ELECTRO-OPTICAL COMPOSITE POLYMER LAYERS FOR HIGH SPEED RADIOPHOTONICS MODULATORS, EXPERIMENT AND MODELING

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ABSTRACT
The properties of polymer materials with embedded electro-optical (EO) chromophores capable for refractive index modulation under the applied electric field are studied. Thin film waveguide structure are manufactured based on SU-8, PMMA and new synthesized fluorine polymers and a number of chromophores like DR1, DR13 and specially synthesized ones. To measure the electro-optic response inside modulator prototype we produced metalized sandwich structures from those composites, polled chomophores by corona or contact polling and measure induced refraction changes $\Delta n = 0.002$ with a prism-coupling method. Special modeling algorithm to precisely determine optical characteristics of each of six layers from prism-coupler data is developed. Adapted fitting procedure allows to extract electro-optics coefficient values of inner layers. Under the influence of intense short wavelength radiation this material refractive index decreases on $\Delta n = 0.01 - 0.03$, that allows one to create a waveguide with a photo mask method or by direct laser writing.

Keywords: electro-optical polymer, refraction, prism-coupler, layer reflection modeling, waveguide.

1. INTRODUCTION

The efforts of the researchers are directed to the synthesis of new chromophores possessing a large EO coefficient in the telecommunication (1.5 μm wavelength) C-band, an increase of the concentration of chromophores in the polymer matrix in the absence of agglomeration, a reduce of the applied voltage, and a better temporal and temperature stability of the EO materials. The latest achievements in this direction are presented in the reviews of Dalton, Sullivan and Bale (2010); Kajzar, Lee and Jen (2003). This work is based on an interdisciplinary approach that includes chemical, optical and modeling directions: 1) Synthesis of new polymers and chromophores. 2) Optical methods for characterization and evaluation of electro-optical response. 3) Modeling and fitting prism-coupler data to obtain linear and nonlinear optical parameters of multilayer planar waveguide structure. The final our goal is the manufacturing of compact high-speed electro-optical modulators for the telecommunications C-band of wavelengths 1530-1565 nm.

New monomers based on halogenated acrylates with a record low absorption coefficient in the telecommunications C-band have been synthesized. Monomers have a high activity in the process of radical photopolymerization and are capable for the formation of polymer waveguides. New chromophores (not described earlier) have been synthesized, possessing a high electro-optical coefficient r_{33}. Composite polymeric materials have been created, both of the guest-host and of the side-chain type. Methods for measuring the EO of the coefficients r_{13} and r_{33} of polymeric composites, including second-harmonic generation and resonant excitation of waveguide modes using a prism-coupler have been developed. Composite films are oriented (poled) using a corona discharge or contact polarization, we obtained the EO coefficient in a planar waveguide $r_{33} = 4\text{-}20$ pm/V. The calculation algorithm has been developed that describes the reflection of TE and TM of polarized electromagnetic waves from a multilayer structure, including a polymeric buffer layer, a composite waveguiding layer, and semitransparent metal electrodes. The code takes into account the optical constants and thicknesses of all layers and allows obtaining exact value of r_{33} when compared with the experimental angular spectra. A new method for the formation of Mach-Zehnder waveguide interferometers is proposed, based on the effect of photodestruction of a composite under the action of intense visible radiation – Sokolov et.all. (2017).

2. METHODS AND RESULTS

With the introduction of EO chromophores in the polymer matrix and polling them it is possible to control the refraction of light in such a composite medium under the external electric field. This effect is used in the manufacturing of high-speed integrated optical modulators based on EO composites. As the first step we produced a nonlinear optical film of polymethylmethacrylate (PMMA) or SU8 with

embedded chromophore DR13 into it. By side-chain method we were able to increase chromophores concentration in transparent polymer to 25%.

The obtained absorption characteristics on Figure 1 are consistent with the literature data, EO chromophores like DR1 and DR13 has a strong absorption line with a center near 510 nm and bandwidth of 100 nm. Note that, depending on the type of matrix (solvent, polymer, etc.) into which the chromophores are embedded, their absorption peak can be shifted by 10-20 nm toward larger or shorter wavelengths.

