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Fabrication of TiO₂ Grating with Composites of Azobenzene Polymer and TiO₂ Nanoparticles[†]

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We have used the formation of surface relief gratings (SRG) on azobenzene polymers to manipulate TiO₂ nanoparticles and to fabricate TiO₂ nanoparticle gratings. Suspensions of an azobenzene polymer (PDO3) and TiO₂ were used to spin coat thin films on glass slide substrates. By interfering coherent light from an Argon laser on the surface of the PDO3-TiO₂ composite films, SRGs were fabricated. Atomic force microscopic images of the SRGs show TiO₂ nanoparticles dispersed throughout the sample, and in particular, at the peaks of the SRG after oxygen plasma treatment. The lateral forces acting on the azobenzene polymer during the SRG fabrication drag the TiO₂ nanoparticles. These results indicated that it is feasible to create TiO₂ nanoparticle gratings with the composites.

Keywords: SRG structure; azobenzene polymer; TiO₂ nanoparticles

1 Introduction

Nanostructure fabrication is of fundamental importance for many industries including semiconductors, magnetic storage, sensors and photonics among others. Several techniques to fabricate nanostructures using block copolymer self-assembly for a variety of applications have been reported by Hamley (1). A potential optical application of nanoparticles has been demonstrated by Sanchez et al, by recording high diffraction efficiency volume holographic gratings with composites of TiO₂ nanoparticles-photopolymers (2).

We have explored a novel way to manipulate titanium dioxide (TiO₂) nanoparticles and to fabricate micron and sub-micron TiO₂ patterns. These TiO₂ structures can be readily used as a template for sensor fabrication. The surface relief TiO₂ structures with increased surface areas will find applications in dye sensitized solar cells (3, 4).

The study presented in this paper is based on the property of azobenzene functionalized polymers, which can undergo trans-cis isomerization when exposed to coherent light beams. The trans-cis isomerization leads to the fabrication of surface relief grating (SRG) structures on the surface of

azobenzene polymer thin film (5, 6). There have been extensive investigations with this class of polymers for the past 15 years, (7–11). In this research, we extended the SRG formation to composites films of azopolymers and TiO₂ nanoparticles. Suspensions of an azobenzene polymer and TiO₂ nanoparticles were prepared and thin film samples were spin-coated. By interfering two polarized light beams on the surface of these thin films, SRGs were fabricated. A TiO₂ grating was fabricated by simply exposing the fabricated SRG to oxygen plasma to remove the azopolymer.

2 Experimental

2.1 Materials

An azobenzene polymer functionalized with the Disperse Orange 3 (DO3) dye was utilized in the investigation. The azopolymer is denoted as PDO3 (5). This polymer contains the azobenzene chromophore attached to the main-chain, as shown in Figure 1. The absorption peak of the azopolymer is located around 450 nm. The TiO₂ particles with sizes ranging from 25 nm (single particles) to 5 micron (clusters of the small nanoparticles) were used. The suspensions were prepared by dissolving PDO3-TiO₂ (5 wt% PDO3) in 1,4-dioxane. The PDO3 polymer and the TiO₂ nanoparticles were crushed together in a mortar in order to break apart the larger clusters of TiO₂ particles. Then 1,4-dioxane was slowly added into the mortar and mixed together to form a uniform suspension. The suspension was then sonicated for

[†]Dedicated to the memory of Professor Sukant K. Tripathy.
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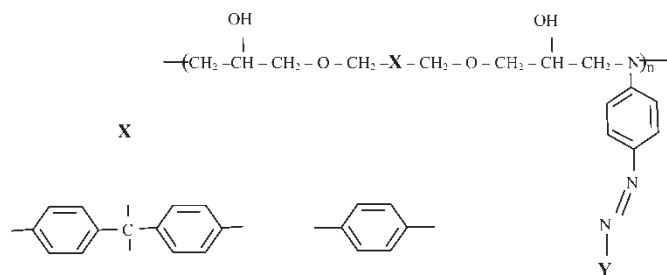


Fig. 1. Chemical structure of PDO3 polymer.

one hour to make it more homogeneous. The composite films were produced by spin-coating from the homogeneous suspensions of 77 wt% PDO3 and 23 wt% TiO₂ and 70 wt% PDO3 and 30 wt% TiO₂ onto glass slide substrates. The speed of the spinner was set at 600 rpm, which yielded thin films with a thickness around 1 micron. The thin film samples were dried overnight in a vacuum oven at 70°C to remove the remaining solvent.

