

Optical microfabrication of highly reflective volume Bragg gratings

Vincent K. S. Hsiao, Tzu-Chau Lin, Guang S. He, Alexander N. Cartwright,^{a)} and Paras N. Prasad

Institute for Lasers, Photonics and Biophotonics, State University of New York at Buffalo, New York 14260-1920

Lalgudi V. Natarajan and Vincent P. Tondiglia
Science Applications International Corporation, Ohio 45431

Timothy J. Bunning
Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio 45433

(Received 25 August 2004; accepted 19 January 2005; published online 24 March 2005)

An approach for fabricating wide-bandwidth and highly reflective Bragg grating structures with the technique of holographic photopolymerization of a liquid crystal (LC) polymer composite is presented. The key to this fabrication method that distinguishes it from previous methods is the use of a nonreactive solvent, acetone, to dissolve the photoinitiator and coinitiator in an acrylate monomer/LC mixture. The addition of acetone results in the creation of controllable periodic voids inside the thin film after the acetone evaporates. Peak reflectivity as high as 80% and a broad reflection bandwidth of 80 nm were observed in the reflection gratings formed with acetone present in the starting mixture. It was estimated from a fit to the experimental data that the resulting index mismatch was approximately 0.2; consistent with the presence of air voids. It is determined that tunable wavelength, diffraction efficiency, and bandwidth of reflection notches can be achieved by backfilling with fluids of different refractive indices. © 2005 American Institute of Physics. [DOI: 10.1063/1.1880435]

There have been a number of studies determining the ability to form both static and switchable Bragg grating structures using a photopolymer system with holographic interferometry.¹⁻⁴ These structures have demonstrated application to color filters for display systems.⁵ Moreover, extensions of making periodic structures with this holographic formation have demonstrated the optical microfabrication of switchable photonic band-gap crystals.^{6,7} As a review, in the standard acrylate photopolymer system used for electrically switchable gratings, syrups containing a monomer, a photoinitiator, a coinitiator, and liquid crystals (LCs) are sandwiched together and irradiated by an optical grating that is formed by the interference of two coincident coherent laser beams. In this manner, the monomer is polymerized in the bright regions of the resulting optical grating and the LCs are forced to diffuse and then phase separate in the dark regions of the optical grating. For a given thickness, the diffraction efficiency (DE) of these holographically written gratings is determined by the refractive index (RI) mismatch between the polymerized region and the LC-rich region.⁸⁻¹⁰ The presence of phase separated LC domains imparts the electro-optic variability.

Recently, much research has focused on the study of the role of each constituent material in the acrylate photopolymer system.^{11,12} Moreover, additional components, such as nonreactive fluorine-rich biphenyl molecules and surfactants, have been added to the system and the threshold field for electro-optic switching decreases from 11 to 3 V/ μm and the relaxation time increases from 156 to 312 μs .¹³ Generally, in order to reduce the viscosity of the monomer and to ensure the homogeneity of the syrups, a reactive solvent,

N-vinylpyrrolidinone (NVP), is used.¹⁴ NVP helps to dissolve the photoinitiator and coinitiator and aids in a homogeneous dispersion of the LCs in the syrup. In addition, NVP is also involved in the chemical reaction that forms the crosslinking polymer structure during the photopolymerization process. In the recent experimental study reported here, we have found that instead of NVP, acetone could be used as a nonreactive solvent to dissolve the syrup. Interestingly however, it was observed that immediately after the two-beam interferometric exposure of the prepared syrup sandwiched by two glass plates, acetone coexisted with the polymerized film and no grating was observed. Subsequent evaporation of acetone from the film induced by the removal of one of the two substrates led to the development of strong reflection (passive) notches. The large contrast is the result of

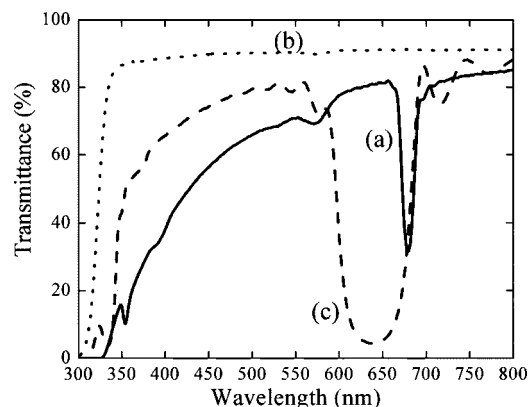


FIG. 1. Transmission spectra of the grating samples, (a) NVP sample; (b) acetone sample without removing cover slide; and (c) the same sample as (b) but acetone was evaporated by removing the cover slide. The ratio of acetone: LC: photopolymer was 20:20:60 by weight percentage.