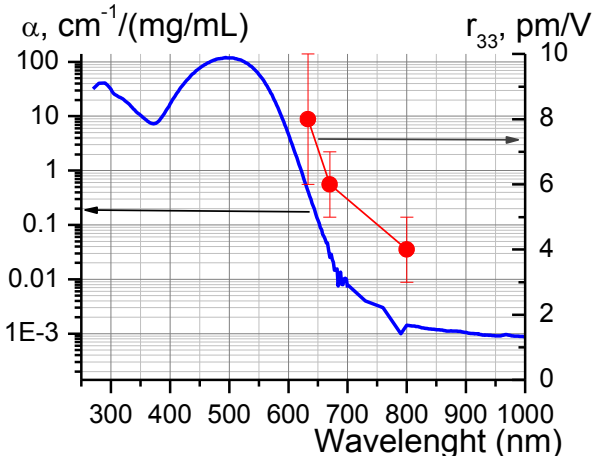

Figure 1. The absorption spectrum of the chromophore DR13 (solution in chlorobenzene) normalized to the concentration of the chromophore is the left axis. The right axis is the measured EO coefficient r_{33} for three wavelengths.

P polymer films were deposited on a substrate by spin-coating method. After forming thin film and drying it at 60° C for several hours, the solvent was evaporated from the polymer material. Films of PMMA/DR13 composite with thickness h_1 = 4-5 μm were deposited on quartz (SiO_2) and silicon (Si) substrates with thermally grown oxide layer of SiO_2. That is sample S1. Sample S2 was formed on a quartz substrate with a copper layer previously deposited on it with a thickness h_0 = 1 μm (lower electrode). For the mechanical and electrical protection of the PMMA/DR13 film, a layer of photoresist SU-8 with thickness h_2 was applied to it, see Fig. 2. Sample S3 was produced on a low-resistance silicon (LR Si) plate with a thermally grown oxide layer (h_1) 3.5 μm thick, onto which the PMMA/DR13 film (h_2) was deposited.

With the method of the prism coupling adapted for a metallized film structure we studied optical and electro-optical properties of the polymer composite. To measure the electro-optic response we polled chomophores by a corona or contact polling method and analyzed the induced refraction changes with original prism-coupling modeling method

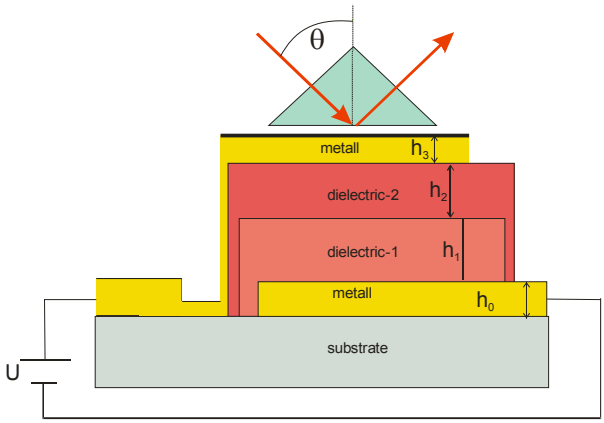

Figure 2: A sketch of a planar multilayer waveguide and coupling prism for measuring reflection angular spectra.

In the reflection angular spectra several quasi-waveguide modes are excited in a stack of thin films. One of the films contains oriented chromospheres, the upper metal film is semitransparent, conducting Cu layer of 30 nm. A sequence of dark resonances (m-lines) - Horsthuis and Krijnen (1989) - is measured in this structure when incidence angle θ is scanned for S or P-polarization.

