CHEMISTRY OF MATERIALS

VOLUME 14, NUMBER 7 JULY 2002

© Copyright 2002 by the American Chemical Society

Communications

Creating Periodic Three-Dimensional Structures by Multibeam Interference of Visible Laser

Shu Yang,*,[†] Mischa Megens,[†,‡] Joanna Aizenberg,[†] Pierre Wiltzius,[†,||] Paul. M. Chaikin,[‡] and William B. Russel[§]

Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey 07974, and Departments of Physics and Chemical Engineering, Princeton University, Princeton, New Jersey

Received May 9, 2002
Revised Manuscript Received June 3, 2002

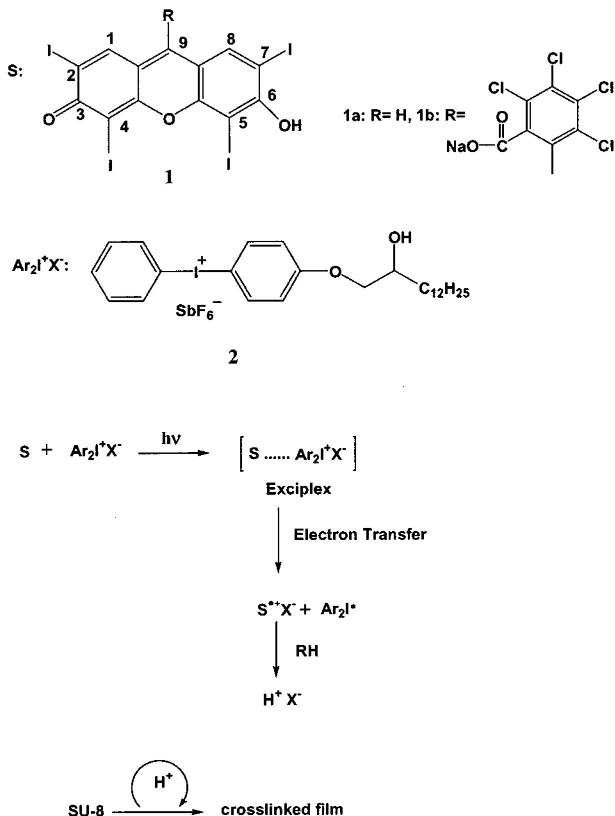
Porous materials have potential applications in photonic crystals,[1] membranes,[2] and data storage[3] and as catalyst supports.[4] Increasing interest in these areas has driven extensive research efforts to explore novel materials and processes. Although significant progress has been made in the development of new lithographic procedures for the fabrication of two-dimensional (2D) structures, it remains technologically challenging to rapidly create highly ordered, true three-dimensional (3D) structures with submicrometer periodicities and comply with demands such as controlling defects in a large area and fabrication at low cost. Self-assembly of block copolymers,[5] crystallization of colloidal particles,[6,7] and soft lithography[8] are simple and fast techniques for the 3D fabrication, yet random defects are inevitable in large areas. Two-photon absorption at near-IR[3,9] on photosensitive materials is a promising lithographic technique to construct defect-free 3D structures. However, the serial pinpoint writing in a two-photon process may not be suitable for massive production. In comparison, the multibeam interference method is much faster and more straightforward, and Turberfield and co-workers[10] have successfully demonstrated the construction of 3D structures using UV light with a pulse laser. Unfortunately, to obtain good reproducibility of interference patterns using a pulsed laser is still challenging, and the low efficiency of the penetration of UV light may limit the thickness of the films, thus hampering the broader application of the multibeam interference method on a variety of photosensitive materials. Here, we report an alternative lithographic route based on interference of three or four beams of visible light in continuous wave (cw) mode and laser-initiated cationic polymerization of epoxy. The novelty of this method lies mainly on two aspects. First, cw laser offers stable beam output and the resist is sensitized by visible light, which is more flexible and applicable to a wide range of photosensitive materials. In the visible region, the transmission increases significantly; therefore, interfer-

* To whom correspondence should be addressed.
† Lucent Technologies.
‡ Department of Physics, Princeton University.
§ Department of Chemical Engineering, Princeton University.
|| Current address: Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana–Champaign, Urbana, IL.

