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A widely tunable refractive index in a nanolayered photonic material

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A class of composite polymer films is described in which the refractive index can be varied by simple mechanical forces. The films are comprised of 1024 alternating layers of an elastomer and a glassy polymer. When the layer spacing is much less than the wavelength of the probe light, these materials behave as effective medium composites. The layer thickness of the elastomer component and thus the effective index of the composite can be varied by compressing the composite. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1738513]

Light is used to sense, communicate, process, and store information in a multitude of applications. Control devices are essential for the transmission and use of this data. Materials with an easily variable refractive index can be used to create devices that switch, attenuate, shutter, filter, or phase shift optical signals. Electro-optical and $\chi^{(3)}$ effects are used to drive refractive index changes, but the index changes are relatively small.[1,2] Optical switching by thermal and microfluidic effects have also been described recently.[3–6] We report a class of nanolayered polymeric materials that possess a large and dynamically variable refractive index. They can provide an approach to these functions. Our ability to fabricate elastomeric polymer structures with many thousands of layers and features down to about 10 nm makes this technology feasible.[7] The initial examples of nanolayered polymers show reversible refractive index changes of greater than 0.013. In this communication, we discuss the fabrication of the polymers, show that they possess a variable refractive index, and investigate the mechanism of the large index changes we observe.

Investigations of multilayer polymer films were underway as early as 1969.[8] Recently, there has been renewed interest in multilayer polymer optics. The reflective properties of these films can be manipulated to create a variety of filters, reflectors, omnidirectional mirrors and photonic band gap materials.[9–11] We demonstrate the ability to manipulate the refractive index in these materials. The nanolayered composite structures described here comprise alternating layers of polymers (Fig. 1) chosen to have differences in both the index of refraction and the elastic moduli. These materials possess a modulation in the refractive index n across the polymer film with a period corresponding to the layer thickness. The optical properties of such films depend on the layer thickness and the wavelength of the light used to probe the material. When the layer thickness is $\lambda/4n$, the polymer is effectively a one-dimensional (1D) photonic crystal. It shows a high reflectivity at the wavelength λ [Fig. 2(a)]. The essential difference in our materials is that the average layer thickness is substantially less than $\lambda/4n$ [Fig. 2(b)]. The optical properties of such films are those of an effective medium composite. The material is transparent at the probe wavelength λ, and the refractive index normal to the film is, to a good approximation, the thickness-weighted average of the indices of the component polymers.[12] Because the component polymers are chosen so that the elastic moduli of the polymers differ, applied pressure will change the relative layer thickness and hence the refractive index of the film.

To study the properties of effective medium composite materials, polymers consisting of 1024 alternating layers of the elastomer, poly(ethylene-octene) (EO), and the glassy polymer, polycarbonate (PC) were fabricated using a continuous multilayer co-extrusion process.[13] PC possesses both a substantially larger refractive index and a substantially larger elastic modulus than poly(ethylene-octene). Three composite films were fabricated with the elastomer comprising 50%, 75%, and 90% of the total thickness, respectively. Fabrication of the nanolayered materials is described in detail elsewhere.[14] The individual layer thickness ranged from 20 to 220 nm. However, the combined thickness of an EO/PC layer pair in all of the films was about 240 nm. This is less than one-quarter wavelength at 1.546 μm, where the refractive index was measured. The layer structure of the (50/50) material was confirmed by atomic force microscopy studies.

For these initial studies, the refractive indices of the composites were measured using a modified prism-coupling instrument (Metricon) in a refractometer mode.[15] Pressure was applied uniformly, perpendicular to the layers, over a film area of 0.78 mm^2 by an air-driven piston. The applied pressure was measured using a calibrated force sensor (Flexiforce). The refractive index perpendicular to the nanolayers (TE) at 1.546 μm as a function of applied pressure for the three different multilayer structures is shown in Fig. 3. In each of the layered polymer materials shown in Fig. 3, the effective refractive index of the composite polymer film varied with the applied pressure. The data were recorded with both increasing and decreasing pressure. The variation in this refractive index is reversible and reproducible. The multilayer film with 90% elastomer exhibits the greatest index change as the applied pressure is increased. At approximately 40 MPa, the observed index change is about 16% of

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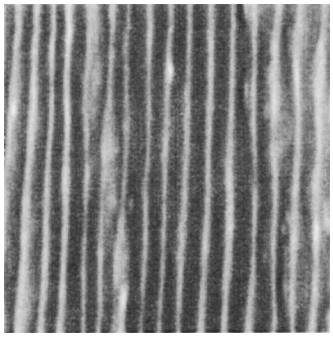

FIG. 1. Atomic force microscope phase image of a cross section of (50/50) elastomer/glassy polymer film. Image is taken in tapping mode. Each layer is 50 nm. There are a total of 1024 layers in the film.

the index difference between the component polymers. At the same applied pressure, the refractive index change for both the 75% and 50% elastomeric films were similar, about 11% of the index difference between the component polymers.

