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Waveguide electro-optic modulators based on self-assembled material systems

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Abstract: Fabrication and characterization of electro-optic modulators based on the novel organic electro-optic materials composed of self-assembled superlattices (SAS) were presented, both wet-dipping self-assembly and vapor phase deposition approaches were discussed. Prototype waveguide electro-optic modulators were fabricated using SAS films integrated with low-loss polymeric materials functioning as partial guiding and cladding layers. Promising electro-optic thin film materials including DTPT and PEPCOOH grown from the vapor phase were used for fabrication and test of electro-optic prototype modulators. Finally, the EO coefficient of tens of pm/V was obtained, which can sufficiently support high-speed and small size EO modulators.

Key words: electro-optical modulator; waveguide modulator; self-assembled material; superlattice; vapour deposition

1 Introduction

Organic materials have advantages such as lower dispersion, higher modulation frequency, and lower power of operation compared with inorganic materials for application in electro-optic (EO) devices[1-2]. There are several groups who have reported the fabrication of poled polymer-based EO modulators. Electro-optic coefficients higher than those of lithium niobate have been achieved with microstructural acentricity of the polymeric materials by application of an external electric poling field[3]. Another approach for fabricating nonlinear waveguides is based on the vapor phase deposition of nonlinear thin films[4].

We describe here an approach to fabricating and characterizing organic EO modulators using multilayer self-assembled superlattices (SAS) as the guiding layer and commercial low-loss polymers as the cladding layers. The SAS layers are intrinsically acentric and have relatively large EO responses without the requirement of external electric field poling. Electro-optic parameters such as the half-wave voltage and the effective electro-optic coefficient have been evaluated. Promising electro-optic thin film materials including DTPT and PEPCOOH grown from the vapor phase also have long-range crystalline-like order giving molecular alignment, even for micrometer-thick film. The films have been fabricated and tested for electro-optic prototype modulators by integrating them with polymeric waveguiding layers on semiconductor substrates.

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2 Waveguide electro-optic modulator based on SAS materials

A promising alternative approach to achieving nonlinearity has been demonstrated by the growth of intrinsically acentric SAS layers of polymer materials, which exhibit strong second harmonic generation and EO modulation effects without external electric field poling. Previously we had fabricated EO modulator using a three-step process for the SAS layers, and the growth of SAS layers took relatively long time.

Recently, a new, expeditious two-step process has also been developed and used for the growth of SAS films. With this process the SAS film can be grown at a rate of about 40 min per bilayer (alternating chromophore and capping layer), and it is at least one order of magnitude more rapid than the three-step deposition method.

Fig. 1 shows the design structure and an SEM image of the cross-section of an SAS-based waveguide EO modulator fabricated on a GaAs substrate. The lower Au electrode layer was deposited using a standard E-beam evaporation process. An SiO_2 layer was then deposited by the PECVD method. The EO-active SAS layers were then grown on the SiO_2 layer, and were next covered with a layer of the robust, electronic grade polymer BCB. The BCB layer functions as part of the guiding core since it has a good refractive index match with the SAS materials.

Next, a low refractive index CYTOP polymer was spin-coated on top of the BCB layer. Both CYTOP and BCB exhibit good transparency over a wide wavelength range from the ultraviolet to infrared and are commercially available. The spin coating conditions were adjusted for a Cytop layer having a thickness of 1.8 μm, and a BCB layer having a thickness of 1.5 μm. In order to form uniform films, each layer was baked in a conventional oven with nitrogen gas flow after spin coating. Ridge waveguide patterns were next fabricated by etching the BCB to the SiO_2 surface using RIE. Another layer of CYTOP was spin-coated on the ridge structure to form a buried waveguide and to reduce the upper metal contact loss of the optical modes of the waveguides. The widths of the resulting waveguides range from 2.0 to 6.0 μm. The total thickness of the upper CYTOP cladding layer is about 2 μm. Finally, the top gold electrode was fabricated by using E-beam evaporation and lift-off methods.

