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Fabrication of Gold Nano-Structures with Azopolymer Templates†

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Fabrication of gold nano-patterns has been demonstrated employing surface relief structures created on films of an azobenzene-functionalized polymer as templates. The surface relief templates were photoinscribed on the azopolymer films in one-step with two laser beams. Thin layers of gold were over-coated on the polymer templates by thermal evaporation. Gold lines of a few hundred nanometer width were successfully fabricated by pyrolyzing the azobenzene polymer. Sub-micron gold dots were also created. The resulting gold structures exhibited the same periodicity as the polymer templates.

Keywords: azopolymer; surface relief grating; template; pyrolyze

1 Introduction

The continuous miniaturization of electronic and photonic devices over the past few decades has necessitated the development of adaptable high-throughput nanoscale fabrication techniques. One of the most significant challenges to the realization and large-scale manufacture of devices is the fabrication process. The most commonly adopted techniques for the fabrication of highly ordered arrays of micro and nanostructures include lithography using photons (1), electrons (2) or ions printing (3), embossing (4), molding (replication using masters, such as micro-contact printing techniques) (5), soft lithography (6), projection photolithography (7) and scanning probe based lithography (8–11). These ordered structures offer great potential for photonic (12), electronic (13), and sensor (14) applications. The fabrication processes essentially involve inscription (writing) and/or replication. Although writing and replication are, in most cases, different kinds of processes, replication always requires the fabrication of a "master" or a "mask". Writing nanostructures or "making masters" is often done by serial techniques such as writing with a focused beam of electrons or ions. Moreover replication based techniques, such as soft lithography require the maintenance of masters/masks. Although active research is being pursued in existing technologies, well-controlled and intricate arrays with higher resolution are possible only by X-ray lithography or electron-beam lithography or scanning probe techniques. However, these methods are limited by long processing time and high production cost.

We previously explored a novel and simple methodology for fabricating ordered periodic structures of titanium oxides at the sub 100 nm scale employing azobenzene polymer templates (15). It is well-known that optical manipulation of azobenzene functionalized polymeric materials in the solid state at modest intensity is a non-thermal process (16, 17). When illuminated with a coherent light of appropriate wavelength, the azobenzene groups undergo a reversible *trans-cis-trans* isomerization process and an associated orientation redistribution of the chromophores. Holographic surface relief gratings (SRGs) with intricate structures showing large surface modulation (>3000 Å) can be easily photoinscribed on the azopolymer films at modest light intensities without any subsequent processing steps. The efficient *trans-cis-trans* isomerization is necessary for motion of the chromophores, which drag the polymer chains in the direction of field gradient. We have demonstrated that these surface relief patterns created on azobenzene polymer films can be readily used as templates to fabricate submicron/nano structures of metal dioxide. Titania nanoparticles, with a mean diameter of less than 10 nm, were deposited selectively on the surface of the SRG formed on azopolymer films (on glass substrates) using sequential electrostatic layer-by-layer deposition with a polyelectrolyte, poly(4-styrene sulfonate) (SPS). The nano-layered assemblies of SPS and titania were

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†Dedicated to the memory of Professor Sukant K. Tripathy

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then heated to a suitable temperature in air to aggregate the colloids further along the grooves of the SRG. At higher temperatures (around 500°C), the polymer scaffolding is pyrolyzed, leaving behind highly ordered patterned array of titania nanowire with line-widths less than 150 nm in a relatively large area (>1 cm^2). The formation of TiO_2 nanostructures using SRGs created on azopolymer films was also reported by Kim et al. (18) utilizing a controlled sol-gel reaction of a titanium precursor, titanium isopropoxide. In order to control and reduce the hydrolysis rate of the titanium precursor, HCl was added to the precursor solution. The precursor solution was then spin-coated on the SRGs and heated up to 425°C to remove the polymer template. TiO_2 nanowire array with a line-width of 250 nm were achieved. The novelty of the fabrication method using the azopolymers SRG templates lies in its simplicity and adaptability to obtain structures in the neighborhood of a hundred nanometers without the use of very expensive instrumentation that was typically used.