To verify that the index changes are due to the nanolayered structure, the refractive index of samples of pure EO and pure PC were measured under the same experimental conditions. Pure PC showed no refractive index change within the experimental resolution (0.0002). For pure EO, a refractive index change of 0.0012 was observed at the maximum applied pressure. The index changes in the nanolayered polymer were more than an order of magnitude larger than that observed for the pure component materials.

To investigate the mechanism of the index change, we first consider the refractive index n as a function of applied stress due to a change in the elastomer layer thickness. This, according to the appropriate effective medium theory for a layered effective medium, is

$$n \cong \frac{n_0 - n_2 x\left(\frac{\sigma}{E}\right)}{\left[1 - x\left(\frac{\sigma}{E}\right)\right]}, \tag{1}$$

where n_0 is the composite index at zero strain, n_2 is the elastomer index (1.4772), x is the fractional thickness of the elastomer layer, σ is the applied pressure, and E is the elastic modulus of the elastomer layer. In order to apply Eq. (1), knowledge of the modulus E is needed. E can be determined directly from a reflection spectrum of the film. The layer thickness is less than $\lambda/4n$ at 1.546 μm; however, at shorter wavelengths, $\lambda/4n$ approaches the layer thickness and a reflection spectrum is observed. In the current samples, the

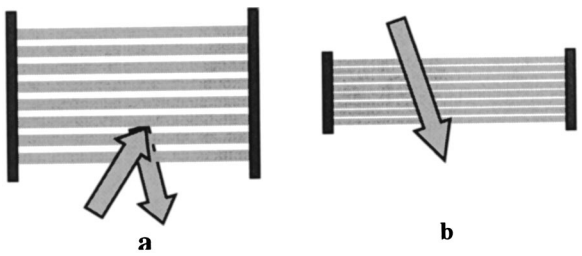

FIG. 2. Nanolayer polymer film as (a) 1D photonic band gap material when the layer thickness is $\lambda/4n$. (b) Effective medium composite when the layer thickness is less than $\lambda/4n$.

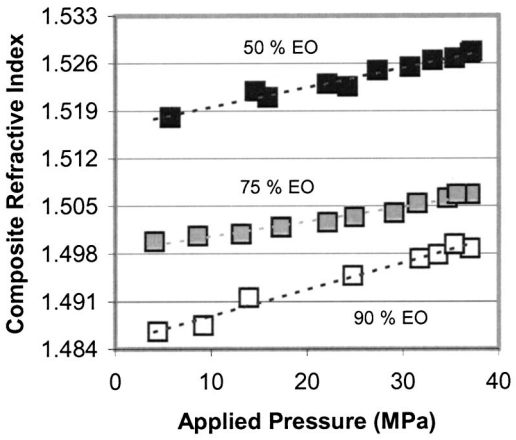

FIG. 3. Reversible refractive index variation at 1.546 μm as a function of applied pressure in 50%, 75%, and 90% elastomeric films. All films are layered EO and PC.

reflection spectrum appears near 600 nm. The reflection spectrum depends on the layer thickness and E can be determined from a study of the pressure dependence of the reflection spectrum. The modulus for the EO layer in both the 75% and 50% elastomeric films was found to be on the order of $(1.5 \pm 0.4) \times 10^2$ MPa. We did not observe reflection spectra from the 90% EO sample, so that we could not determine E using this method.

Figure 4 shows the experimental refractive indices for the 50% elastomeric composite material (squares) compared to the indices calculated from Eq. (1) (solid line). The change in EO layer thickness with pressure accounts for about half of the observed index change in the composite polymer. If both the layer thickness and the index of the nanolayered EO are allowed to vary with pressure, the observed pressure dependence of the composite can be fit (dashed line) assuming pressure dependence of the EO nanolayer is 3×10^{-4} per MPa. However, this implies that refractive index change with pressure in nanolayered EO differs from what we measured in bulk EO.