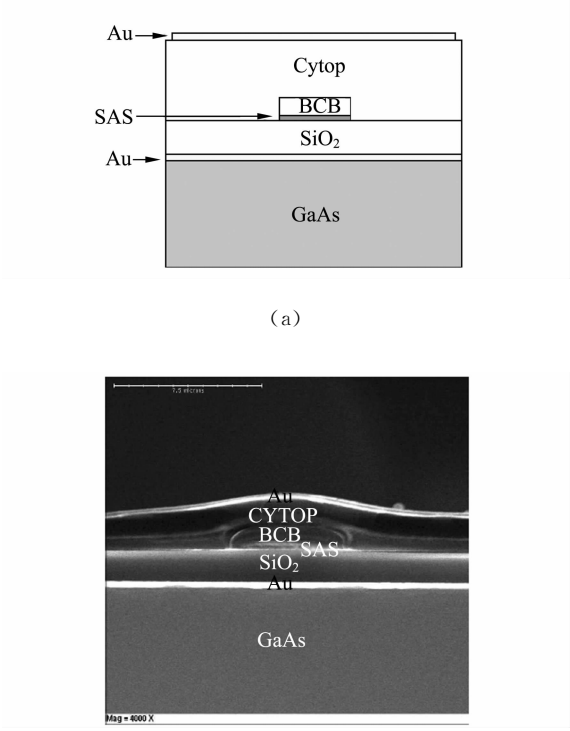

Fig. 1 (a) Design structure of the EO modulator and (b) a SEM image of the cross section of the traveling wave EO phase modulator.

Fig. 2 shows the setup for the measurement of the EO response of the SAS-based waveguiding EO modulators. A diode pumped Nd:YAG laser operating at 1064 nm was used as the light source. The light was coupled into and out of the ridge waveguide using a pair of 40× micro-

scope objectives. The device was operated by launching both TE and TM modes in the waveguide. The light beam propagates through a polarizer oriented at 45° with respect to the vertical direction before the objectives. The EO response was measured by end-firing the laser beam into one of the cleaved facets of the sample. Then the light went through an analyzer oriented perpendicular to the orientation of the polarizer. The modulated light signal was then coupled to a photodetector and monitored by an oscilloscope. Fig. 3 shows the typical EO response of a SAS-based EO modulator measured from the oscilloscope traces. In this figure, traces 1 and 2 represent the applied electrical signal and the response of the EO modulator, respectively. The half-wave voltage V_π was esti-

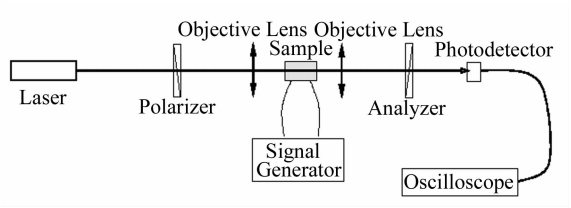

Fig. 2 Setup for the measurement of the EO response of waveguiding EO modulators.

mated to be about one hundred volts for the EO modulator sample shown. The effective EO coefficient r is related to the half-wave voltage V_π by $r=\frac{\lambda d}{n_{\text{eff-opt}}^3 V_\pi L \Gamma}$, where λ is the wavelength of the optical wave, d the distance between the lower and the upper electrodes, $n_{\text{eff-opt}}$ the effective optical refractive index, L the length of the electro-optic interaction region, and Γ the overlap integral factor of the optical and the external electric fields, $\Gamma=\frac{d}{V}\frac{E_e|E_o|^2\mathrm{d}x\mathrm{d}y}{|E_o|^2\mathrm{d}x\mathrm{d}y}$, where the E_e and E_o are the amplitudes of optical field, and external electric field under an applied voltage of V, respectively.

The effective EO coefficient r is estimated to be 23 pm/V. A longer waveguide (cm level) and thicker SAS films (at the μm level) will help

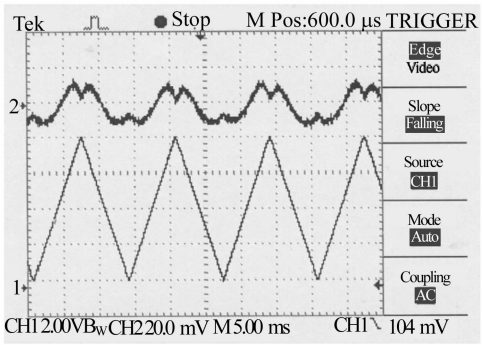

Fig. 3 EO response of an SAS-based modulator monitored by oscilloscope traces. The upper trace is the modulator output waveform, and the lower trace is the applied electrical signal.

to achieve a much lower V_p.

