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Electrically Switchable Gratings Formed Using Ultrafast Holographic Two-Photon-Induced Photopolymerization

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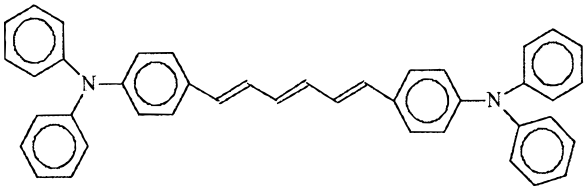
The infrastructure of the telecommunication, display, and future computing industries will rely heavily on the ability to switch information rapidly and with high contrast between two or more different states. The recent development of switchable diffractive elements using polymer-dispersed liquid crystals fills this void.[1−4] Lightweight, compact, cheap optical elements whose properties can be swiftly and easily switched using an applied voltage have been demonstrated.[5−8] These elements are formed using one-photon holographic photopolymerization of a reactive monomer mixed with inert liquid crystal material. The holographic overlap of two coherent beams results in a spatially modulated intensity pattern caused by the constructive and destructive interference of the incoming light. Because the rate of polymerization is related to the local intensity, spatially periodic polymerization occurs and subsequent phase separation results in the formation of planes (150 nm to several microns spacing) of small (50−200 nm) liquid crystal (LC) domains separated by dense polymer regions.

The advantages of using holography over lithography and other surface-mediated structures are that small periods ($<1\ \mu$m) with high aspect ratios (>50) can be formed (Bragg gratings), processing is single step, and various complex structures can be written (including reflection gratings). The morphology formed is related to the interference pattern established by the holographic overlap and subsequent polymerization response of the monomer. The balance between the polymerization propagation and phase separation controls the final morphology of the two-phase composite. Methods to skew this balance and thus the final morphology across the Bragg period are currently being investigated. Better control of the physical processes will lead to better control of the final morphology that determines the electro-optical performance of holographic optical elements. One such method, reported here uses an ultrafast holographic two-photo-induced polymerization process to drive the phase separation.

Two-photon-induced photopolymerization (TPIP) has recently been the focus of several groups interested in MEMS (micro-electro-mechanical system) fabrication within bulk structures.[9−11] The high intensity within the confocal region of the short pulse initiates the reaction and forms solid polymer. Rastering the sample or beam in a two-dimensional pattern followed by subsequent translation in the third dimension allows for complex, micrometer-sized structures to be formed. Although this technique has been used to demonstrate complex three-dimensional microfabrication, drawbacks include a lack of speed and a lack of resolution. Recently, a holographic two-photon-induced photopolymerization (H-TPIP) technique using an ultrafast laser[12−14] was utilized to fabricate complex permanent gratings. Advantages of this approach include the ability to write structures in parallel and the formation of small structural features (50 nm). In the work reported here, we utilize H-TPIP to induce localized phase separation of an initially soluble LC into sheets of polymer-dispersed liquid crystal (PDLC) droplets separated by polymer lamellae.

The two-photon absorber used was selected from the bis(diphenylamino) stilbene family as they have been shown to be efficient two-photon polymerization initiators for three-dimensional optical data storage and fabrication.[9,15] Bis(diphenylamino) diphenyl hexatriene, **I**, has a two-photon absorption cross section of 1.55 ×



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(1) Sutherland, R. L.; Natarajan, L. V.; Tondiglia, V. P.; Bunning, T. J. *Chem. Mater.* **1993**, *5*, 1533.

(2) Tanaka, K.; Kato K.; Tsuru, S.; Sakai, S. *J. Soc. Inf. Display* **1994**, *2*, 37.

(3) Crawford, G. P.; Fiske, T. G.; Silverstein, L. D. *Proc. Imaging Sci. Technol./Soc. Inf. Display* **1995**, *3*, 52.