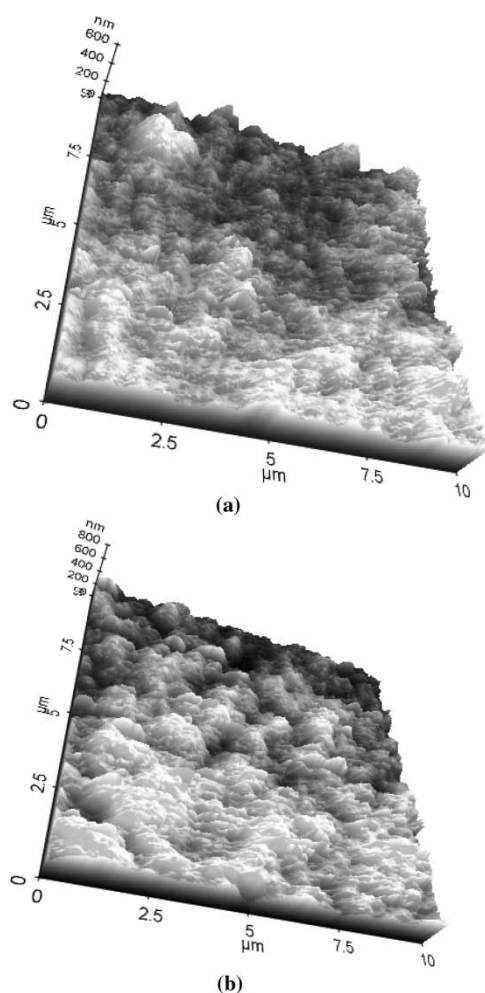


Fig. 2. Texture of PDO3-TiO₂ composite films: (a) 23 wt% of TiO₂ and (b) 30 wt% of TiO₂.

2.2 Atomic Force Microscopy Measurements

The surface topography of the polymer thin films was obtained with an atomic force microscope (AFM). The AFM was operated in contact mode with the scans rate of 1 Hz.

The topographic images of the polymer thin films are shown in Figures 2 (a and b), and the measured roughness are 64 nm for the film with 23 wt% TiO₂ and 76 nm for the film with 30 wt% TiO₂, respectively. The film surfaces are very rough and large clusters of TiO₂ are visible throughout the surfaces. The rough surface of the samples scattered the incident laser beams during the SRG formation, consequently limiting the SRG formation.

3 Results and Discussion

3.1 Surface Relief Grating Fabrication

The samples were illuminated with continuum coherent polarized beams from an Ar⁺ laser at 514 nm. The absorption of the laser beams causes the azobenzene chromophores to undergo a trans-cis isomerization process, leading to a change in their orientation with respect to the incident polarization. As a result, the polymer migrates away from the regions where the laser beams interfere constructively to the regions of destructive interference. As the polymer migrates, it also carries the TiO₂ nanoparticles along the same path. This process results in the formation of SRG structures on the surface of the composite films of the azopolymer and TiO₂ nanoparticles. The SRG fabrication is strongly dependent on the polarization orientation of both writing beams (6). The polarization of the laser beam was set at 45° with respect to s-polarization. Figure 3 shows the experimental setup used to write the SRG structures. In the present study the intensity of the Ar⁺ laser beam was set at 80 mW/cm². The incident angle of the laser beams was set at 14 degrees, leading to SRGs with a periodicity of 1 micron.

The samples used in the investigation were the composite thin films of the azopolymer and TiO₂ nanoparticles. Thus, as the polymer that contains the azobenzene chromophores undergoes trans-cis transformation leading to the SRG formation during the writing process, TiO₂ nanoparticles are dragged by the polymer to the peaks of the SRG structures. Figure 4 (a) shows a SRG on a PDO3 film. By comparison,

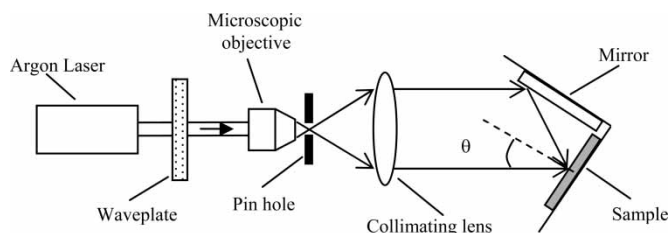


Fig. 3. Experimental setup for fabricating SRG structures.

as can be seen in Figures 4 (b and c), the crests of the SRGs contain TiO₂ nanoparticles and TiO₂ clusters are also observed in some regions on the thin films.

