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Enhanced electro-optic response of layered composite materials

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We have constructed a multilayered composite material consisting of alternating layers of rf-sputtered barium titanate and spin-coated polycarbonate containing a third-order nonlinear optical organic dopant. The effective nonlinear susceptibility of the composite describing the quadratic electro-optic effect was measured to have the value $\chi^{(3)}=(3.2+0.2i)\times 10^{-21}\pm 25\%$ $(\mathrm{m/V})^2$. The real part of this value is a factor of $3.2\pm 50\%$ times larger than that of the doped polycarbonate, which is the dominant electro-optic component of the composite. We have modeled the experiment by using both effective medium theory and by solving the wave equation for our multilayered system, and we find that these approaches give consistent predictions which are in good agreement to the experimental results. © *1999 American Institute of Physics.* [S0003-6951(99)03117-4]

Many applications in modern optical technology require the use of materials with a large electro-optic response. Examples include the photonic control of phased array radar,[1] satellite-to-satellite data links that will require data transfer rates during the next decade of 50–100 Gbits/s,[2] and optical fiber links of 1 Tbit/s.[3] The present approaches to improving materials (e.g., improved organic chromophore design) have resulted in characteristics that are within a small factor of being satisfactory for application. Therefore, new approaches are in order and in this letter, we describe a technique that can be used to increase the value of essentially any electro-optic material by forming a composite out of that material. In the present work, we deal with the quadratic electro-optic effect, although the technique can be applied to the linear electro-optic effect as well.

Our approach entails forming a composite material consisting of alternating layers of an electro-optic material (designated material *a* in the ensuing analysis) and a buffer material (designated material *b*) having a different linear dielectric constant. A theoretical analysis[4] of such a situation shows that the effective nonlinear susceptibility describing the quadratic electro-optic effect $\chi^{(\mathrm{eff})}_{ijkl}(\omega';\omega,\Omega_1,\Omega_2)$ is related to that of the electro-optic constituent *a* by the relation

$$\chi^{(\mathrm{eff})}_{ijkl}(\omega';\omega,\Omega_1,\Omega_2)=f_a\left[\frac{\varepsilon_{\mathrm{eff}}(\omega')}{\varepsilon_a(\omega')}\right]\left[\frac{\varepsilon_{\mathrm{eff}}(\omega)}{\varepsilon_a(\omega)}\right]\left[\frac{\varepsilon_{\mathrm{eff}}(\Omega_1)}{\varepsilon_a(\Omega_1)}\right]\times\left[\frac{\varepsilon_{\mathrm{eff}}(\Omega_2)}{\varepsilon_a(\Omega_2)}\right]\chi^{(a)}_{ijkl}(\omega';\omega,\Omega_1,\Omega_2). \tag{1}$$

Here, f_a represents the volume fill fraction of component *a*; Ω_1 and Ω_2 represent low (e.g., kHz) frequencies, ω and $\omega'=\omega+\Omega_1+\Omega_2$ represent optical frequencies, and ϵ_{eff} is the effective linear susceptibility of the composite material, which is given by

$$\frac{1}{\varepsilon_{\mathrm{eff}}}=\frac{f_a}{\varepsilon_a}+\frac{f_b}{\varepsilon_b}, \tag{2}$$

for fields polarized perpendicular to the plane of the layers (the *z* direction in the following) and by $\varepsilon_{\mathrm{eff}}=f_a\varepsilon_a+f_b\varepsilon_b$ for fields polarized along the plane of the layers. Equation (1) predicts that the effective nonlinear susceptibility can exceed that of the electro-optic component of the composite. For instance, in Fig. 1 we plot the enhancement in the electro-optic response (that is $\chi^{(3)}_{\mathrm{eff}}/\chi^{(3)}_a$) as a function of the fill fraction f_a for the *zzzz* tensor component, which is the component displaying maximum enhancement. In preparing this figure, we have used our best laboratory estimates of the optical constants appropriate to the sample described below, namely $\varepsilon_a(\omega)=2.5$, $\varepsilon_a(\Omega)=2.9$, $\varepsilon_b(\omega)=4$, and $\varepsilon_b(\Omega)=15$. We see that enhancements as large as approximately a factor of three are possible for this choice of materials. This theory predicts that the maximum response would be obtained for a 17% fill fraction of the electro-optic component. However, in our experimental studies we used a fill fraction of approximately 50% to avoid difficulties associated with the preparation of very thin layers of the electro-optic component. In earlier work,[5] we demonstrated a 35% enhance-

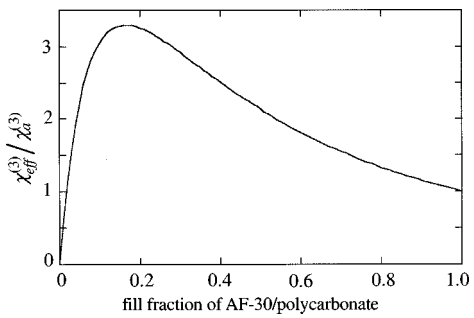

FIG. 1. Predicted enhancement of the electro-optic response plotted as a function of the fill fraction of the doped-polycarbonate constituent of the layered composite material.

