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Patterning Flexible Substrates Using Surface Relief Structures in Azobenzene Functionalized Polymer Films

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A novel method for maskless micro-patterning of polymeric substrates is presented. First, an azobenzene functionalized polymer film is spin-coated on a Poly (ethylene terephthalate) (PET) sheet. Then surface relief structures are optically inscribed on the polymer film by interference of laser beams. The patterned azobenzene functionalized film is then etched in the plasma chamber such that the gratings are transferred to the PET substrate. Finally, any remaining azobenzene functionalized polymer is dissolved away using an appropriate solvent. This method of patterning can be broadly applied to a variety of flexible/polymeric substrates and the resolution is not limited by the substrate thermo-mechanical properties.

Keywords: Maskless micro-patterning of plastics, azobenzene functionalized polymers, surface relief structures, optically induced grating, etching

1. Introduction

Organic and polymeric materials based devices present several unique advantages such as flexibility; being lightweight and amenable to roll-to-roll processing, that can potentially result in high-throughput low-cost devices. One of the most significant challenges to the realization and large-scale manufacture of these devices is the fabrication process. Conventional photolithography cannot be directly extended (without modification) to the fabrication of flexible organic devices, as the substrates used are often not completely planar and are also easily affected by chemical solvents (1). In this communication, we report a fairly simple and inexpensive method for micro-patterning (over areas greater than a few square inches) a variety of substrates including flexible plastic sheets.

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The most commonly adopted techniques for the fabrication of patterned micro and nanostructures include (1) lithography using photons (2), electrons (3) or ions, printing (4), hot-embossing (5), molding (replication using masters), soft lithography (6) and scanning probe based lithography (7–10). Although active research is being pursued in existing technologies such as projection photolithography (11), higher resolution becomes possible only by using shorter wavelength radiation such as ultra-violet, extreme-ultra-violet, and X-rays. However quartz lenses are no longer transparent in these wavelengths and new materials or reflective optics are required. X-ray lithography is routinely used to fabricate structures as small as 40 nm. The high production cost for the masks has to some extent impeded the progress of this technology in the sub-micron regime.

Conventional photolithography is most commonly used for transferring geometric patterns from a pre-fabricated mask onto the surface of a substrate. The steps involved are coating of a photoresist film, soft baking, mask alignment and optical exposure, developing, hard baking, etching and removal of the remaining photoresist film. There are two

major factors that limit the ability to extend conventional photolithography to cost-effective large area patterning of polymeric substrates. First, the fabrication of photomasks is fairly expensive but one of the most crucial steps that determine the ultimate resolution of the patterns generated using lithography. Secondly, the removal of photoresist during processing often involves the use of strong bases and/or organic solvents that are not suitable for patterning polymeric substrates. While other techniques such as hot-embossing can be used for the large-scale, micro-patterning of polymeric substrates, the suitability and resolution of these technique are often limited by the thermo-mechanical properties of the polymers (12,13).

2. Experimental

The smooth side of a PET film used for inkjet printable transparency film was cleaned with ethanol. The azobenzene-functionalized polymer was dissolved in spectroscopic grade 1, 4-dioxane and filtered through a 0.45 μm membrane filter. The solution was then spin-coated on the PET substrate and dried in a vacuum oven overnight at 80°C. The film thickness was controlled at 0.5 μm by adjusting the solution concentration and spin speed. Surface relief structures were fabricated on the polymer film by interference of the two laser beams at 488 nm from an Argon (Ar+) laser with an intensity of 160 mW/cm^2 using a simple experimental set-up (14). The polymer film with gratings was etched in a Plasma Etcher with RF of 13.56 MHz and power of around 50 watts in an oxygen atmosphere (pressure 150 millitorr).