^{a)} Author to whom all correspondence should be addressed; electronic mail: anc@buffalo.edu

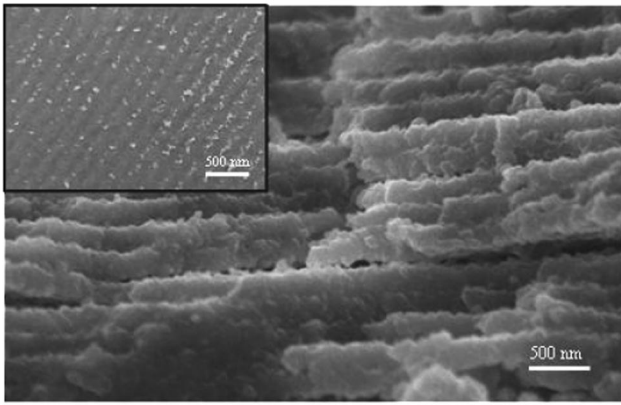


FIG. 2. LVSEM and BFTEM (inset) images of the grating structure of the acetone sample.

the index difference between the high index of the polymer and the low index of the void generated while the acetone evaporated. In direct contrast to the addition of nonreactive fluorine-rich biphenyl molecules reported earlier,¹³ the acetone is not intended to improve the electrical properties and, in fact, the formation of voids makes electrical switching difficult. However, the addition of acetone allows functional porous polymeric structures for sensing applications¹⁴ to be easily fabricated. Morphological results and the optical shape and depth of the notch indicate the formation of periodic voids on a length scale commensurate with Bragg reflection in the visible. Using this method, high DE, and wide bandwidth gratings can be obtained.

The prepolymer syrup employed for this study consisted of an acrylate monomer (~60%) (Dipentaerythritol hydroxypenta acrylate from Aldrich), LCs (~20%) (TL213, $n_0=1.527$ $n_e=1.766$, from EM Industries, Merck), a coinitiator (N-phenylglycine, from Aldrich), a photoinitiator (Rose Bengal, from Spectra Group Limited), and acetone (~20%) (from Aldrich). A reference sample, which contained NVP instead of acetone, was also prepared for comparison purposes. For simplicity, we will refer to these samples as the NVP sample and the acetone sample. The writing beam for the interferometry was the 514 nm line generated by an argon-ion laser. The laser was expanded with a $4\times$ microscope objective and collimated with a 20 cm focal length lens. The grating was written with a one-beam setup in which the writing laser beam enters a right-angle prism and self-interferes with its internally reflected beam.¹⁵ The laser power was adjusted to 100 mW and this interference pattern was incident on the sample for an exposure time of 30 s. The reflectivity of the resulting reflection gratings was measured by a Shimadzu UV-3101PC spectrometer working in the transmission spectra mode. The grating morphology was measured via low voltage scanning electron microscopy (LVSEM) and bright-field transmission electron microscopy (BFTEM).

For the typical photopolymer syrup utilizing liquid crystals with NVP, the reflection grating was formed and observable during the holographic writing as shown in Fig. 1(a). The reflection notch centered at 675 nm typically possessed 30–50% DE and a narrow bandwidth (20–30 nm). This notch appears almost immediately and grows in magnitude during the early part of the holographic exposure. In contrast, for samples containing acetone rather than NVP, no notch is

observed upon holographic exposure as shown in Fig. 1(b). This suggests a uniform RI profile across the thickness of the cell. However, once the top substrate of the cell was removed, a deep notch centered at 640 nm, with considerably more bandwidth and reflectivity than the NVP sample, is formed as indicated in Fig. 1(c). The breadth of the notch is indicative of a large RI profile, similar to standard HPDLC gratings, wherein the LC has been removed and replaced by air.⁶ The depth of the notch (80%) for such a thin film (~3 microns) also is supportive of a large RI profile.

We speculate that upon initial holographic exposure, a grating in crosslink density must form due to the spatially periodic polymerization profile; however, because the sample is swollen with acetone, any initial periodic structure is homogenized and thus little RI profile and no reflection notch are observed. Upon evaporation of acetone, the highly crosslinked regions (high intensity) collapse upon themselves, leaving dense polymer layers separated by voids (air) that are formed in the lightly crosslinked regions (low intensity). During the photopolymerization process, more acetone migrates toward the low intensity regions which become polymer deficient due to the low rate of polymerization. Upon removal of acetone, a lightly crosslinked highly porous local morphology is developed. Due to the holographic illumination, this structure is periodic with a length scale dictated by the writing geometry and initial laser wavelength.

