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2010 Nanotechnology 21 165301

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Proximity field nanopatterning of azopolymer thin films

Robert H Lambeth¹, Junyong Park³, Hongwei Liao², Daniel J Shir², Seokwoo Jeon³, John A Rogers^{1,2} and Jeffrey S Moore^{1,2}

¹ Department of Chemistry, Beckman Institute, University of Illinois, Urbana, IL 61801, USA

² Department of Materials Science and Engineering, Seitz Materials Research Laboratory,

University of Illinois, Urbana, IL 61801, USA

³ Department of Materials Science and Engineering, KAIST Institute for Nanocentury, Korea Advanced Institute of Science and Technology, 305-701, Daejeon, Republic of Korea

E-mail: jrogers@illinois.edu and jsmoore@illinois.edu

Received 17 December 2009, in final form 5 March 2010 Published 26 March 2010 Online at stacks.iop.org/Nano/21/165301

Abstract

A method for inscribing surface relief gratings in azopolymer thin films via proximity field nanopatterning is reported. Azopolymers prepared by ring opening metathesis polymerization were cast as thin films and brought into conformal contact with transparent polydimethylsiloxane phase masks. Irradiation of the film surface through the phase masks induces mass transport of azopolymer that generates surface relief structures on the basis of the intensity modulation of the light by structures on the phase mask. The experimental images obtained matched well with those produced by optical simulation. A wide variety of structures could be inscribed in the film surface which depended on the molecular weight of the azopolymer and irradiation time. Control experiments conducted suggest that the process is entirely photonic and that the presence of the phase mask on the film surface did not affect the inscription process.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Azobenzene functionalized polymers (azopolymers) are a unique class of photo-responsive materials and are well studied due to their wide applicability in a variety of applications [1, 2]. Many applications take advantage of the photo-induced isomerization from the more stable trans form to the less stable cis form. Relaxation from the cis isomer back to the trans isomer can occur thermally on a timescale of seconds to minutes or photochemically on a timescale of picoseconds. The isomerization process can have a profound effect on the physical and optical properties of materials which contain the azobenzene chromophore as a parent molecule or as a dopant. One of the most interesting phenomena associated with the photo-isomerization process is massive macroscopic motions of the polymer chains leading to physical deformation of the material well below the glass transition temperature [3]. Irradiation of a flat, isotropic film surface with an intensity distribution of plane

polarized light results in a transfer of an optical pattern to the film surface. The research groups of Natansohn/Rochon and Tripathy/Kumar were the first to observe the optomechanical response of azobenzene functionalized polymers (azopolymers) to irradiation with interference patterns of plane polarized light [4, 5]. Since these initial discoveries, much effort has been devoted to understanding the mechanism of mass transport, developing structure–property relationships and identifying possible applications.

Recently, we reported a new method for the preparation of well-defined azopolymers using ring opening metathesis polymerization (ROMP) [6]. This provided an alternative to other conventional methods such as free radical polymerization or condensation polymerization where control over the macromolecular structure or functional group intolerance was limiting. We also investigated the response of our material prepared by ROMP to irradiation with a simple interference pattern of linearly polarized light and observed surface modulations comparable to those produced in similar materials under similar conditions. The typical setup involves impinging an expanded and collimated beam from an argon laser source on the surface of the film creating a sinusoidal wave pattern. While this method is certainly effective for generation of surface relief gratings, it has several limitations. The maximum amplitude of relief depth is typically achieved when the angle between the beams is $14^{\circ}-15^{\circ}$ limiting the effectiveness of the process when smaller or larger periodicities are desired [7]. The types of surface structures are also very limited beyond simple gratings. Construction of more complex patterns requires multiple recordings or complex, cumbersome laser setups. We propose a new method for generating the necessary light intensity distributions needed to induce macroscopic motions based on a soft lithographic approach known as proximity field nanopatterning (PnP) [8]. This procedure allows for the fabrication of new types of surface relief structures in azopolymer thin films.

PnP is a photolithographic technique which involves the exposure of photosensitive materials through soft, conformable phase masks [9]. Spin casted photosensitive materials, typically photopolymerizable resists, are brought into intimate contact with the phase mask via generalized adhesion forces [10-12]. The conformable phase masks are made of transparent, flexible materials such as polydimethylsiloxane (PDMS) or perfluoropolyethers (PFPE) [13] with various relief structures of surface. Passage of light through the phase mask generates a complex 3D intensity distribution of light in the photosensitive material. Removal of the uncured photoresist through developing process results in free standing 3D nanostructures, replicating the intensity distribution [14]. Abbe theory of image formation can account for all aspects of the optics of this process. In particular, the surface relief structures on the phase masks cause phase shifts between light passing through raised and recessed areas. A transmission function can be represented in terms of these phase shifts. Fourier components of the transmission function, some of which are propagating and the others are evanescent, define complex intensity distributions immediately adjacent to the surface of the mask via interference of the propagating modes. The shape, areal coverage, height, and refractive index of phase masks define the intensity distributions.