At room temperature, the modulation characteristics of this device exhibit negligible relaxation over a period of several months. Experiments show that the SAS has good thermal stability during the fabrication process involving different polymer curing conditions (at 130 ~ 150℃ for hours) and e-beam deposition.

The SAS materials also exhibit excellent stability under proton irradiation. Two SAS samples (22 bilayers and 24 bilayers) were irradiated to test the stability properties in simulations of orbiting satellite environments. The UV-vis spectra of the irradiated samples show almost the same $\lambda_{\max}$ and the absorption intensities as those before irradiation (Fig. 4). SHG measurements also reveal negligible decay in

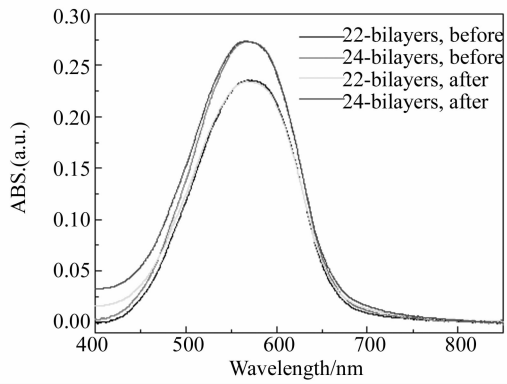

Fig. 4 UV-spectra of SAS before and after irradiation

nonlinearity after the irradiation. Additional measurements will be next carried out under higher proton fluxes. We are currently studying the modulation voltages as a function of the structural parameters.

3 Electro-optic modulator based on novel self-assembled thin film of DTPT from vapor phase deposition

The NLO-active chromophore (5-{4-[2-(4, 6-diamino-[1, 3, 5] triazin-2-yl)-vinyl]-benzylidene}-pyrimidine-2, 4, 6-trione (DTPT) containing H-bond donor and acceptor modules was first designed and synthesized. The SA thin films were grown from the vapor phase of DTPT on treated substrates. As the first step for the growth of self-assembled DTPT thin films, a melamine group template was anchored on 5 mm × 5 mm substrates with 3-amonopropyltrimethoxysilane functionalization. The reaction of 6-chloro-1,3,5-triazine-2,4-diamine with 1-propylamine was first carried out in solution to optimize the functionalization reaction conditions for the substrates. The pyrimidine-2,4,6-trione and 4, 6-diamino-1, 3, 5,-trizine-2-yl substituents form longitudinally directed triple H-bonds between neighboring molecules with only head-tail bonding allowed. Intermolecular longitudinal H-bonding interactions force the chromophore molecules to preferentially align in the desired direction (head-tail, perpendicular to the substrate surface) as thin solid films from the vapor phase (Figure 5). Out-plane non-centrosymmetric microstructures are achieved in the deposited films, and the acentricity is intrinsic. Since H-bonding is far stronger than van der Waals forces, the dipolar orientation has high temporal stability with robust film mechanical and environmental properties.

A diffusion-pumped vacuum deposition apparatus ($\sim 1.33 \times 10^{-6}$ Pa) was used to grow thin films at a rate of 0.05～0.2 nm/s on substrates with temperature of 100℃. This approach is at least one order of magnitude more rapid than the two-step siloxane-based solution deposition methodology. A calibrated quartz crystal microbalance was used to monitor the film growth rate and thickness. The adherent, stable SA thin films exhibit appreciable nonlinear responses, characterized by second harmonic generation (SHG) at a wavelength of 532 nm, and a high chromophore surface density. The regularity of the SA thin films has been demonstrated by absorption spectra and SHG responses of samples having different thickness parameters. The SA thin films can be grown on SiO_2, plasma treated polymers, and glass substrates.

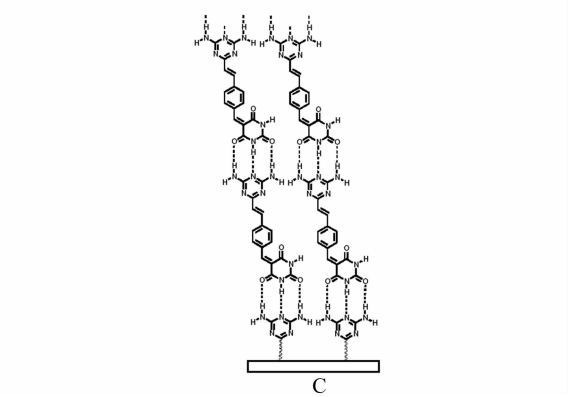

Fig. 5 SA of DTPT on a functionalized substrate through H-bonds. Out-plane order is achieved.