(4) Pogue, R. T.; Sutherland, R. L.; Schmitt, M. G.; Natarajan, L. V.; Siwecki, S. A.; Tondiglia, V. P.; Bunning, T. J. *Appl. Spectrosc.* **2000**, *54*, 1.

(5) Date, M.; Naito, N.; Tanaka, K.; Kato, K.; Sakai, S. *Proc. Int. Disp. Conf.* **1995**, *15*, 603.

(6) Domash, L.; Chen, Y.-M.; Gomatam, B.; Gozewski, C.; Sutherland, R. L.; Natarajan, L. V.; Tondiglia, V. P.; Bunning, T. J.; Adams, W. W. *SPIE Proc.* **1997**, *3143*, 182.

(7) Domash, L.; Chen, Y.-M.; Gozewski, C.; Haugsjaa, P.; Oren, M. *SPIE Proc.* **1997**, *3010*, 214.

(8) Natarajan, L. V.; Sutherland, R. L.; Bunning, T. J.; Tondiglia, V. P. *SPIE Proc.* **1998**, *3292*, 44.

(9) Cumpston, B. H.; Ananthavel, S. P.; Sarlow, S.; Dyer, D. L.; Ehrlich, J. E.; Eyskine, L. L.; Heikal, A. A.; Kuebler, S. M.; Lee, I.-Y. S.; McCord-Maughon, D.; Qin, J.; Roeckel, H.; Rumi, M.; Wu, X.-L.; Marder, S. R.; Perry, J. W. *Nature* **1999**, *398*, 51.

(10) Joshi, M. P.; Pudavar, H. E.; Swiatkiewicz, J.; Prasad, P. N.; Reinhardt, B. A. *Appl. Phys. Lett.* **1999**, *72*, 170.

(11) Maruo, S.; Nakamura, O.; Kawata, S. *Opt. Lett.* **1997**, *22*, 132.

(12) Kirkpatrick, S. M.; Baur, J. W.; Clark, C. M.; Denny, L. R.; Tomlin, D. W.; Reinhardt, B. R.; Kannan, R.; Stone M. O. *Rapid Commun. Appl. Phys. A* **1999**, *69*, 461.

(13) Kirkpatrick, S. M.; Denny, L. R.; Stone, M. O. *SPIE Proc.* **2000**, *3951*, 102.

(14) Stone, M. O.; Baur, J. W.; Sowards, L. A.; Kirkpatrick, S.M. *SPIE Proc.* **2000**, *3934*, 36.

(15) Albota, M.; Beljonne, D.; Bredas, J.-L.; Ehrlich, J. E.; Fu, J.-Y.; Heikal, A. A.; Hess, S. E.; Kogej, T.; Levin, M. D.; Marder, S. R.; McCord-Maughon, D.; Perry, J. W.; Rumi, H. R. M.; Subramaniam, G.; Webb, W. W.; Wu, X.-L.; Xu, C. *Science* **1998**, *281*, 1653.

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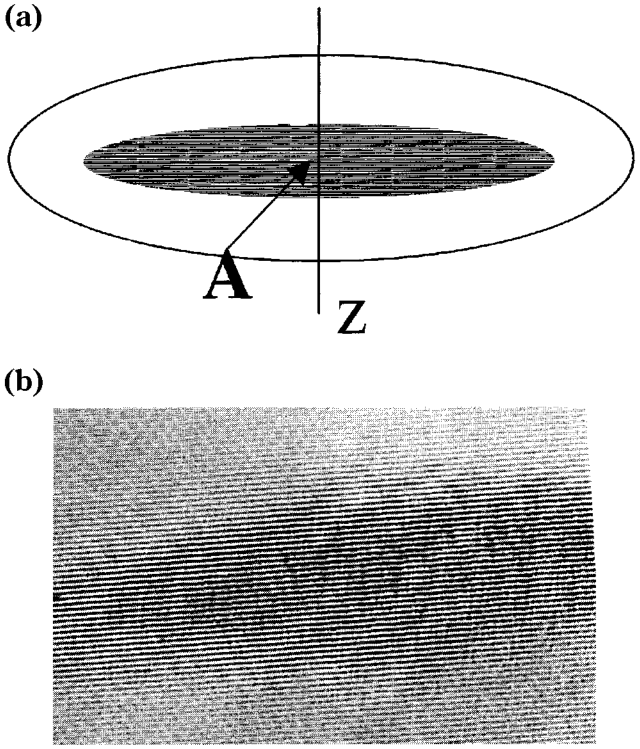