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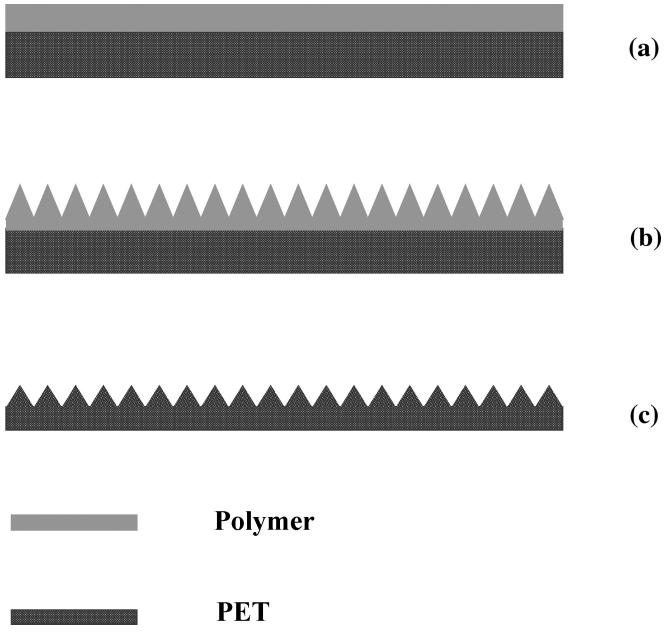
3. Results and discussion

A novel method that can be broadly applied to the patterning of a variety of flexible/polymeric substrates and not limited by the substrate thermo-mechanical properties is presented. The patterns are first inscribed as surface relief structures by optical interference technique on the surface of an azobenzene functionalized polymer that has been coated on the polymer film to be patterned. Sub-micron features can be accurately obtained on azopolymer surface over reasonably large areas (> 6 square centimeter) by adjusting the angle between two interfering beams. This single-step process does not require a mask/master or developing procedure. Although, if desired the patterning of the azo-polymer is also possible by exposure through a conventional mask as with a conventional resist.

Simple post-processing techniques such as oxygen plasma processing or reactive ion etching is used to transfer these intricate sub-micron structures on polymer film present immediately below the azopolymer. Thus, the grating structures that are optically inscribed on the azopolymers are translated to inscriptions on flexible substrates without using photomasks.

Azobenzene-functionalized polymer thin films have been extensively explored for the fabrication of surface-relief structures upon exposure to an interference pattern. The mechanism of this process is based on the photoisomerization and photoinduced anisotropy of the azobenzene groups in the polymer chains. Upon irradiation with polarized light of an appropriate wavelength, azobenzene chromophores will undergo photoinduced reorientation through trans-cis-trans isomerization and initiate the mass transport process, which begins on the free surface of the polymer film and continues through into the bulk. Surface relief gratings (SRGs) can be formed at temperatures well below the glass transition temperature (Tg). This phenomenon has been investigated on a variety of azobenzene-functionalized polymers (14–19).

Since the modulation depth of surface relief gratings is related to the light exposure time, the power and the polarization direction of the writing beams, the feature of the grating patterns can be accurately controlled. Grating spacing from a few microns to submicron can be easily obtained by changing the angle between two interfering beams of the writing beams. In addition, more complicated surface structure, such as "egg-crate", hexagonal and other gratings, can be easily fabricated on the azobenzene functionalized polymer films by simply superposing various recording patterns (20). We have successively patterned an Indium Tin Oxide



Sch. 1. Schematic outline of the procedure used to pattern PET layer: a) a PET sheet was spin-coated with an azobenzene polymer film; b) surface relief gratings were inscribed on the polymer film using two coherent interfering laser beams; c) the sample was etched in a plasma-etcher with oxygen until all the azobenzene polymer disappeared and then rinsed with 1,4-dioxane.