We have recently further extended this novel optical patterning technique to fabricate nanostructures of metals. Gold nano-patterns have been successfully created using the SRG templates. Arrays of gold nanowires and submicron gold dots were easily created. The experimental details and results are presented.

2 Experimental

An azobenzene functionalized epoxy polymer (diglycidyl ether of Bisphenol A and 4-(4′-nitrophenylazo) phenyl amine (Disperse orange 3), which exhibited efficient surface relief grating formation characteristics, was utilized (17) in the study. The chemical structure of the azopolymer is shown in Figure 1. The T_g of the polymer was determined to be 102°C by differential scanning calorimetry. The azobenzene functionalized epoxy polymer (5 wt%) was dissolved in 1,4-dioxane. Optical quality films of the azobenzene polymer were obtained by spin-coating the filtered polymer solution onto microscope glass slides. These films were then dried in a vacuum oven at 60°C overnight.

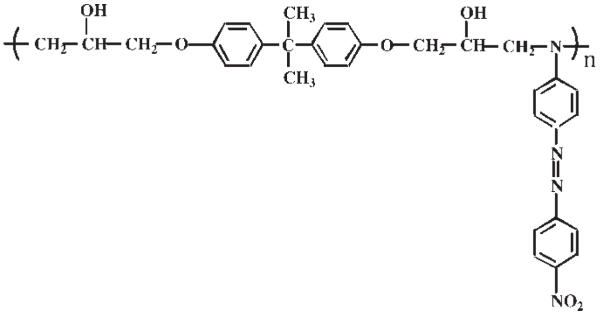

Fig. 1. Chemical structure of the azobenzene chromophore functionalized epoxy-based polymer.

The polymer SRG templates with a grating spacing about 1 μm were employed to fabricate nanostructures of gold. These templates were photoinscribed on the azopolymer films by using two laser beams at 515 nm from an Argon ion laser with an intensity of 100 mW/cm^2. The grating spacing was adjusted by varying the angle between the two laser beams. To achieve optimized recording, the polarization of the incident laser beam was chosen to be 45° polarized with respect to s-polarization. Grating formation was monitored with a low power HeNe laser at 633 nm by measuring the power in the first-order diffracted beam during the writing process. The “egg-crate” SRG template used for fabricating submicron gold dot structures was formed by sequentially recording two SRGs perpendicular to each other.

Thin gold (Au) film about 50 nm thick was simply overcoated on the SRG template by thermal evaporation in vacuum. The gold over-coated SRG templates were then heated to 500°C for 2 h in air to pyrolyze the azobenzene polymer. The step-by-step fabrication procedure of the gold nanostructures is shown in Figure 2.

Atomic force microscopy (AFM, in contact mode) and scanning electron microscopy (SEM) were utilized to investigate the surface relief patterns of the gold nanostructures. Energy dispersive microanalysis with X-rays (EDAX) was employed to confirm the presence of gold in the nanostructures and to obtain the X-ray mapping of the gold patterns. The EDAX analysis of the gold nanostructures was performed at an accelerating voltage of 15.0 kV.

3 Results and Discussions

The surface relief templates were photofabricated on the azopolymer films. Figure 3 shows a three-dimensional AFM view of a SRG created on the azobenzene polymer film. A periodic surface relief structure was observed as a result of

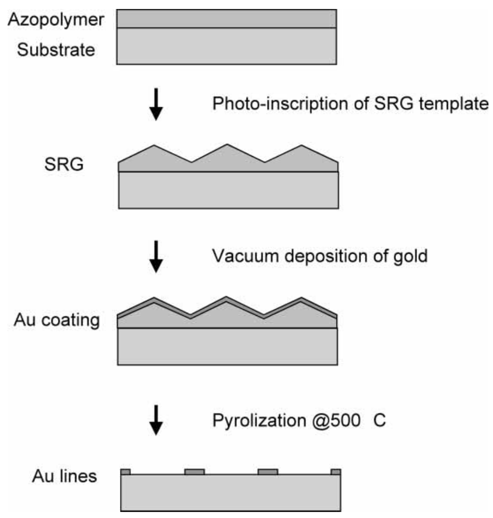

Fig. 2. Experimental procedure to create nano-scale gold structures.