(1) Polman, A.; Wiltzius, P. *MRS Bull.* **2001**, *26*, 608.
(2) Boyle, T. J.; Brinker, C. J.; Gardner, T. J.; Sault, A. G.; Hughes, R. C. *Commun. Inorg. Chem.* **1999**, *20*, 209.
(3) Cumpston, B. H.; Ananthavel, S. P.; Barlow, S.; Dyer, D. L.; Ehrlich, J. E.; Erskine, L. L.; Heikal, A. A.; Kuebler, S. M.; Lee, I. Y. S.; McCord-Maughon, D.; Qin, J. Q.; Rockel, H.; Rumi, M.; Wu, X. L.; Marder, S. R.; Perry, J. W. *Nature* **1999**, *398*, 51.
(4) Morey, M. S.; Davidson, A.; Stucky, G. D. *J. Porous Mater.* **1998**, *5*, 195.
(5) Edrington, A. C.; Urbas, A. M.; DeRege, P.; Chen, C. X.; Swager, T. M.; Hadjichristidis, N.; Xenidou, M.; Fetters, L. J.; Joannopoulos, J. D.; Fink, Y.; Thomas, E. L. *Adv. Mater.* **2001**, *13*, 421.
(6) Vlasov, Y. A.; Bo, X.-Z.; Sturm, J. C.; Norris, D. J. *Nature* **2001**, *414*, 289.
(7) Colvin, V. L. *MRS Bull.* **2001**, *26*, 637.
(8) Yang, P. D.; Rizvi, A. H.; Messer, B.; Chmelka, B. F.; Whitesides, G. M.; Stucky, G. D. *Adv. Mater.* **2001**, *13*, 427.
(9) Belfield, K. D.; Ren, X. B.; Van Stryland, E. W.; Hagan, D. J.; Dubikovsky, V.; Miesak, E. J. *J. Am. Chem. Soc.* **2000**, *122*, 1217.
(10) Campbell, M.; Sharp, D. N.; Harrison, M. T.; Denning, R. G.; Turberfield, A. J. *Nature* **2000**, *404*, 53.

10.1021/cm0256007 CCC: $22.00 © 2002 American Chemical Society
Published on Web 06/25/2002

Scheme 1. General Scheme of Photosensitized Cationic Polymerization (S, Sensitizer; RH, Solvent or Epoxy Monomer)



ence of visible light will provide a more even exposure throughout the thick films and better control of the interference pattern. Second, we control the photochemistry carefully by the addition of an amine neutralizer to eliminate the background exposure caused by non-coplanar polarization of the multiple beams. Then, the polymerization is controlled in a two-step reaction (exposure and postexposure bake) without perturbing the interference patterns. A series of 2D and 3D defect-free porous structures with periods of 0.9–8 μm in an area larger than 1 mm are created by this method.

Epon SU-8 is a multifunctional epoxy derivative of a bisphenol-A novolac.[11] It is chosen here as a photosensitive material because of (i) its high solubility in many organic solvents that enables preparation of thick films and (ii) its high transparency in the near-UV and visible region.[12] Here, we formulated the resists based on visible-laser-initiated cationic polymerization of epoxides.[13,14] This initiating system typically includes a photosensitizer, which absorbs the visible light and electron transfers to an onium salt via the formation of a charge-transfer complex to generate the acids (see Scheme 1). The photoacids initiate ring-opening reactions of epoxy groups and the acids are regenerated in the subsequent steps.[15] The polymerization is thus chemically amplified, resulting in a highly cross-linked film. Detailed studies of the mechanism of photosensitization can be found elsewhere.[13,15,16]

We studied the photosensitizing efficiency of two xanthene dyes, 2,4,5,7-tetraiodo-6-hydroxy-3-fluorone (**1a**, H–Nu 535 from Spectra Group Limited) and Rose Bengal (**1b**, from Aldrich). Consistent with the literature,[17] we found that **1a** with a small hydrogen group at the C-9 position has a much higher quantum yield to donate electrons to the oxidizing agents compared to **1b**.