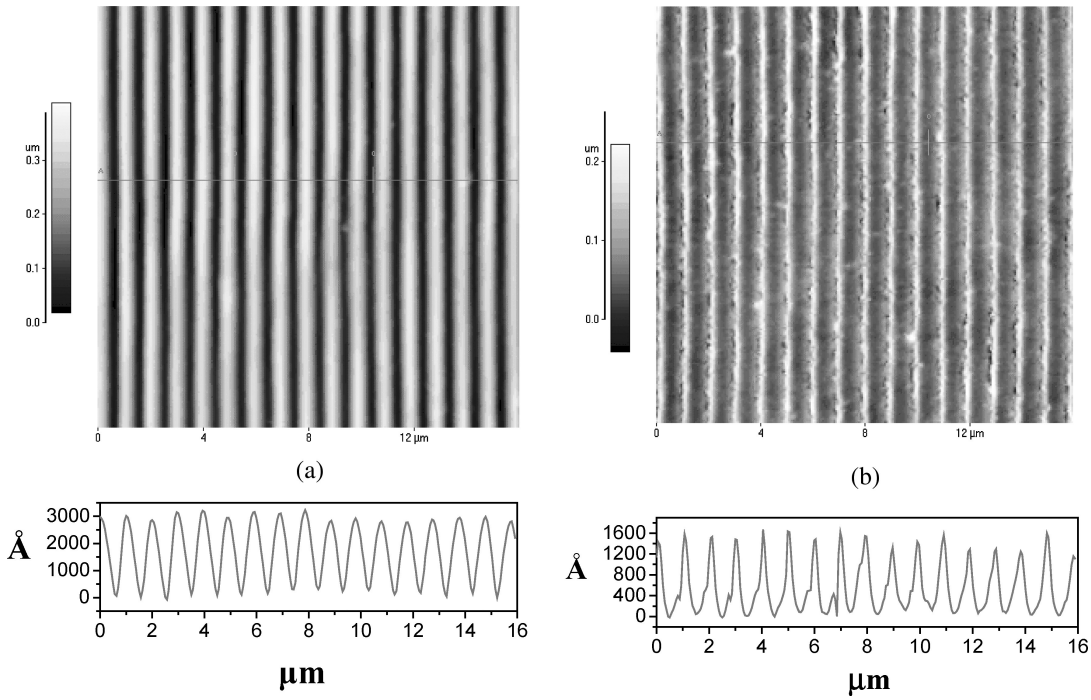


Fig. 1. AFM images and line-profile measurements of: a) gratings on the polymer film; b) patterned PET film.

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layer on a glass substrate using surface-relief structures formed on azobenzene functionalized polymer film (21). The present study extends this technique to patterning flexible substrates and demonstrates the creation of intricate structures on Polyethylene terephthalate (PET).

First, an azobenzene functionalized polymer film was spin-coated from dioxane solution on a PET film as illustrated in (Scheme 1a). Then a surface relief grating was inscribed on the azopolymer film (Scheme 1b). The sample with the surface relief grating was etched in oxy-