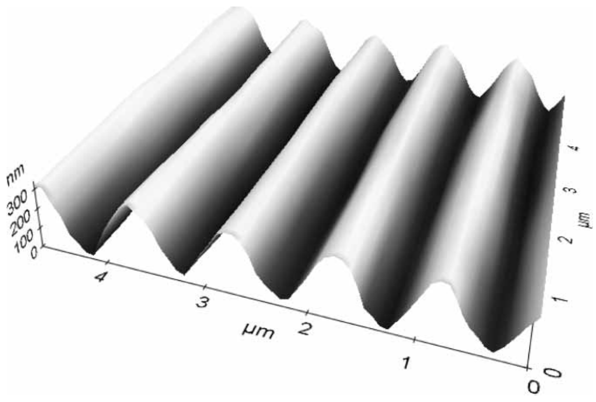

Fig. 3. A three-dimeniosnal AFM view of an SRG formed on an azopolymer film.

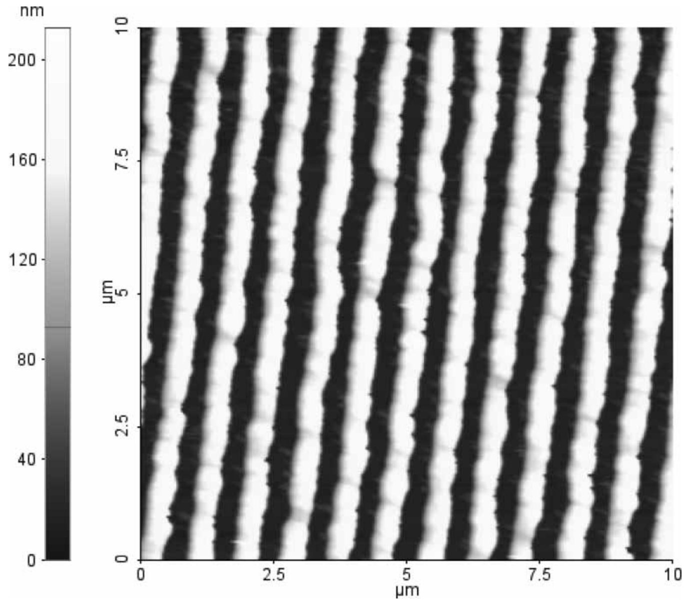

Fig. 4. A two-dimensional AFM image of a gold relief nanowire array.

recording the interference pattern created by the two laser beams. Large surface modulation about 300 nm was measured with a grating spacing of 1 μm. Nanowire array of gold was created using the SRG photoinscribed on the azopolymer film as the template. A two-dimensional AFM image of a gold relief nanowire array, after pyrolyzing the azopolymer at 500°C, is depicted in Figure 4. The depth of the surface relief pattern was determined to be about 160 nm. The gold nanostructure exhibited the same period as that of the azopolymer template.

The EDAX analysis of the fabricated nanostructure provided a verification of the formation of gold nanowire array. The EDAX spectrum of the nanowire array is shown in Figure 5. The gold Mα X-ray line at 2.12 keV was clearly observed, which confirmed the presence of gold in the nanowire array. SEM image of the gold relief structure is shown in Figure 6(A), revealing the gold nanowires with a line-width of 250 nm. Further examination of the gold nanowire array was accomplished by mapping of the EDAX gold Mα X-ray line in the same area as that for the SEM. Figure 6(B) shows the EDAX mapping of gold Mα X-ray line of the gold nanostructure. Clean gold