Former work of PnP mostly used photopolymerization chemistry to form multi-dimensional structures. For example, in negative tone resists, the regions exposed to light above the photocrosslinking threshold can polymerize and become insoluble during developing process while the underexposed regions remain soluble; vice versa in positive tone resists. Thus, inverse structures can be formed depending on the photocrosslinking chemistry of the resist. This process differs significantly from azopolymers in that the structures formed in azopolymer films are from the migration of the material and not from photopolymerization. This unique property of azopolymers could be advantageous, because developing or post-curing processes are not required further, which simplifies overall fabrication processes. Since the polymer migrates from regions of high intensity to regions of low intensity, the resulting structures are similar to that of the positive tone resists. Here, we report the new patterning capabilities when



Figure 1. Chemical structure of azopolymer.

PnP is applied to azopolymer thin films. The scope of possible patterns, influence of irradiation time on structure formation, and influence of polymer molecular weight on irradiation time are described.

2. Experimental details

2.1. Materials

The azopolymers where prepared by the ROMP of a Disperse Red 13 functionalized norbornene monomer with Grubbs' 3rd generation catalyst. The molecular weight of the polymer is adjusted simply by varying the ratio of monomer to catalyst. The structure of the polymer is shown is figure 1. Full synthetic details are described elsewhere [6]. The PDMS phase masks used in this study were fabricated according to previously reported procedures [8].

2.2. Characterization

Atomic force microscopy (AFM) images were obtained on a Digital Instruments Multimode Nanoscope IIIa operating in tapping mode. Scanning electron microscopy (SEM) images were captured on a Phillips XL30 ESEM-FEG operating at an accelerating voltage of 5 kV. Samples were coated with a thin layer of gold/palladium. The molecular weight and polydispersity of the polymers were estimated in THF at 30 °C with a Waters 515 HPLC pump, Viscotek TDA model 300 triple detector and a series of three ViskoGEL HR high resolution columns (1 × G3000 HR, 2 × GMHHR-H mixed bed) at a flow rate of 1.0 ml min⁻¹. Molecular weight data are reported as polystyrene equivalents. The optical simulations of expected 3D azopolymer structures were calculated by rigorous coupled wave analysis using the GSOLVER(Grating Solver Development Co.).

2.3. Irradiation geometry

Light from an argon laser source at 488 nm is passed through a spatial filter, expanded and collimated. Passage through a $\lambda/4$ plate converts the light to circularly polarized light (CPL) which passes through the phase mask to generate an intensity distribution of light. Unless otherwise mentioned, the laser power was measured to be 150 mW cm⁻². The phase masks are placed on the surface of the thin film leading to conformal contact to the surface without the need for applied pressure. The same phase mask can be used repeatedly without destroying the relief structures on the phase mask surface. The



Figure 2. Schematic of PnP process.

films were spin cast from filtered solutions of cyclopentanone ranging in concentration from 200–400 mg ml⁻¹ depending on the molecular weight of the polymer onto piranha treated glass slides. This procedure generally resulted in 1–2 μ m thick films with very little surface modulation (1–2 nm) as confirmed by AFM. A schematic of the PnP process is described in figure 2.

3. Results and discussion

The different types of structures that could be produced were initially explored using various phase masks with different types of relief structures varying in size, shape, arrangement, and periodicity. By passing of light through these phase masks, the generated high diffraction beams forms 3D interference intensity distributions in thin film photopolymers. Thin films were cast from azopolymers with a molecular weight of 5 kDa and were irradiated for 15 min. Examples of the various types of possible structures are shown in figure 3. A wide variety of different patterns were readily inscribed on the surface of thin films. The size, shape, arrangement and periodicity of the surface structures are controlled by the relief structures on the surface of the phase mask. The geometry of the phase masks defines a relatively small number of propagating modes (3-9) that interfere to form the structures in figure 3. The nulls in intensity, which are similar to those reported in near field phase shift lithography, that occur in each phase boundary are clearly observed (ring shapes in figures 3(A)–(C) correspond to the edges of the raised posts on the phase mask). As expected, the material migrated from regions of high intensity to regions of low intensity forming structures analogous to a positive tone photoresist. Features sizes ranged from 40 to 225 nm for the examples shown. Also, these various structures are theoretically simulated in figure 2 based on calculations of 3D intensity distributions using rigorous coupled wave analysis. The experimentally fabricated surface structures of thin film azopolymer are exactly consonance with results of optical simulation. This initial study demonstrated the utility of PnP to readily create complex surface structures. After exploring the range of possible structures, the inscription process itself was investigated in more detail in terms of molecular weight of the azopolymer and irradiation time.