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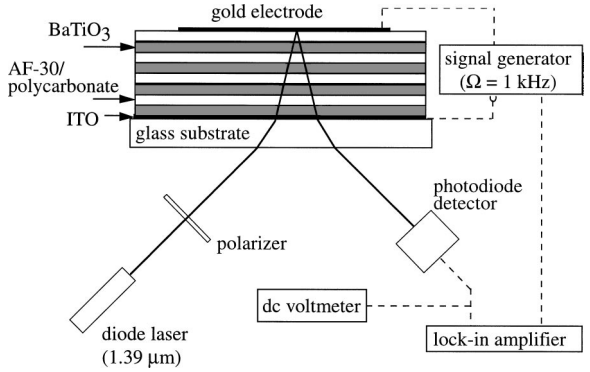

FIG. 2. Sample geometry and experimental arrangement used to measure the electro-optic response. The variation of the reflectivity of the structure is measured as a function of the applied voltage.

ment in the third-order susceptibility describing degenerate four-wave mixing in a layered composite material. The present work differs in that it demonstrates enhancement of the third-order susceptibility describing the electro-optic effect and demonstrates a numerically much larger enhancement.

The sample studied in our experiments is illustrated in Fig. 2. A layer of indium tin oxide (ITO) was deposited on a microscope slide to act as the bottom electrode of our structure. Four layer pairs consisting of alternating 100-nm-thick layers of the electro-optic material and the buffer material were next deposited on top of the bottom electrode, and finally a 300-nm-thick layer of gold was deposited to serve as the top electrode. The electro-optic material was polycarbonate doped at 10% by weight with 5-benzothiazol-2-yl-2-[5-benzothiazol-2-yl-3,4-didecyloxy(2-thienyl)]-3,4-didecyloxy-thiophene (see Fig. 3) which will be referred to as AF-30 in the remainder of this letter. This material was deposited by spin coating. The buffer layer consisted of rf-sputtered barium titanate ($BaTiO_3$); this material was selected because of the large values of its optical and low-frequency dielectric constants. The linear refractive indices were measured by ellipsometry and were determined to have the values 1.58 ± 0.03 for the doped polycarbonate and 1.98 ± 0.04 for the sputtered barium titanate. The low-frequency (1 kHz) dielectric constants were measured using a commercial LCR meter and were found to be 2.9 ± 0.01 for the doped polycarbonate film and 15 ± 1.5 for the barium titanate.

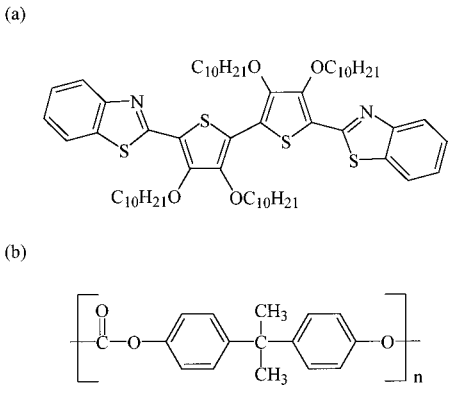

FIG. 3. Chemical structure (a) of the electro-optically active dopant molecule 5-benzothiazol-2-yl-2-[5-benzothiazol-2-yl-3,4-didecyloxy(2-thienyl)]-3,4-didecyloxythiophene, and (b) of the polycarbonate host.

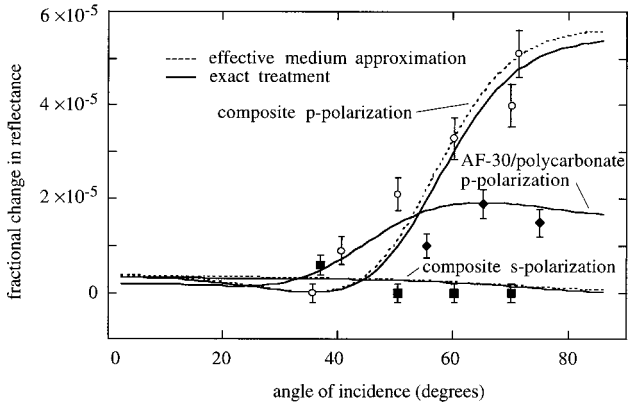

FIG. 4. Fractional change in reflectance plotted as a function of the angle of incidence both for a layered composite material and for a homogeneous layer of the doped polycarbonate material. The continuous curves represent theoretical predictions calculated both using the effective medium approximation and taking explicit account of the layered nature of the material sample. Each theoretical curve depends on one free parameter, the value of $\chi^{(3)}$. The values of $\chi^{(3)}$ determined from these fits are quoted.