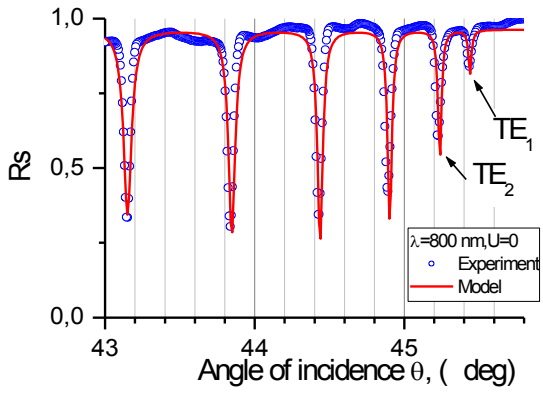

Figure 3: The Angular Reflection Spectrum Rs(θ) of six layers sample in the case of TE (S) polarization of the incident radiation. The solid line is the modeling, the circles are the experiment. The wavelength is λ = 800 nm. Sample S1

The algorithm for calculating the coefficients of reflection of TE(Rs) and TM(Rp) polarized laser beams from multilayered anisotropic structure (see Fig. 2 and 3) is developed. It allows to determine the characteristics of all films in a multilayer structure.

Besides the thicknesses of the layers h_1, h_2, h_3 and their permittivities ε_1, ε_2, ε_3, on Rs and Rp influences the thickness of the air gap H_i between the sample and the prism and the refractive index N_p. The numerical program (written in FORTRAN) takes into account the wavelength λ, complex refraction and thickness h_i of each layer, takes into account the anisotropy of the

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composite polymer film, characterized by the values of n_o and n_e. Expressions for the reflection coefficients have the form

$$R_s(\theta)=\left|\left(\frac{k_z-i\gamma^{II}}{k_z+i\gamma^{II}}+A_s e^{-2\gamma^{II}H_i}\right)\Big/\left(1+\frac{k_z-i\gamma^{II}}{k_z+i\gamma^{II}}A_s e^{-2\gamma^{II}H_i}\right)\right|^2 \quad (1)$$

$$R_p(\theta)=\left|\left(\frac{k_z-i\varepsilon_p\gamma^{II}}{k_z+i\varepsilon_p\gamma^{II}}+A_p e^{-2\gamma^{II}H_i}\right)\Big/\left(1+\frac{k_z-i\varepsilon_p\gamma^{II}}{k_z+i\varepsilon_p\gamma^{II}}A_p e^{-2\gamma^{II}H_i}\right)\right|^2 \quad (2)$$

Where $k = 2\pi/\lambda$ is the wave vector in vacuum, $k_z = kN_p\cos(\theta)$ is the projection of the wave vector of the electromagnetic wave in the prism (see Fig.2), $\gamma^{II}=k\sqrt{(N_p\sin\theta)^2-1}$, is z- projection of the wave vector in the gap between the measuring prism and the sample, $\varepsilon_p = N_p^2$ the dielectric constant of the prism. Angle dependent complex parameters A_s and A_p determine the reflections of the light beam in the layers of the thin-film structure.

$$A_s=\left(\frac{\gamma^{II}-\gamma^{III}}{\gamma^{II}+\gamma^{III}}+B_s e^{-2\gamma^{III}H_m}\right)\Big/\left(1+\frac{\gamma^{II}-\gamma^{III}}{\gamma^{II}+\gamma^{III}}B_s e^{-2\gamma^{III}H_m}\right),$$

$$A_p=\left(\frac{\varepsilon_m\gamma^{II}-\gamma^{III}}{\varepsilon_m\gamma^{II}+\gamma^{III}}+B_p e^{-2\gamma^{III}H_m}\right)\Big/\left(1+\frac{\varepsilon_m\gamma^{II}-\gamma^{III}}{\varepsilon_m\gamma^{II}+\gamma^{III}}B_p e^{-2\gamma^{III}H_m}\right),$$