Figure 1. A schematic of the cat's-eye shape (a), a result of the complex optics, and a micrograph (b) of the grating using optical microscopy (periodicity corresponds to 3 μm).

10^{-20} GW/cm^4 as measured by Z-scan analysis.[16] Photopolymer formulations were made using 0.5% of this amine, a highly functional free-radical polymerizable monomer dipentaerythritol pentaacrylate (DPHPA) 57%, a reactive diluent *N*-vinyl pyrrolidinone (NVP) 10%, and nematic liquid crystal E7 32%. No co-initiator was used. The syrup was homogenized using sonication and sandwiched between ITO-coated glass slides separated by 8-μm-diameter glass rod spacers. The cell was sealed on all the sides with epoxy glue.

The optical setup used to write the grating structures was a variation of a standard transmission-type holographic configuration. Details of the ultrafast laser and optical configuration (90 fs, 950 μJ (500 Hz) pulse at 800 nm) are discussed in ref 12. Samples were exposed for 60 s. Electron microscopy was performed on a low-voltage scanning electron microscope (LVSEM). Optical microscopy was performed on a Nikon Optiphot microscope in transmission. An electric field (amplified 2-kHz square wave) was used to modulate the diffracted (He–Ne) energy.

Upon illumination, a small iridescent region in the form of a narrow line was observed between the substrates. This iridescence is characteristic of a transmission grating and corresponds to diffraction from planes of different refractive indices. Because of the complexity of the optical setup and the coherence length of the 90-fs pulse, the resulting overlapped area resembles a cat's eye as shown in Figure 1a. Within the most efficient overlap of the two beams (A), sharp gratings are observed with phase contrast microscopy (Figure 1).

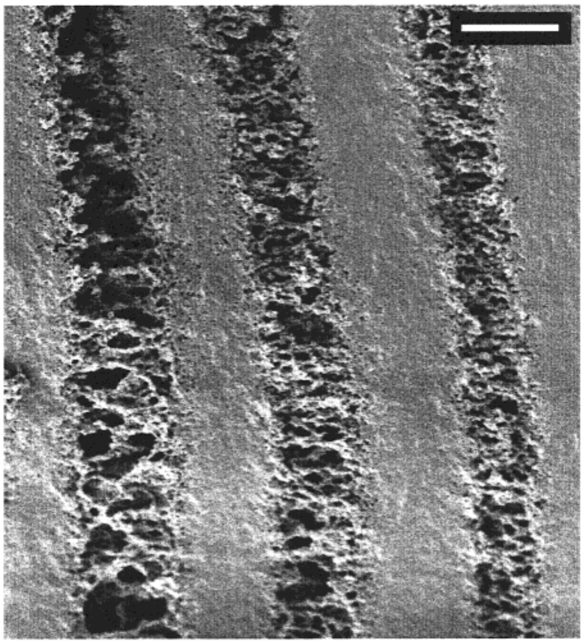

Figure 2. LVSEM micrographs of the cross-sectional surface. The dark areas correspond to domains wherein the liquid crystal molecules have been extracted. The scale bar corresponds to 1.5 μm.

Polymerization of the acrylate monomer occurred in the entire overlap region as indicated by solidification of the prepolymer syrup. Polymerization proceeds by free-radical initiation by anion radicals,[17] which is formed due to electron transfer from the excited amine to the monomer following two-photon absorption. An advantage of this formulation is the absence of a co-initiator needed to act as an electron acceptor to produce a free radical.