When an intense polarized laser beam interacts on the surface of an azopolymer film, the surface of the azopolymer film starts to deform. As a result, a lateral migration of the polymer chains occurs attributed to lateral force acting on the azopolymer as described in references (12 and 13). During the SRG formation process with the composite film, the azopolymer moves from one region to another region. The TiO₂ nanoparticles proceed along with the azopolymer. Figures 4 (b and c) show SRG structures with TiO₂ nanoparticles dispersed throughout the sample and notably in the peaks of the SRG.

The diffraction efficiencies for the SRGs formed on the composite films with 23 wt% and 30 wt% of TiO₂ nanoparticles are approximately 7% and 6%, respectively. These are low when compared with the efficiency of 23% from a SRG on a PDO3 film, written under the same conditions. The lower efficiency can be attributed to lesser azobenzene polymer available for SRG inscription, where the TiO₂ nanoparticles do not contribute to the SRG formation. Another factor responsible for the lower diffraction efficiencies is the scattering of the writing beams impinging upon the rough surface of the samples (as shown in Figures 2 (a and b)). It is remarkable that the strength of the lateral forces acting on the azobenzene polymer during the SRG formation

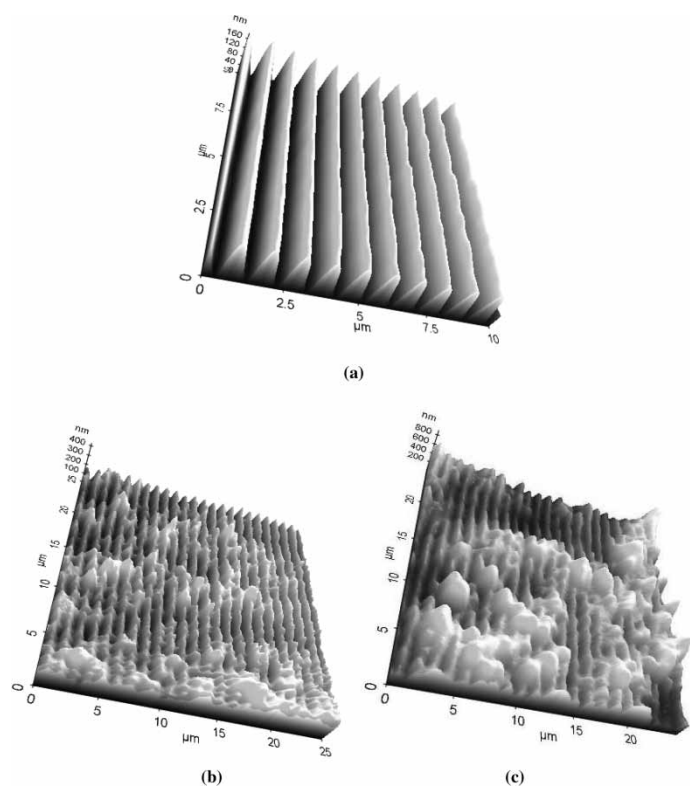


Fig. 4. SRG structures written on (a) a PDO3 film, and on the PDO3-TiO₂ composite films with (b) 23 wt% of TiO₂ and (c) 30 wt% of TiO₂.

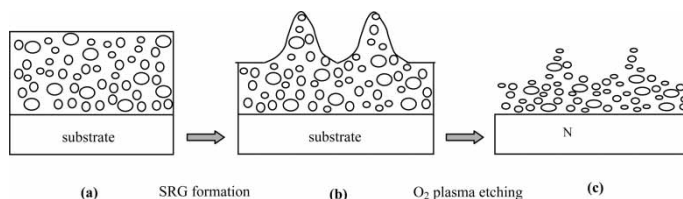


Fig. 5. Schematic diagram of the fabrication process: (a) a representation the composite thin film; (b) SRG structure; and (c) a TiO₂ grating after oxygen plasma etching.

is sufficient to indirectly move TiO₂ particles from regions where the polarized laser beams interfere constructively (valley) to regions of destructive interference (peaks).