where H_m is the thickness of the upper semitransparent metal electrode,

$$B_s=\left(\frac{\gamma^{III}-\gamma^{IV}}{\gamma^{III}+\gamma^{IV}}+C_s e^{-2\gamma^{IV}H_1}\right)\Big/\left(1+\frac{\gamma^{III}-\gamma^{IV}}{\gamma^{III}+\gamma^{IV}}C_s e^{-2\gamma^{IV}H_1}\right),$$

$$B_p=\left(\frac{\varepsilon_{1y}\gamma^{III}-\varepsilon_m\gamma^{IV}}{\varepsilon_{1y}\gamma^{III}+\varepsilon_m\gamma^{IV}}+C_p e^{-2\gamma^{IV}H_1}\right)\Big/\left(1+\frac{\varepsilon_{1y}\gamma^{III}-\varepsilon_m\gamma^{IV}}{\varepsilon_{1y}\gamma^{III}+\varepsilon_m\gamma^{IV}}C_p e^{-2\gamma^{IV}H_1}\right),$$

where H_1 is the thickness of the upper anisotropic polymer layer,

$$C_s=\left(\frac{\gamma^{IV}-\gamma^{V}}{\gamma^{IV}+\gamma^{V}}+\frac{\gamma^{V}-\gamma^{VI}}{\gamma^{V}+\gamma^{VI}}e^{-2\gamma^{V}H_2}\right)\Big/\left(1+\frac{\gamma^{IV}-\gamma^{V}}{\gamma^{IV}+\gamma^{V}}\frac{\gamma^{V}-\gamma^{VI}}{\gamma^{V}+\gamma^{VI}}e^{-2\gamma^{V}H_2}\right),$$

$$C_p=\left(\frac{\varepsilon_{2y}\gamma^{IV}-\varepsilon_{1y}\gamma^{V}}{\varepsilon_{2y}\gamma^{IV}+\varepsilon_{1y}\gamma^{V}}+\frac{\varepsilon_s\gamma^{V}-\varepsilon_{2y}\gamma^{VI}}{\varepsilon_s\gamma^{V}+\varepsilon_{2y}\gamma^{VI}}e^{-2\gamma^{V}H_2}\right)\Big/\left(1+\frac{\varepsilon_{2y}\gamma^{IV}-\varepsilon_{1y}\gamma^{V}}{\varepsilon_{2y}\gamma^{IV}+\varepsilon_{1y}\gamma^{V}}\frac{\varepsilon_s\gamma^{V}-\varepsilon_{2y}\gamma^{VI}}{\varepsilon_s\gamma^{V}+\varepsilon_{2y}\gamma^{VI}}e^{-2\gamma^{V}H_2}\right),$$

where H_2 – is the thickness of the lower anisotropic polymer layer. Here, $\varepsilon_1 = \varepsilon_{1x}x + \varepsilon_{1y}y + \varepsilon_{1z}z$, $\varepsilon_2 = \varepsilon_{2x}x + \varepsilon_{2y}y + \varepsilon_{2z}z$ are the permittivity tensors of polymer films 1 and 2; $\gamma^{III}=k\sqrt{(N_p\sin\theta)^2-\varepsilon_m}$, $\gamma^{VI}=k\sqrt{(N_p\sin\theta)^2-\varepsilon_s}$, ε_s is the permittivity of the substrate. In the case of TE polarization of the incident light wave $\gamma^{IV}=k\sqrt{(N_p\sin\theta)^2-\varepsilon_{1x}}$, $\gamma^{V}=k\sqrt{(N_p\sin\theta)^2-\varepsilon_{2x}}$, and In the case of TM polarization $\gamma^{IV}=k\sqrt{(N_p\sin\theta)^2\varepsilon_{1y}/\varepsilon_{1z}-\varepsilon_{1y}}$, $\gamma^{V}=k\sqrt{(N_p\sin\theta)^2\varepsilon_{2y}/\varepsilon_{2z}-\varepsilon_{2y}}$.

We note that in z-projections of wave vector γ^{IV}, γ^{V} in layers h_1 and h_2 imaginary parts of the corresponding refractive index (extinction coefficient) m_i are introdused $\varepsilon_i=(n_i+im_i)^2$. Namely m_i determines the width of the observed m-lines.