A difference in the pressure dependence of the index between EO in nanolayers and EO in bulk is plausible if the nanolayered EO is partially constrained from expanding in the layer plane by the adjacent rigid PC layers, or equiva-

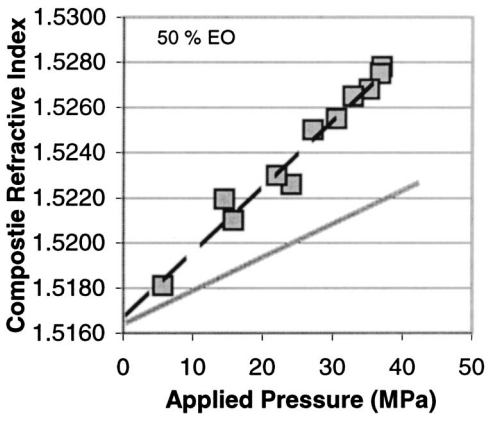

FIG. 4. The refractive index normal to the layers as a function of applied pressure for EO/PC (50/50) (squares) compared to the expected index change due to elastomer layer thickness alone (solid line). The dashed line includes a pressure-dependent index for nanolayered EO.

lently, if the Poisson ratio of the nanolayered EO is smaller than that of bulk EO. A smaller Poisson ratio means that the density of nanolayered EO increases faster with pressure than does the bulk. Since the refractive index is approximately proportional to the density, n will also be more sensitive to pressure in nanolayers. In this context, it seems consistent that the modulus for nanolayered EO measured is about eight times larger than that for bulk EO, again suggesting that the properties of the elastomeric EO nanolayers differ from those in the bulk due to the adjacent, rigid PC layers.

In summary, we have demonstrated that the refractive index of nanolayered EO/PC composite polymers varies reversibly by as much as 0.013 or ~16% of the index difference between the component polymers with pressures of about 40 MPa. The observed index changes are sufficient to be useful for optical processing. The mechanism for the dynamically variable index includes both changes in elastomer layer thickness and a pressure dependence of the elastomer index. Some properties of the elastomeric EO nanolayers differ from those in the bulk, perhaps due to the adjacent, rigid polymer layers.

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[1] M. E. Van der Boom, G. Evmenenko, P. Dutta, and T. J. Marks, Adv. Funct. Mater. **11**, 393 (2001).
[2] S. R. Marder, B. Kippelen, A. K.-Y. Jen, and N. Peyghambarian, Nature (London) **388**, 845 (1997).
[3] B. J. Eggleton, A. K. Ahuja, K. S. Feder, C. Headley, C. Kerbage, M. D. Mermelstein, J. A. Rogers, P. Steinvurzel, P. S. Westbrook, and R. S. Windeler, IEEE J. Sel. Top. Quantum Electron. **7**, 409 (2001).
[4] P. Mach, M. Dolinski, K. W. Baldwin, J. A. Rogers, C. Kerbage, R. S. Windeler, and B. J. Eggleton, Appl. Phys. Lett. **80**, 4294 (2002).
[5] C. Kerbage, R. S. Windeler, B. J. Eggleton, P. Mach, M. Dolinski, and J. A. Rogers, Opt. Commun. **204**, 179 (2002).
[6] J. M. Weissman, H. B. Sunkara, A. S. Tse, and S. A. Asher, Science **274**, 959 (1996).
[7] E. Baer, Macromol. Symp. **104**, 31 (1996).
[8] J. T. Alfrey, E. F. Gurnee, and W. J. Schrenk, Polym. Eng. Sci. **9**, 400 (1969).
[9] M. F. Weber, C. A. Stover, L. R. Gilbert, T. J. Nevitt, and A. J. Ouderkirk, Science **287**, 2451 (2000).
[10] A. C. Edrington, A. M. Urbas, P. DeRege, C. X. Chen, T. M. Swager, N. Hadjichristidis, M. Xenidou, L. J. Fetters, J. D. Joannopoulos, Y. Fink, and E. L. Thomas, Adv. Mater. (Weinheim, Ger.) **13**, 421 (2001).
[11] M. Ibanescu, Y. Fink, S. Fan, E. Thomas, and J. Joannopoulos, Science **289**, 415 (2000).
[12] R. J. Gehr and R. W. Boyd, Chem. Mater. **8**, 1807 (1996).
[13] EO (EG 8200) and PC (Calibre 200-14) are both manufactured by The Dow Chemical Company. The processing temperatures are 220 and 270 °C, for EO and PC, respectively. The secant modulus in tension for EO is 4.0 MPa (100%) and 2300 MPa (2%), for PC.
[14] J. S. Shirk, R. G. S. Pong, S. R. Flom, A. Hiltner, and E. Baer, in *Defense Applications of Nanostructured Materials*, edited by A. Miziolek (American Chemical Society, Washington, DC, in press).
[15] In this mode, the refractive index is found from the critical angle for TE incident light. For these polymers, the measurement accuracy using this technique is uncertain, but is estimated to be ±.005. The index parallel to the layers was also measured using TM incident light. A small birefringence is observed, but it remains constant, within the experimental uncertainty, as the pressure is increased.