In our experimental setup, **1a** is selected as a photosensitizer and diaryliodonium hexafluoroantimonate (**2**, SR1012 from Sartomer) is chosen as a photoacid generator because of low reduction potential of iodionium salts for energy transfer. They were first dissolved in tetrahydrofuran (THF) and then mixed with SU-8 (from Shell Chemical) in a weight ratio of 1:2.5:100, respectively, to form a clear solution. The solution was cast or spun at a speed of 200 rpm on a cover glass and baked in an oven at 65 °C to evaporate the THF and to obtain a solid 4–10-μm-thick film. The baking time was determined by time-resolved Fourier-transform infrared (FT-IR) spectroscopy following the disappearance of the solvent peak at 924 and 1076 cm^{-1} (C–O–C stretching). In the FT-IR experiment, the film was cast on a KBr window and mounted on a Mettler hot stage (FP82HT) in the sample compartment of a Nicolet Megna-IR 560 spectrometer. The resolution was 4 cm^{-1}.

The exposure of the films was conducted at room temperature on a horizontal stage with three or four non-coplanar beams of an argon ion laser (Coherent Innova 90) for ~1 s. The laser generated 514-nm light in a continuous wave (cw), which provided a uniform beam profile and stable output of 1 W. The beam diameter was several millimeters and the beam geometry is arranged in a way similar to that in the reference.[10] After the exposure, the film was baked in the oven at 65 °C for 25 min to accelerate the cationic polymerization of epoxy. The unexposed film was removed by propylene glycol methyl ether acetate (PGMEA), followed by drying in a supercritical CO_2 dryer (CPD 7501 from Polaron Range) to avoid pattern collapse. We found that the low surface tension of supercritical CO_2 is especially advantageous in removing solvents from films with high porosity and high aspect ratio features.

The relatively high glass transition temperature of SU-8, 50 °C, plays an important role in minimizing the acid diffusion before the postexposure bake. Polymerization during exposure is not desired because it would disturb the original interference pattern because of the change of refractive index of the cross-linked film. When the film is exposed at room temperature and then baked at 65 °C, the beam interference stage is separated from the film cross-linking stage.

The partially nonparallel polarization of three or four non-coplanar laser beams produces a non-zero background of optical intensity ($I_0 > 0$) and, therefore, a non-zero background of generated acids ($C_0 > 0$) (Figure 1). This results in the formation of shallow patterns

(11) Shaw, J. M.; Gelorme, J. D.; LaBianca, N. C.; Conley, W. E.; Holmes, S. J. *IBM J. Res. Dev.* **1997**, *41*, 81.

(12) Lee, K. Y.; LaBianca, N.; Rishton, S. A.; Zolgharnain, S.; Gelorme, J. D.; Shaw, J.; Chang, T. H. P. *J. Vac. Sci. Technol. B* **1995**, *13*, 3012.

(13) Bi, Y. B.; Neckers, D. C. *Macromolecules* **1994**, *27*, 3683.

(14) Hua, Y. J.; Crivello, J. V. *Macromolecules* **2001**, *34*, 2488.

(15) Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci: Polym. Chem. Ed.* **1978**, *16*, 2441.

(16) Crivello, J. V. *J. Polym. Sci. Part A: Polym. Chem.* **1999**, *37*, 4241.

(17) Zhang, X. P.; Neckers, D. C. *J. Org. Chem.* **1993**, *58*, 2614.

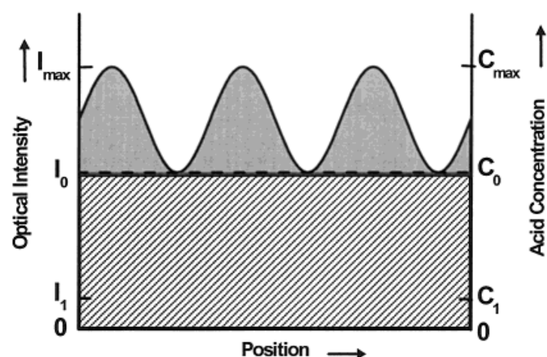


Figure 1. Non-zero backgrounds (slashed area) of the light intensity and the resulting acid concentration generated in the interference pattern of nonorthogonally polarized beams.