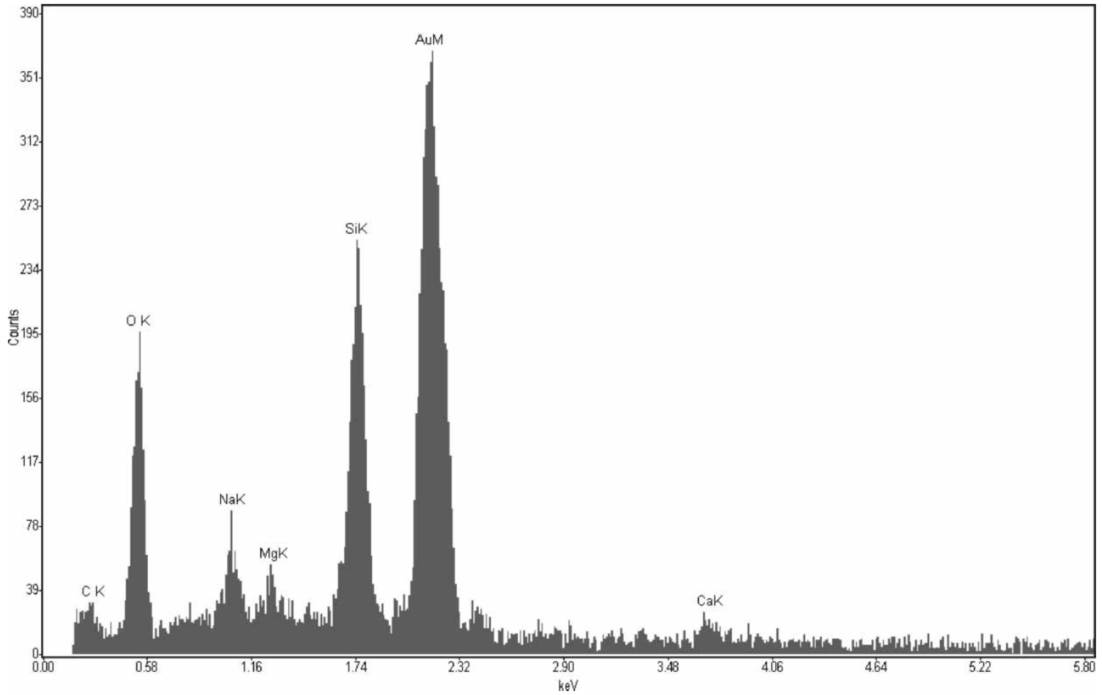

Fig. 5. EDAX spectrum of the gold nanowire array.

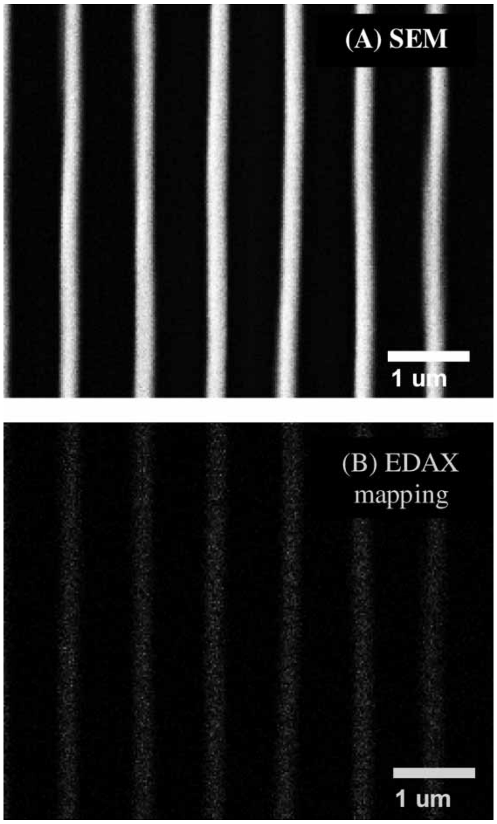

Fig. 6. SEM image and EDAX mapping of Au Mα X-ray line of a gold nanowire array.

nanowire array was obtained. No residual of gold deposit was presented in the areas between the gold nano lines. This evidently indicated that the simply photoinscribed surface relief patterns on the azopolymer films can also be readily employed as templates for the fabrication of gold nanostructures.