The experimental setup used to measure the electro-optic response is also shown in Fig. 2. An electrical voltage was applied to the sample and the change in optical reflectivity was measured as a function of the angle of incidence. This method was chosen because it is possible that there are strong multiple reflection effects at the wavelength of interest due to the proximity of the ITO band edge that would make interferometric methods[6–8] and the Teng and Man method[9–12] difficult to analyze. Also, the Teng and Man method was developed for poled polymer systems where there is only one undetermined tensor coefficient. Additionally, since no strong Fabry-Pérot resonances were present, methods utilizing transmission resonances[13,14] were also not practical. In our setup, an optical beam at 1.37 μm wavelength was obtained from a semiconductor diode laser and could be rendered either *s* or *p* polarized at the sample. The reflected signal was detected by a photodiode and measured by a lock-in amplifier. We experimented with a variety of applied electrical signals and found that the most reliable measurements could be performed by applying a variable dc voltage in the range -20–20 V superimposed on a 40 V peak ac signal at 1 kHz. We then measured the 1-kHz-modulated component of the reflected signal as a function of the applied dc voltage and determined the part of the response varying as the product $E(\Omega)E(0)$. The results of this measurement are shown in Fig. 4, both for the composite sample and for a homogeneous sample of the doped polycarbonate film. We were unable to make reliable measurements of the electro-optic response of the homogeneous barium titanate films, which display a much smaller quadratic electro-optic effect.

The value of the electro-optic coefficient was extracted from the data shown in Fig. 4 by fitting theoretical curves to the data. The theoretical curves depend on the electro-optically induced change in the refractive index as well as on the linear optical properties of the materials that comprise the sample. By investigation of a homogeneous film of polycarbonate doped with an organic material very similar to AF-30, it was concluded that signals due to electrostriction, electromechanical vibration, trapped charge movement, and heating

effects[6,13] in the AF-30/polycarbonate were small compared with the signal due to refractive index changes. We use the literature values of the linear refractive indices $0.4494+8.7245i$ for gold[15] and $0.674+0.2168i$ for indium tin oxide,[16] as well as the measured values for the barium titanate and doped polycarbonate films which were quoted above. We then calculate the Fresnel reflection coefficient at each interface, and take full account of interference effects in calculating the intensity of the reflected signal. We calculate the intensity using two different procedures. One procedure is to treat the composite material as a single layer with effective optical constants given by Eqs. (1) and (2). The other procedure is to take explicit account of the reflection at each interface of the composite stack. It is seen from Fig. 4 that these two procedures give consistent predictions, and that the best-fit theoretical curves are in good agreement with the experimental data. From these fitted curves we are able to determine the value of $\chi^{(3)}$ through use of the readily deduced relation

$$\Delta n = 3\chi^{(3)} E(\Omega) E(0)/n. \tag{3}$$

We find that $\chi^{(3)}_{zzzz} = 1.0\times 10^{-21}\,(\mathrm{m/V})^2 \pm 25\%$ for the doped polycarbonate film and that $\chi^{(3)}_{zzzz} = (3.2+0.2i)\times 10^{21}\,(\mathrm{m/V})^2 \pm 25\%$ for the composite material. Errors in the susceptibilities are obtained from the uncertainties in the layer thicknesses and indices, and observed signals. The susceptibility uncertainties are then calculated from the computer program used to obtain the susceptibilities. The real part of $\chi^{(3)}$ is thus measured to be $3.2\% \pm 50\%$ times larger for the composite material than for the doped polycarbonate. The measured enhancement of $\chi^{(3)}$ of $3.2\% \pm 50\%$ is in good agreement with our best theoretical estimate of the enhancement. We see from Fig. 1 that for a fill fraction $f = 0.5$, our best laboratory estimate of this value, the expected enhancement in $\chi^{(3)}$ is a factor of 2.1.

In summary, we have fabricated a composite electro-optic material for which the electro-optic response as expressed in terms of a $\chi^{(3)}$ susceptibility, is $3.2 \pm 50\%$ times larger than that of the electro-optic component of the composite. This enhancement is sufficiently large to suggest that the fabrication of composite materials is a viable approach to the development of superior electro-optic materials.

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