Bulk viscosity scales with the first power of molecular weight ($\eta \propto MW$) up to the point of chain entanglement so

Table 1. Comparison of vertical feature size in surface relief

 structures prepared from azopolymers of varying molecular weight.

Mn (calc) (kDa)	Mn (GPC) (kDa)	Vertical feature size ^a (nm)
5	4.4	100
20 40	19.9 38.7	65 40
100	91.2	15

^a Vertical feature size defines the average distance from the peak of the surface relief structures to the trough.

it is anticipated that polymers with longer chain lengths will experience lower rates and extent of surface deformation. It has previously been shown that molecular weight can have a significant effect on the rate of flow of the material and the size of the relief structures produced. Barrett et al initially observed this effect in azopolymer/PMMA blends [15]. Increasing the molecular weight of the PMMA relative to the azopolymer molecular weight lead to a reduction in feature size and inscription rate. Börger et al directly evaluated the effect of azopolymer molecular weight on inscription rates [16]. In their study, well-defined azopolymers were produced by the atom transfer radical polymerization (ATRP) of trimethylsilyl-protected 2-hydroxyethyl methacrylate followed by deprotection and coupling with the azo unit. They also observed a modulation of relief depth and inscription rate with increasing molecular weight. Given our ability to directly prepare azopolymers in a high throughput fashion via ROMP, a series of azopolymers of varying molecular weight were prepared and the size of the relief structures was evaluated. Thin films were coated from polymers with molecular weights of 5, 20, 40, and 100 kDa and irradiated for 5 min at 150 mW cm⁻² with a phase mask consisting of recessed circular holes with diameters of 670 nm and a periodicity of 970 nm. The results are summarized in table 1. As anticipated, the sizes of the relief structures decreased with increasing molecular weight over the time frame of irradiation. Thus, for producing surface relief structures in the shortest time possible, low molecular weight polymers are preferred. This study provides a nice example of the usefulness of ROMP for rapidly producing well-defined polymers of varying molecular weight for determining structure-property relationships.

The affect of irradiation time on the growth of the relief structures was also investigated. It was expected that the size of the features in the film surface would become saturated after a finite amount of time that depends on the light intensity distribution, orientation of chromophores, and surface tension created in the film surface. An azopolymer with molecular weight of 5 kDa was irradiated at room temperature through a phase mask consisting of recessed circular features with diameters of 670 nm and periodicities of 960 nm for varying amounts of time. The results are summarized in figure 4 and table 2.

The surface features were evaluated for times ranging from 5 to 25 min. Distances from the peak height of the relief structures to the troughs in between the relief structures (D_1) and in the center of the relief structures (D_2) was measured. After 5 min, features in the film surface were on the order on



Figure 3. AFM images and accompanying optical simulations of representative 2D surface structured azopolymer thin films. Each film was irradiated at room temperature for 15 min with an argon laser at 488 nm and 150 mW cm⁻². The optical simulations of expected 3D azopolymer structures were calculated by rigorous coupled wave analysis using the GSOLVER (Grating Solver Development Co.). Patterns generated from phase masks with relief structures with diameters (*d*) or widths (*w*) (nm) and periodicities (*p*) (nm) of: (A) hexagonal array of circular posts, *d* = 600, *p* = 800; (B) hexagonal array of circular posts, *d* = 1120, *p* = 1500; (C) square array of rounded square posts, w = 760, *p* = 1000; (D) line array, w = 300, *p* = 600; (E) square array of recessed circular holes, *d* = 670, *p* = 970.



Figure 4. Section analysis of AFM images of azopolymer thin films irradiated with an argon laser at 488 nm and 150 mW cm⁻² through a phase mask consisting of a square array of recessed circular holes, d = 670, p = 970.

Table 2.	Vertical features	sizes D_1	and D_2 as a	a function of time.
	Irradiation time ((min)	$D_{\rm c}$ (nm)	$D_{\rm e}$ (nm)

Irradiation time (min)	D_1 (nm)	D_2 (nm)
5	97	57
10	185	91
15	225	121
20	228	122
25	230	122

100 nm and grew in a non-linear fashion and eventually began to level off ca. 15 min of irradiation. The continued growth was accompanied with a loss of resolution in the features. The non-linear growth and eventual cessation of significant growth could result from a lack of addressable chromophores in the film or from surface tension. Since CPL was used, any chromophore orientated in the *z*-direction will not absorb photons and undergo isomerization. As the relief structures grow, the flow rate of polymer into regions of low intensity is slowed because the surface tension created produces a counter flow. Thus, as the number of chromophores that can be addressed becomes limited and the surface tension becomes too great, polymer flow begins to slow.

