured and Al coated polymer surfaces. Transmission is drastically decreased when a thin Al coating is applied on the nanostructured surface.

Figure 9. (a) Water contact angles of polymer surface without and (b) with nanostructures. (c) Water contact angles of Al coated surface without and (d) with nanostructures. The nanostructures modify the surfaces from hydrophilic to hydrophobic.

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