It is believed that during the pyrolysis process the surface relief structure on the azopolymer film started to planarize at a temperature close to the Tg of the polymer and the coated gold film migrated into the grooves and aggregated. Further migration occurred at higher temperature where the polymer template softened. Finally, at 500°C the azopolymer template was completely pyrolyzed and the gold was fused together forming the nanowire array.

Submicron array of gold dots was also fabricated using the "egg-crate" SRG template created on the azopolymer films. SEM image of the gold relief structure is shown in Figure 7(A), revealing a 2-dimensional array of gold dots of 400 nm. EDAX mapping of gold Mα X-ray line in the same area as that for SEM scanning offered a proof of the presence of gold in the submicron dot array. The EDAX gold Mα X-ray line mapping of the gold relief structure is shown in Figure 7(B). Residual gold deposits were observed apart from those occurring at the expected periodic positions, possibly due to a small amount of excessive gold coating on the template. We are further exploring the fabrication process of gold nanostructures with fine-control of the gold deposition process and the surface modulation depth of the SRG templates. It is expected that these residual deposits in the gold dot array can be minimized by the fine-tuned steps in the gold coating process and by the optimized surface profiles of the relief templates on the azopolymer films.

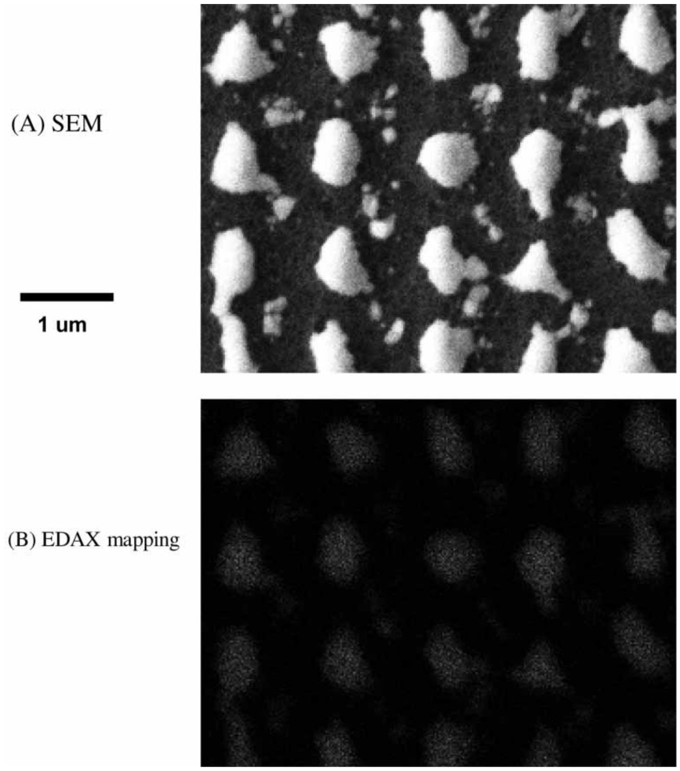

Fig. 7. SEM image and EDAX mapping of Au Mα X-ray line of a submicron array gold dots.

4 Conclusions

In conclusion, we have successfully extended the novel and simple fabrication technique employing the azopolymer templates to the formation of gold nanostructures. Arrays of gold nanowire and submicron dots were produced. These arrays exhibit the same periodicity as the azopolymer templates. These results clearly demonstrated that the simple fabrication method employing the surface relief structures created on the azopolymer as templates is capable of creating metal patterns with a few hundred nanometers features.

5 Acknowledgements

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