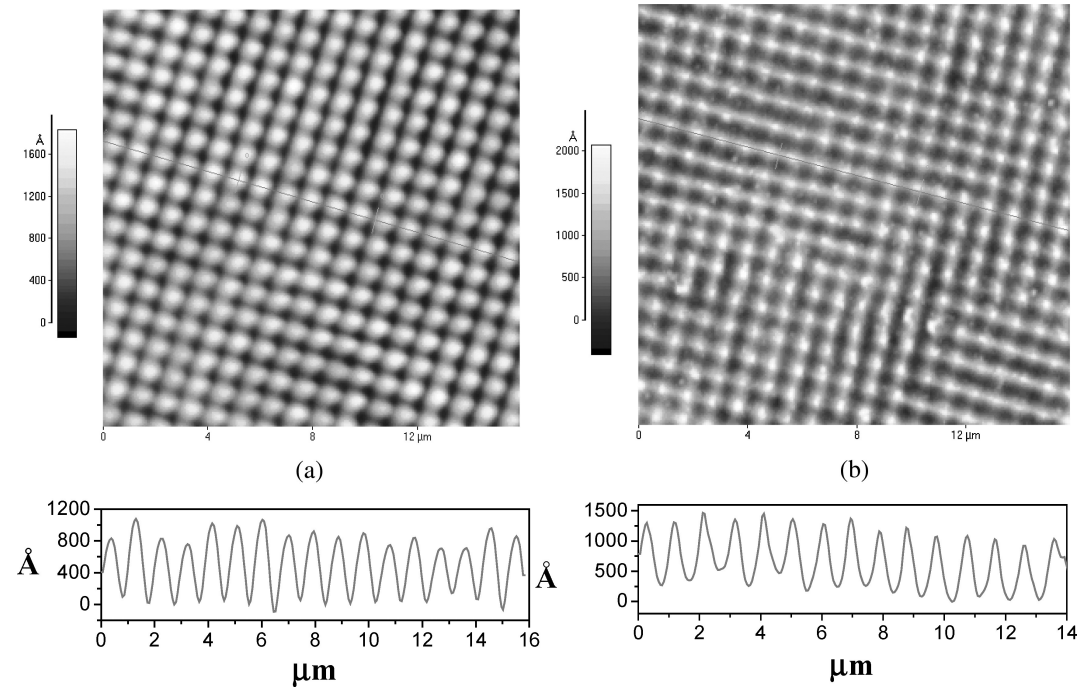

Fig. 2. AFM images and line-profile measurements of: a) 'egg-crate' gratings on the polymer film; b) patterned PET film.

gen plasma. Finally, the remaining azobenzene functionalized polymer was removed by a solvent to give a patterned substrate (Scheme 1c). Thus, the grating structures that are optically inscribed on the azopolymers are translated to inscriptions on flexible plastic sheets without using photomasks.

The azobenzene-functionalized polymer used was an epoxy-based azopolymer PDO3, which was synthesized from diglycidyl ether of bisphenol A and 4-(4′-nitrophenylazo) phenyl amine (14). Then a surface relief grating was inscribed on the azopolymer film with thickness 0.5 μm by interference of the laser beams at 488 nm from an Ar+ laser with the incidence angle of 14°. The polarization of the interfering beams was linear with the plane of polarization at an angle of 45° with respect to the s-polarized beam. The surface relief gratings were investigated using atom force microscopy (AFM) in the contact mode under ambient conditions. A surface modulation depth of about 3000 Å and the grating spacing of around 1 μm were observed (Figure 1a).

The sample with the surface relief grating was etched in a Plasma Etcher with RF at 13.56 MHz and power of around 50 watts in an oxygen atmosphere (pressure 150 milli-torr). During the etching process, the grating in the valleys was first removed all the way to the surface of the PET layer. Subsequently, the exposed PET layer began to be etched simultaneously. Thus after the azopolymer layer was etched away, the gratings were transferred to the PET sheet. Any traces of azobenzene polymer that remained on the surface were removed by rinsing with 1,4-dioxane. After plasma etching, gratings with depth of around 1300 Å and spacing of around 1 μm was transferred to the PET substrate as seen in Figure 1b.

The 'egg-crate' like structure on the polymer film (Figure 2a) was easily created by recording two orthogonal gratings in succession at the same place. After etching in oxygen plasma cleaner and rinsing with 1,4-dioxane, a patterned PET sample with 'egg-crate'-like structure was successfully obtained (Figure 2b).

4. Conclusions

In conclusion, we have demonstrated a novel, facile method for patterning flexible plastic layers by combining photoindued surface relief gratings inscription on an azobenzene functionalized polymer with plasma etching. This patterning method may offer tremendous potential towards maskless fabrication of periodic substrates over large areas for electronic and photonic device applications. This method of micro/sub-micron patterning is also not restricted by thermo-mechanical properties of the polymer film and therefore broadly applicable to a wide variety of flexible substrates. In addition this facile method for submicron scale patterning of substrate (over areas greater than a few square centimetre) is of great importance to other emerging areas of materials science, nanotechnology, nanophotonics and microelectronics.

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