3.2 Oxygen Plasma Etching

To obtain a TiO₂ grating from the SRG formed on the composite film, the polymer scaffold in the SRG structures

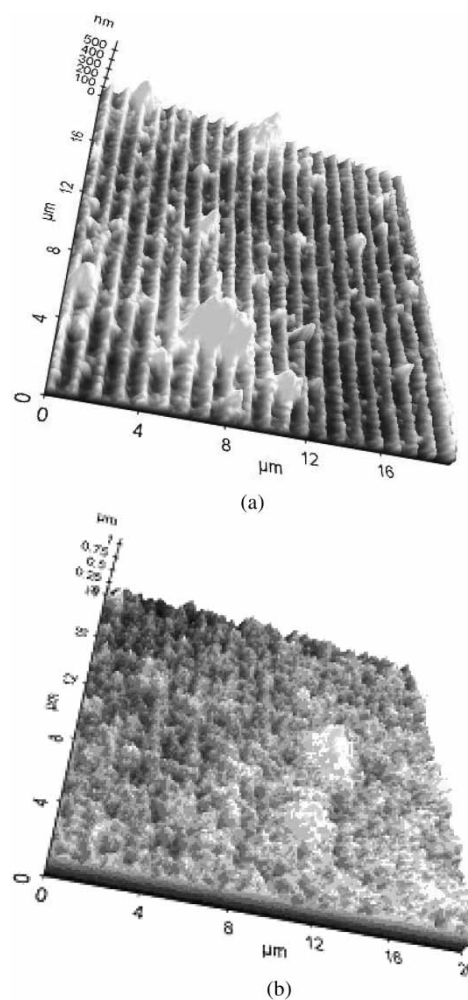


Fig. 6. (a) AFM image of the SRG structure on a PDO3-TiO₂ composite film with 30 wt% TiO₂, and (b) AFM view of the same sample after the oxygen plasma treatment.

needs to be removed, which can be done by oxygen reactive plasma etching. The SRG formed on the composite film with the higher concentration of TiO₂ (30 wt%) was selected for the study. The SRG sample was placed in the plasma chamber, which was evacuated to 1 Torr. Oxygen gas was introduced into the chamber bringing the pressure to 4 Torr. The oxygen plasma was formed in the chamber when the power of the RF source reached 200 Watts. The sample was then treated under the plasma for 20 min. The oxygen plasma treatment completely removed the azopolymer from the sample, resulting in a TiO₂ thin film with a relief structure on the surface.

After the plasma etching treatment, 70 wt% of the polymeric material in the SRG structure was removed, yielding an eroded TiO₂ grating. Figure 5 schematically depicts the steps of the fabrication process. Figure 5 (a) shows the composite film prior to any processing with TiO₂ dispersed throughout the azopolymer film and the circles of different sizes represent the TiO₂ nanoparticles and clusters. Figure 5 (b) is a representation of the SRG on the composite film, where TiO₂ nanoparticles moved along with the azopolymer during the grating formation. Figure 5 (c) shows the SRG structure after the oxygen plasma etching. The TiO₂ grating is covered with holes due to removal of the polymer. Figures 6 (a and b) show the AFM images of the corresponding steps illustrated in Figures 5 (b and c), respectively.

Figure 6 (a) shows the PDO3-TiO₂ SRG structure prior to oxygen plasma etching where TiO₂ nanoparticles are visible at the peaks of the SRG structure. The peaks of SRG are higher than the surface of the azobenzene polymer-TiO₂ thin film prior to SRG fabrication, suggesting that the lateral forces acting on the azobenzene chromophore during the SRG formation are able to move TiO₂ nanoparticles from one region to another in the composite film. Figure 6 (b) shows the sample after being subjected to oxygen plasma etching. Even through the TiO₂ grating is less pronounced and the sample surface is rough, one can clearly see the trend of the relief structures of the TiO₂ grating. The TiO₂ grating is very shallow and its diffraction efficiency is of the order of 0.5%.

4 Conclusions

Using the properties associated with the formation of SRG structures on azobenzene polymer, SRGs on thin films of PDO3-TiO₂ composites were fabricated. AFM studies indicated the distribution of TiO₂ particles throughout the samples and in particular at the peaks of the SRG structures. TiO₂ nanoparticles migrated along with the azopolymer to

form the surface relief structures. These results suggested that the lateral force acting on the azopolymer during SRG formation is strong enough to move the TiO₂ nanoparticles as well. This lateral force is capable of manipulating the nanoparticles, and consequently fabricating the submicron structures on the composite films. A TiO₂ grating was achieved by etching the polymer away under oxygen plasma treatment. Complex structures will be fabricated using the composites of azopolymers and nanoparticles.

5 Acknowledgments

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