To examine the volume grating, LVSEM was performed on fracture planes parallel to the substrates (fracture parallel to *z*). These cross-sectional images clearly indicate the formation of a bulk grating consisting of alternate regions of small LC domains separated by dense polymer (Figure 2). The period is ≈3 μm, consistent with the optical micrographs, and the thickness is ≈8 μm. The LC regions consist of domains that range in size from 20 nm to several hundred nanometers. Only 25–30% of the periodicity is composed of the LC-rich regions with the remainder being mostly polymer.

The presence of a well-defined grating structure observed in the SEM images clearly indicates localized differences in the polymerization rate lead to anisotropic diffusion and phase separation processes. However, the localized confinement of the LC droplets into well-defined planes is promising as previous work at these spacings using one-photon holography indicated much less confinement.[18] In this latter case, droplets were observed throughout the polymer-rich region and the percentage of the Bragg period occupied by the LC-rich region was larger. A much smaller volume of reactive syrup is initiated by the two-photon process (localized to the high-intensity region). This results in a more

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[16] Natarajan, L. V.; Kirkpatrick, S. M.; Sutherland, R. L.; Fleitz, P. A.; Cooper, T. M.; Sowards, L. A.; Spangler, C. W.; Reeves, B. *SPIE Proc.* **1999**, *3798*, 183.

[17] Odian, G. *Principles of Polymerization*, 2nd ed.; John Wiley: New York, 1981.

[18] Bunning, T. J.; Natarajan, L. V.; Tondiglia, V. T.; Sutherland, R. L. *SPIE Proc.* **1996**, *2651*, 44.

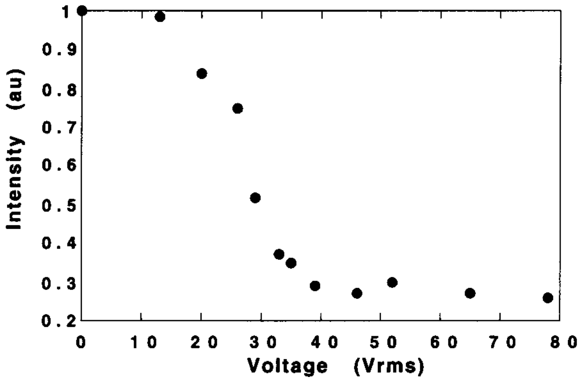

Figure 3. Electrical response of the second-order (far-field) diffracted spot upon application of an electric field.

localized distribution of radicals in the high-intensity regions during the initial stages of the polymerization. Compared to a one-photon polymerization mechanism where the number of radicals is proportional to the intensity profile, the polymerization rate outside the high-intensity regions is lowered. Consequently, the LC molecules have more time to diffuse out of these regions into the low-intensity regions before being trapped. Thus, more of the LC is confined to the low-intensity region upon phase separation. The ability to skew the LC domain distribution using two-photon holography would be an important design option in the fabrication of high-performance phase-separated structures.

The grating structure is a Raman-Nath grating (relative to the He−Ne wavelength) and exhibits several diffracted orders. A clear modulation of the diffracted intensities are observed. A decrease in the second-order intensity is accompanied by an increase in the first order diffracted intensity. The switching curve is shown in Figure 3. After 40 V_{rms}, the diffracted intensity of the second order has been minimized. The switching field of 5 V/μm is promising for such small domain sizes.

This work shows that ultrafast holographic two-photon-induced photopolymerization (H-TPIP) and subsequent phase separation can be used to form electrically switchable gratings. Good delineation of the polymer-rich and LC-rich regions exists for a sample with a grating spacing of 3.0 μm. This delineation is sharper than what has been shown before with a comparable monomer/LC material system and conventional one-photon holography. This work demonstrates the potential for using two-photon holography to control domain size distribution in phase-separated diffractive structures.

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