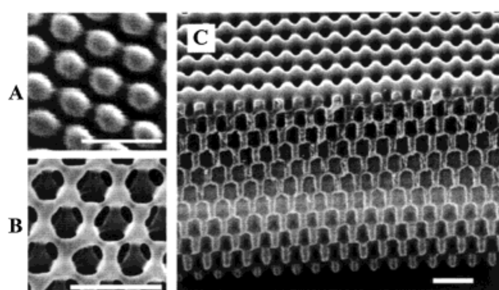


Figure 2. Scanning electron micrographs of micropatterned 3D films. (A–B) Top view of the fcc-like structures formed in the absence (A) and in the presence (B) of TEA. (C) Cross section of the fractured, continuously porous film shown in (B). The top surface is a (111) plane and the fractured surface is a (100) plane. The scale bar is 2 μm.

without fully opened holes throughout the films (Figure 2A). Although the non-zero background of the interference intensity might be minimized by fine-tuning of beam polarization, we suggest an alternative chemical approach by introducing triethylamine (TEA) in the resist. Thus, tedious optimization of polarized beams can be avoided and the unnecessary polymerization can be further reduced during exposure. Conventionally, aliphatic amine, such as TEA, is considered as a terminator for the cationic polymerization because of its high basicity and is carefully avoided.[13] We anticipated that the addition of an appropriate amount of TEA would partially neutralize local photoacids generated during exposure by I_0, thus eliminating the homogeneous crosslinked background. However, the addition of amine should not interfere with the polymerization during postexposure bake. Several controlled experiments were performed to study the role of TEA in the multibeam interference process. First, TEA in increasing concentrations was added to the film. At the molar ratio of TEA/**1a** = 0.03:1, open holes were observed, indicating the neutralization of background acids at the concentration of $C_1 \ll C_0$ (Figure 1) and the resulting partial removal of the crosslinked background. With further increase of the TEA concentration, the porosity of the patterned films increased. At TEA/**1a** = 0.3:1, highly porous patterns with fully opened holes throughout the films were obtained (Figure 2B,C). It suggests that the amine concentration was close to the threshold acid concentration, C_0, and the background is nearly removed. The interference pattern was completely washed out when the TEA concentration reached a 1:1 molar ratio of **1**, apparently near C_{max} (see Figure 1).

Time-resolved FT-IR spectroscopy has been used to study the extent of photoinitiation and polymerization of both films with and without amine. Films were exposed to a single laser beam for 1 min and were then put into the FT-IR chamber to collect infrared spectra. The kinetics of the curing process at 65 °C was monitored by following the decrease of absorbance at 914 cm^{-1} (asymmetrical ring stretching of epoxy). The results suggest that while the addition of TEA removes the non-zero background, the polymerization of epoxy during postexposure baking is not inhibited nor significantly retarded compared to that in the films without TEA. By varying the concentration of amine, exposure time, intensities, beam orientations, and polarizations, films with different lattice constants (0.9–8 μm), symmetry (hexagonal, square, and face-centered cubic), and porosity (10–70%) have been created defect-free in an area larger than 0.1–1 mm.

In conclusion, by interference of multiple non-coplanar laser beams and taking advantage of the stable output of a cw laser and high transparency of resist films for visible light, we microfabricate various 2D and 3D porous structures, defect-free, in a large area within seconds. We believe that this lithographic procedure is applicable to a wide range of photosensitive materials and provides a flexible way to engineer porous materials for potential applications in catalysis, data storage, and photonic band gaps.

Acknowledgment. The authors would like to thank E. Reichmanis, P. Mach, and F. Houlihan for helpful discussion.

CM0256007