Electro-optic waveguide modulators fabricated with DTPT have a three-layer stack configuration. The lower cladding layer was 2.5 μm SiO_2 deposited by PECVD on a highly N-doped GaAs substrate. The electro-optically active DTPT SA thin films (about 1.4 μm thick) were grown on SiO_2 via the aforementioned vapor deposition procedure. Since DTPT has a relatively large refractive index (～1.8 at a wavelength of 632.8 nm), simulation and experiment showed that this thickness is sufficient for DTPT to function exclusively as the guiding layer of the

waveguide. A layer of polymer CYTOP was next used for the protection of the DTPT surface during processing. After spin coating and curing the polymer CYTOP layer, optical ridge waveguide patterns (3～6 μm wide) were formed by standard photolithography and dry reactive ion etching (DRIE) the polymer layers down to the SiO_2 layer. Another layer of CYTOP (about 1.4 μm) functioning as the top cladding layer, was spin-coated onto the ridge waveguide patterns. The bottom and top electrodes were deposited by electron-beam evaporation of great than 99% purity Au in high vacuum, and the thicknesses were nominally 100, 250 nm, respectively. The bottom electrode was reached by etching back the top electrode, polymer, and the SiO_2 layers using wet etching and DRIE. The metal contact loss of the electrodes for this configuration is about 0.3 dB/cm.

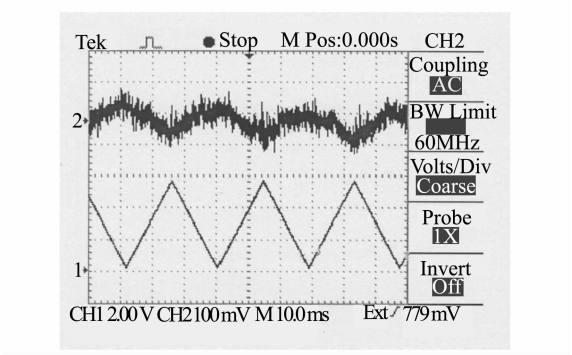

Fig. 6 EO response of a prototype EO modulator based on DTPT thin films. Trace 1 is the applied electrical signal, and trace 2 the response of the EO modulator.

Fig. 6 shows a typical EO response snapshot of the modulator from oscilloscope traces. Trace 1 and trace 2 represent the applied electrical signal and the response signal of the EO modulator, respectively. The effective EO coefficient is thus estimated to be about 0.13 pm/V. The value is in good agreement with the SHG measurement. Future chemical engineering of materials with higher nonlinear coefficients will make this process promising since the growth rate is on the order of ten hours and the thin films are flat enough for good waveguide fabrication.

4 Electro-optic modulator based on novel self-assembled thin film of PEPCOOH from vapor phase deposition

The Structure of PEPCOOH is shown in Fig. 7.

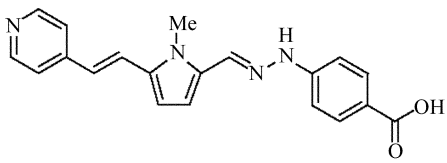

Fig. 7 Chemical structure of PEPCOOH.

The compound has been designed and synthesized with the following criteria in mind: (1) p-excessive and p-deficient heteroaromatics as key donor (D) and acceptor (A) NLO core building-blocks, (2) presence of H-bond donor (DH) and H-bond acceptor (AH) groups to enforce supramolecular alignment upon sublimation, (3) decoupling between D-A (optical) and DH-AH (assembling) actions through proper molecular design, and (4) stabilization of the NLO chromophore by the presence of groups/atoms that inhibit singlet oxygen-promoted decompositions.

Thermal data show that the present chromophore is thermally very stable. More importantly, TGA data indicate that vacuum-deposited film can be prepared without concomitant chromophore decomposition.

PEPCOOH films can be fabricated on a variety of substrates (glass, quartz, silicon, GaAs, Au-coated glass) by vacuum-deposition under the following experimental conditions: deposition rate = 0.02～0.03 nm/s, chamber

pressure ~1.33×10^{-3} Pa, substrate temperature=25-100 ℃. Film polar order parallel to the substrate normal has been unambiguously demonstrated by second harmonic generation measurements.