The thermal stability of the relief structures was also investigated. Annealing at or above the T_g of amorphous azopolymer films often leads to thermal erasure of the surface relief structures [7]. A surface structured film prepared by irradiation for 15 min at 150 mW cm⁻² through a phase mask consisting of recessed circular holes with diameters of 670 nm



Figure 5. (A) Sample geometry consisting of a 1.4 μ m spacer layer sandwiched between a PDMS phase mask and azopolymer thin film. (B) SEM image of spacer layer on surface of azopolymer thin film. (C) AFM image of azopolymer film surface after 15 min of irradiation at 150 mW cm⁻².

and periodicity of 960 nm was placed in an oven at 90° C and the film surface was characterized by AFM at different time intervals. After 1 h of heating, the majority of the relief structure had been erased from the surface and after two hours no relief structures were visible by AFM (results not shown). This result is important for applications where reversible behavior can be taken advantage of such as in information storage. In applications where high stability is required, inclusion of a crosslinking group in the backbone could allow for post-inscription network formation leading to more thermally robust films.

To evaluate whether any physical or thermal effects had an impact on the formation of surface relief structures due to the phase mask being in conformal contact with the film surface, several control experiments were conducted. To remove the phase mask from conformal contact with the film surface, a spacer layer consisting of AZ 5214 photopolymer was deposited on the azopolymer film surface. A thick layer of AZ 5214 was spin coated on the surface of the azopolymer thin film and patterned through a mask aligner to produce a spacer layer consisting of a line array with a height of approximately 1.4 μ m and a width and spacing of 500 μ m. Incorporation of a spacer layer allowed for the intensity distribution generated by the phase mask to be projected on the film surface without bringing the phase mask into conformal contact. The phase mask was brought into conformal contact with the spacer layer and the film was irradiated for 15 min at 150 mW cm⁻² and the resulting surface modulation was characterized by AFM. The resulting relief structures are identical to the previous films prepared with the phase mask in conformal contact with the film surface. This suggests the presence of the phase mask on the film surface does not influence the inscription process. The experimental setup and results are shown in figure 5.

A thermal experiment was also conducted to determine whether formation of the surface relief structures was an entirely photonic process. Barrett *et al* previously demonstrated that surface relief structures could not be formed in films containing an absorbing but non-isomerizing dye (rhodamine G6) suggesting that thermal effects do not play a role [15]. Since our experiments required bringing a phase mask into conformal contact with the film surface, we felt it was important to determine whether any thermal effects were involved. A PDMS phase mask was brought into conformal contact with the film surface and placed in an oven at 150 °C, well above the T_g of the material, for 10 h. AFM analysis indicated no surface relief structures were formed in the film surface. The two control experiments performed strongly suggest that formation of the surface relief structures is an entirely photonic process.

4. Conclusion

We have reported a method for inscribing surface relief gratings in azopolymer thin films via PnP. A variety of structures were easily patterned in the film surface based on the structure of the phase mask. The AFM images obtained matched optical simulations produced with rigorous diffraction analysis. Given the ability to directly prepare polymers of differing molecular weight in a high throughput fashion by ROMP, a relationship between inscription rate and molecular weight was demonstrated. The effect of irradiation time on the growth of the relief structures was also investigated. The inscription was process was monitored from 5 to 25 min during which the growth of the relief structures tapered off with time. As the size of structures increased, resolution was compromised. Several control experiments were conducted which suggested the inscription process is entirely photonic. Bringing the phase mask in conformal contact with the film surface does not appear to influence the process. PnP is a convenient process for preparing surface structured films as multiple recordings, cumbersome laser setups, and postcuring or development are not required. This procedure could potentially impact a number of applications requiring surface modulated film surfaces and could be used for inorganic pattern transfer [17, 18].

Acknowledgments

This work was supported by the Nanoscale Science and Engineering Initiative of the National Science Foundation under NFS Award DMR-0117792 and was carried out in part in the Frederick Seitz Materials Research Laboratory Central Facilities, University of Illinois, which are partially supported by the US Department of Energy under grants DE-FG02-07ER46453 and DE-FG02-07ER46471. This research was also supported by a grant from Center for Nanoscale Mechatronics and Manufacturing, one of the 21st Century Frontier Research Programs, which are supported by Ministry of Education, Science and Technology, KOREA. The authors thank Dr Julio A Soares of the Laser and Spectroscopy Facility for assistance in setting up the argon laser and irradiation geometry. The authors also thank Dr Leilei Yin and Scott J Robinson of the Microscopy suite at the Beckman Institute for assistance in obtaining AFM and SEM data, respectively.

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