When an external electric field E is applied to a composite film with aligned EO chromophores, the m-lines are shifted due to a change in the refraction of the film. This shift depends on the electro-optical coefficient r_{33} for TE polarization and on r_{13} for TE polarization. The sensitivity of the method to a small refraction changes is limited by the width of the m-lines, and accordingly by absorption. Moving to long wavelengths (like 800 nm), where absorption (and m-lines width) is small allows more resize fitting.

Comparison with original analytical model of six-layer structure attenuated total reflection (see Fig. 2 and 4) allows us to determine precisely all optical characteristics. For the example, for the sample used at Fig. 3 determined optical parameters of EO layer are the following: h_2=4.5±0.02 μm is the thicness, n_2=1.5421±0.0005 is the refraction, m_2=(25±1)E-4 is extinction coefficient determining absorption, all that for λ = 800 nm.

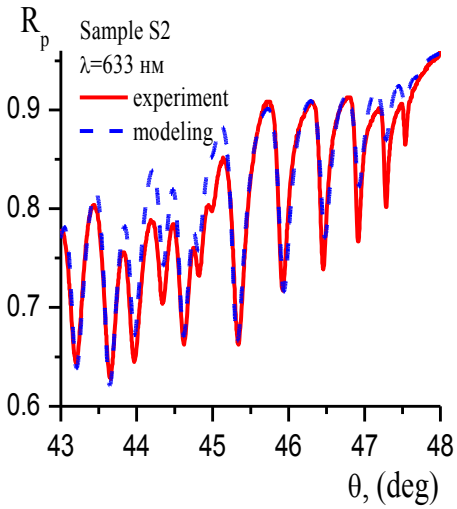

Figure 4. The measured and calculated angular reflection spectrum of Rp(θ) at a wavelength of 633 nm for sample S2.

Fig. 4 shows the measured and calculated dependences of the reflection coefficient Rp(θ) (TM polarization, λ = 633 nm) for sample S2 after alignment of chromophores in the PMMA / DR13 film. The structure parameters were determined from the measured positions of the m-lines after each subsequent layer was deposited. After deposition of all the layers, these parameters were refined by varying them for the best match of the measured and calculated angular spectra Rp(θ).

Sample S2 does not support true waveguide modes in the EO polymer layer h_1, since the refractive index of this layer is lower than that of layer h_2. Nevertheless, the reflection at the boundaries of the layers h_1 and h_2 allows the radiation to propagate in the layer h_1, although with high radiation losses (leaky modes). In Fig. 4 true guided modes excited at high angles of

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incidence (θ = 48 - 45.5 °) they refer to the layer h_2 of SU-8 with DR13 polymer, and the resulting modes at θ <45° refer to the polled layer h_1. The most sensitive to the change in the refractive index are the low-order m-lines.

When analyzing sample S2 at λ = 633 nm, the following thickness values h_j and refractions n_j of layers j numbered, as in Fig. 2: n_3 = 0.16+i*3.37, h_3 = 40 nm, h_2 = 4.80 μm, n_2 = 1.5965 + i*0.002; h_1 = 4.75 μm, $n_{1,o}$ = 1.522 + i*0.002, $n_{1,e}$ = 1.532 + i*0.002, $n_0 = n_3$.

When an external electric field E is applied to a composite film with polled EO chromophores, the m-lines are shifted on $\Delta\theta$ due to a change in the refraction of the film δn see Fig.5.