Figure 2 shows the interior morphology of the evaporated sample which consists of a periodic structure of the crosslinked polymer and small, nanosized holes with an overall periodicity commensurate with the writing geometry. The BFTEM image clearly indicates that the periodic lamellae of inclusions consist of material less dense than the surrounding polymer. Figure 2(b) shows a typical scanning electron microscopy (SEM) image of the resulting grating structure and also reveals periodic nanoscale voids separated by dense polymer layers. The hole diameters (and periodicity) appear to be slightly smaller in the SEM images due to the collapse of the grating, commonly observed due to sample preparation artifacts. Both sets of images yield periodicities commensurate with the notch wavelength. From the optical transmission spectrum, λ_{Bragg} is 635 nm and the average index, n_{ave} , can be estimated at 1.43 by assuming a composition of 60% polymer (1.52), 20% LC (1.6), and 20% air (1.0). Therefore, a calculated optical spacing of 220 nm is in close agreement with that measured from the micrographs.

The reflection efficiency of the volume grating can be expressed by Kogelnik coupled wave theory¹⁶

$$\eta = \frac{1}{1 + (1 - \varepsilon^2/\nu^2)/\sinh^2(\nu^2 - \varepsilon^2)^{1/2}},$$

$$\text{where } \nu = \frac{\pi\Delta n\Lambda}{\lambda_{\text{Bragg}}} \text{ and } \varepsilon = \frac{2\pi\Delta\lambda\Lambda n_{\text{ave}}}{\lambda_{\text{Bragg}}^2}.$$

where $\Delta\lambda$ is the half width half maximum of the spectrum and Δn is modulation of the RI, Λ is the film thickness, and λ_{Bragg} is the reflection wavelength satisfying the Bragg condition. From this equation, the dependence between Δn and n_{ave} is plotted in Fig. 3, using all parameters that were experimentally determined. Once the average RI of the grating is determined we can approximate Δn that would result in an 80% reflection efficiency. According to the volume fraction calculation, the n_{ave} was ~1.43 and the corresponding Δn would be ~0.165. This value is quite similar to the value of

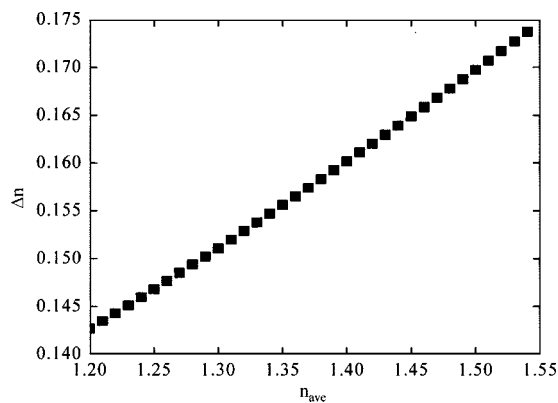


FIG. 3. Index mismatch vs the average refractive index of the grating, where $\eta=80\%$, $\Delta\lambda=40$ nm, $d=3.1$ μm , and $\lambda=640$ nm.

0.20 which we estimated using the Berreman 4×4 matrix method.¹⁷ Savant *et al.*¹⁸ suggested that it is not suitable to use the coupled wave theory for calculating the index mismatch for broad bandwidth reflection gratings, e.g., Lippmann–Bragg broadband holographic grating, and that the coupled wave theory always underestimates the value of Δn . Therefore, the value of Δn for the acetone grating sample is probably larger than 0.17 and this value is very high when compared to DuPont’s holographic photopolymer which has an average Δn around 0.08.^{5,19}

The optical spectra and analysis indicate a large periodic n profile, much larger than can be obtained by periodically phase separated LC voids and polymer ($n_p=1.52$, $n_{\text{LC}}=1.6$ – $\max \Delta n \sim 0.08$). This conclusion leads to the natural question of where the LC resides. Although there may be small amounts of LC at the edges of the air voids, all data support the conclusion that the LC is present (solvated) in the crosslinked polymer and not phase separated. In previous work, no appreciable DE is observed for samples containing less than 18% LC indicating that there is finite solubility of the LC in the crosslinked polymer. Moreover, a lack of any DE in these samples indicates that enough mobility is present in the final system to allow any compositional gradient (and thus DE) formed during the initial part of the holographic exposure to be eliminated. The finite solubility of LC would also be enhanced by the presence of acetone. Also, preliminary attempts to switch these samples were not successful. The evaporation of acetone and formation of voids (and thus a large fraction of air) are clearly the drivers behind the formation of these reflective notches.

Figure 4 shows the potential ease of variability this system provides. Specifically, Fig. 4(a) shows the reflection spectrum of the as produced structure, Figs. 4(b)–4(d) show the reflection spectrum of the film back-filled with acetone ($n=1.36$), chloroform ($n=1.45$), and toluene ($n=1.50$), respectively. As the RI of the solvent is increased, the notch wavelength redshifts due to an overall higher average RI while the notch depth diminishes as the RI difference between the polymer and the solvent filled voids becomes smaller. The large sensitivity of these structures to these slight changes in RI may hold promise in the area of low-cost high fidelity sensing applications.