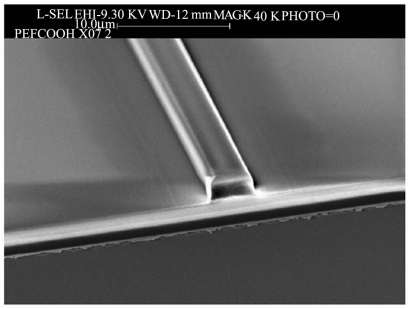

Fig. 8 A typical ridge waveguide of PEPCOOH before top cladding material spin-on.

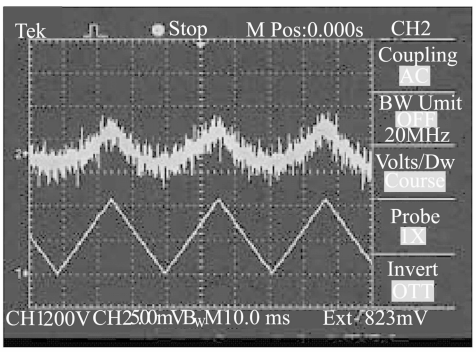

Fig. 8 EO response of a prototype EO modulator based on a PEPCOOH thin film. Trace 1 is the applied electrical signal, and trace 2 the response of the EO modulator.

The process is similar to that of the DTPT EO modulators since PEPCOOH has an even higher refractive index (~1.9 at 632.8 nm) and can function solely as the guiding layer in ridge waveguide structures. Fig. 8 shows a typical ridge waveguide before the top cladding layer is spun-on. Fig. 9 displays an EO response snapshot of the device. The EO coefficient is estimated in the order of tens of pm/V.

Deuteration of the hydrogen bonds should lower the absorption of the materials, and is currently under investigation.

5 Conclusions

Self-assembled superlattices (SAS) are intrinsically acentric and highly cross-linked structures. For organic electro-optics, they offer advantages such as not requiring electric field poling for creating an acentric, EO-active microstructure and having excellent chemical, thermal, and orientational stabilities. In this paper, the two-step all "wet-chemical" self-assembly (SA) approach is reported. Radiation hardness of the SAS films is demonstrated by high-energy proton irradiation experiments. Prototype waveguiding electro-optic modulators have been fabricated using the SAS films integrated with low-loss polymeric materials functioning as partial guiding and cladding layers. Waveguide EO modulators were fabricated using a multistep process including E-beam evaporation, PECVD, spin-coating and curing, superlattice self-assembly, photolithography, RIE, and metal deposition and lift-off techniques. EO parameters such as the half-wave voltage and the effective electro-optic coefficient are reported.

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References:

[1] ZHAO Y G, WU A, LU H L, *et al*. Traveling wave electro-optic phase modulators based on intrinsically polar self-assembled chromophoric superlattices[J]. *Appl. Phys. Lett.*, 2001, 79(5): 587-589.

[2] MARDER S R, KIPPELEN B, JEN A K Y, *et al*. Design and synthesis of chromophores and polymers for electro-optic and photorefractive applications[J]. *Nature*, 1997, 388: 845-851.

[3] SHUTO, Y, AMANO M, KAINO T. Electrooptic light modulation and second-harmonic generation in novel diazo-

dye-substituted poled polymers[J]. *IEEE Trans. Photon. Techn. Lett.*, 1991, 3(11):1003-1006.

[4] FACCHETTI A, ABBOTTO A, BEVERINA L, *et al*. Layer-by-layer self-assembled pyrrole- based donor-acceptor chromophores as electro-optic materials[J]. *Chem. Mater*, 2003, 15(5):33-38.

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Dr. XU Guo-yang received his Ph. D. degree in July 1999 from Chinese Academy of Science, Beijing. He is currently a research associate in Department of Electrical and Computer Engineering, Northwestern University, Evanston, Illinois. His current research interests are photonic devices and integration and electro-optical devices based on nonlinear organic materials.

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Prof. Tobin J. Marks received his Ph. D. degree from MIT in 1970. His research interest is in the areas of organometallics, photonics, MOCVD, and molecular electronics. Now he is a professor in Chemistry and Mechenical Engineering Center. He is AAS Academician.