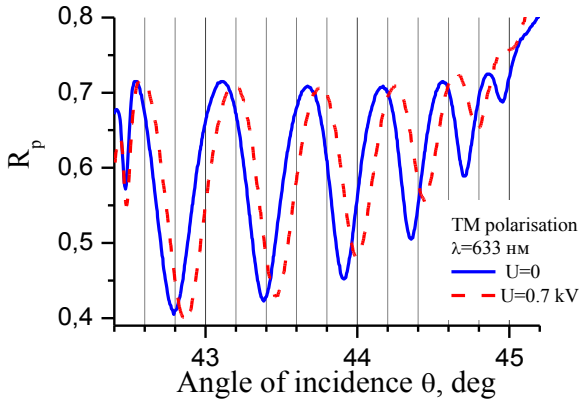

Figure 5: The measured Angular Reflection Spectrum for λ = 633 nm, with and without applied voltage. TM (P) polarization. Sample S3

The largest angular shift of m-lines is observed for TM polarization due to a larger change in the refractive index n_e

$$\Delta\theta_{TM} \propto \delta n_e = -0.5 n_e^3 r_{33} E$$

Using the calculations, we can compare the magnitude of the angular shift of a particular m-line and the change in refraction that leads to such a shift. For example, for λ = 633 nm and for the TM_3 mode in the PMMA / DR13 layer (θ = 44.6 ° in Figures 4), the refraction of change of n_e to 0.0006 results in a shift of the mode angle θ by 0.017°, hence $\Delta n_e = \Delta\theta_{TM}/29$. The resolution of the prism coupler Metricon2010 is Δθ = 0.01°, thus the accuracy of determining the refractive index at low absorption reaches Δn = 0.0001. Thus, the induced changes in the refractive index in the fourth digit can be registered.

The change in the refractive index due to the EO effect is related to r_{ij} and the applied electric field $E_z = U/(h_1 + h_2)$. Let us estimate the value of r_{33}, which leads to the observed variation Δn_e = 0.006 when the control voltage U = 0.3 kV is applied to sample S2. With the total thickness of polymer composite films $h_1 + h_2$ = 9.5 μm, we obtain r_{33} = 8 pm/V. As the distance from the EO resonance decreases, the coefficient decreases (see Figure 1).

At 800 nm, the film is transparent (see Fig. 1), there is already a nonresonance part of the EO coefficient. A further increase in the wavelength does not lead to a significant decrease in r_{33}. To characterize the coefficient EO by the method of prism coupler, the optimum wavelength is the wavelength corresponding to the edge of the absorption band, in the case of DR1 and DR13 dyes this is 670-700 nm. Moreover, the EO coefficient still has a noticeable resonant contribution, and m - the line are already narrow enough.

Using calculation algorithm we relate Δθ and δn and thus we found EO coefficients r_{33} and r_{13} composite PMMA/DR13 in multiple wavelengths (633, 800, 980 nm) near the absorption peak of chromophore (at 520 nm) and far from it. The proposed method allows us to measure the induced external electric field changes in the refractive index in the thin-film light-guiding structure of the real electro-optic modulator with an accuracy of ± 0.0003.

3. CONCLUSSION

Electro-optical response of perspective chromophores embedded into polymer waveguide structure is studied. Modeling is based on analytical solution of Fresnel formulas for six layer system under prism coupling conditions for guided modes excitation. Complex transition and multiple reflections in each layer are taken into account. Adapted fitting procedure to the experimental data allows obtaining optical linear (refraction, absorption, thickness) and nonlinear (EO Pockels effect) properties of each layer.

The sensitivity of the method makes it possible to measure the EO of the coefficients r_{33} and r_{13} for the TE and TM of the polarization of the incident light beam from 2 pm/V, the sensitivity is limited by the breakdown voltage of the metallized structure. The method makes it possible to determine the refractive indices of several dielectric layers (even those covered by a translucent metal film) with an accuracy of ±0.0005, and their thickness with an accuracy of ±0.05 μm.

The advantage of the proposed method in comparison with the known approaches – Nahata and Shan (1993) is that it can be used to measure the characteristics of real polymer EO modulators with a multilayer structure and external electrical contacts for different wavelengths.

The results of the research can be used to create active integrated-optical devices of radio-photonics: waveguide amplifiers, high-speed optical switches and modulators for the telecommunications C-band of the spectrum. The design of integrated - optical modulator for radio-photonics is suggested

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