In conclusion, we have produced high efficiency and broad bandwidth reflection gratings using a holographic recording method. In contrast to standard LC/NVP samples, the grating is not observable until the solvent (acetone)

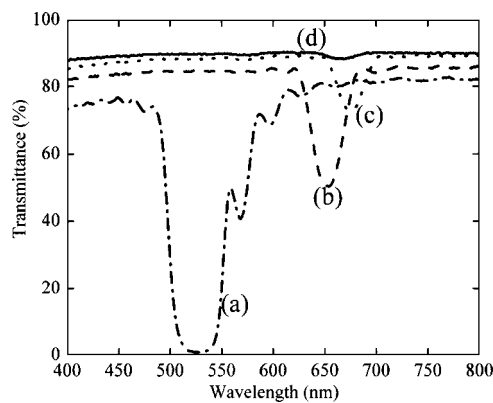


FIG. 4. The spectra of the acetone sample obtained after backfilling with different materials (a) air voids n_{air} ($n=1$) (b) acetone, n_a ($n=1.36$) (c) chloroform n_c ($n=1.45$), and (d) toluene n_t ($n=1.50$).

evaporates. The strong notch reflection is due to the formation of periodic air voids that are left, once the anisotropically crosslinked polymer de-swells. For a very thin film, a deep and broad reflection notch confirms a large RI difference that can arise only from a substantial portion of air voids. The simplicity of this technique shows the potential ability to create high performance reflection gratings of any color, DE, and/or bandwidth.

This work was supported by DURINT Grant No. F496200110358 from the Chemistry and Life Sciences Directorate of the Air Force Office of Scientific Research, and the Air Force Research Laboratory, Materials, and Manufacturing Directorate.

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

²G. S. He, T. C. Lin, Vincent K. S. Hsiao, A. N. Cartwright, and P. N. Prasad, *Appl. Phys. Lett.* **83**, 14 (2003).

³C. C. Bowley and G. P. Crawford, *Appl. Phys. Lett.* **76**, 16 (2000).

⁴N. Suzuki and Y. Tomita, *Appl. Opt.* **43**, 10 (2004).

⁵T. J. Trout, J. J. Schmieg, W. J. Gambogi, and A. M. Weber, *Adv. Mater. (Weinheim, Ger.)* **10**, 1219 (1998).

⁶V. P. Tondiglia, L. V. Natarajan, R. L. Sutherland, D. Tomlin, and T. J. Bunning, *Adv. Mater. (Weinheim, Ger.)* **14**, 3 (2002).

⁷R. L. Sutherland, L. V. Natarajan, V. P. Tondiglia, S. Chandra, D. Tomlin, and T. J. Bunning, *Opt. Express* **10**, 1082 (2002).

⁸T. J. Bunning, L. V. Natarajan, V. P. Tondiglia, G. Dougherty, and R. L. Sutherland, *J. Polym. Sci., Part B: Polym. Phys.* **35**, 2825 (1997).

⁹R. L. Sutherland, V. P. Tondiglia, L. V. Natarajan, and T. J. Bunning, *Appl. Phys. Lett.* **79**, 14 (2001).

¹⁰R. L. Sutherland, L. V. Natarajan, V. P. Tondiglia, S. Chandra, C. K. Shepherd, D. M. Brandelik, and S. A. Siwrecki, *J. Opt. Soc. Am. B* **19**, 3004 (2002).

¹¹T. J. Bunning, L. V. Natarajan, V. P. Tondiglia, R. L. Sutherland, D. L. Vezie, and W. W. Adams, *Polymer* **37**, 3147 (1996).

¹²T. J. Bunning, L. V. Natarajan, V. P. Tondiglia, and R. L. Sutherland, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **320**, 127 (1998).

¹³M. D. Schulte, S. J. Clarson, L. V. Natarajan, D. W. Tomlin, and T. J. Bunning, *Liq. Cryst.* **27**, 467 (2000).

¹⁴F. Cunin, T. A. Schmedake, J. R. Link, Y. Y. Li, J. Koh, S. N. Bhatia, and M. J. Sailor, *Nat. Mater.* **1**, 39 (2002).

¹⁵L. V. Natarajan, C. K. Shepherd, D. M. Brandelik, R. L. Sutherland, S. Chandra, V. P. Tondiglia, D. Tomlin, and T. J. Bunning, *Chem. Mater.* **15**, 2477 (2003).

¹⁶H. Kogelnik, *Bell Syst. Tech. J.* **48**, 2909 (1969).

¹⁷I. J. Hodgkinson and Q. H. Wu (World Scientific, Singapore, 1997).

¹⁸T. Jansson, I. Tengara, Y. Qiao, and G. Savant, *J. Opt. Soc. Am. A* **8**, 201 (1991).

¹⁹T. J. Trout, W. J. Gambogi, and S. H. Stevenson, *Proc. SPIE* **2577**, 94 (1995).