Electro-optic activity of an azopolymer achieved via poling with the aid of silicon nitride insulating layer

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Nonlinear optical chromophore was synthesized to form a guest–host system with a PMMA matrix. Thin polymer films were spin-coated onto the substrates containing an additional insulating layer. The layer material was high resistivity and high transmittance silicon nitride obtained by chemical vapour deposition with plasma enhancement at a relatively low temperature of 150 °C. The presence of the nitride layer allowed for performing the polymer poling in the range of high electric field strengths not attained in structures without the insulating layer. Here, for the first time to the best of our knowledge, the silicon nitride interlayer was used in the poling process.

Keywords: azopolymers, polymer poling, electro-optic activity.

1. Introduction

In recent years electro-optic (E-O) polymers have been considered as promising materials for photonic applications [1]. Due to the unique properties such as large molecular hyperpolarizability, low dielectric constant, low optical absorption in the infrared region and compatibility with microelectronic processes the polymers have been competing with the traditional inorganic materials for fabrication of optoelectronic devices: high-speed E-O modulators, switches and filters. An E-O polymer contains the chromophores, which are nonlinear optical (NLO) molecules embedded in a polymer matrix. The chromophore structure made of the proper electron donor and

electron acceptor groups separated by a π-conjugated bridge gives the molecule both large permanent dipole moment and first hyperpolarizability. The linear E-O effect being a change in the refractive index of a medium caused by an electric field belongs to the second-order nonlinear optical effects, which are forbidden in centrosymmetric materials. A typically utilized spin-coating method gives a polymer film exhibiting no E-O properties due to a random chromophore orientation. Several techniques have been applied for inducing an acentric chromophore order required for E-O activity [2–5]. In a parallel-plate geometry of a common static electric field poling method [3], a polymer film is placed between two electrodes and heated near to the film glass transition temperature. In a state of increased molecule mobility the noncentrosymmetric arrangement of the chromophore dipoles is realized by a high electric field applied across the film. Cooling down the sample in the presence of the field ensures locking in the introduced order to room temperature. The magnitude of an arising E-O material activity is determined by the degree of the imposed polar order. In practice efficient poling involving the highest possible field is not trivial to perform. Defects and impurities of the polymer film may lead to a destructive short circuit even in the fields of a moderate strength (< 100 V/µm). Therefore, it is necessary to use high purity materials and perform a dust-free film processing. Moreover, in order to delay the onset of catastrophic breakdown certain additional methods are applied. They are based on inserting a thin layer of spin-coated material between the NLO polymer and the electrode. In particular, it was shown that in the presence of a siloxane layer the probability of singular dielectric breakdown events was decreased and the limit of avalanche breakdown was shifted to higher poling field strengths [6, 7]. Recently, highly polarizable chromophores were effectively poled using a titanium dioxide layer that significantly blocked excessive charge injection and reduced the leakage current during high field poling [8].

 Here, we report on determination of the E-O activity of a guest–host NLO polymer system containing the synthesized azobenzene chromophores (denoted as AZ-1) and poly(methyl methacrylate) (PMMA) as a matrix material. We investigate a possibility of performing a successful high electric field poling of the polymer using an additional silicon nitride insulating layer obtained by chemical vapour deposition with plasma enhancement and applying a clean environment film preparation conditions.

2. Experiment

2.1. Chromophore synthesis

The AZ-1 chromophore that was N-ethyl-N-(2-hydroxylethyl)-4-(2-cyano-4-nitro-phenylazo)-aniline was prepared by the azo coupling of 2-cyan-4-nitroaniline with 2-(N-ethylaniline)ethanol, *i.e.*, 2-cyan-4-nitroaniline was converted to the corresponding diazonium salt, which was subjected to a coupling reaction with 2-(N-ethylaniline)-ethanol to give the final compound. Details of the synthesis were presented elsewhere [9].

2.2. Sample geometry

For the electric field poling procedure the polymer film was sandwiched between two conducting plates: a 30-nm-thick indium tin oxide (ITO) coated onto a glass substrate and a 100-nm-thick aluminium. An additional 200-nm layer of silicon nitride separated the polymer and the ITO films. Silicon nitride was grown onto the ITO coated glass slides by chemical vapour deposition with plasma enhancement (PECVD) using an Oxford Plasmalab 100 reactor fed with silane (SiH_4) and ammonia (NH_3) as reactive gases. The deposition process was carried out at 150 °C. Before the deposition a narrow strip along the edge of the ITO coated glass slide was mechanically masked with a piece of silicon wafer. An area non-deposited with the nitride was then used for attachment of an electrical contact with the ITO electrode. The aluminum layer, serving as a second electrode, was obtained by sputter deposition onto the top of the polymer film. The same sample geometry was applied in the E-O characterization.

2.3. Guest–host polymer film preparation procedure

The whole procedure of polymer film preparation was performed in a clean-room environment to avoid impurities. A commercially available PMMA purchased from Aldrich and the AZ-1 chromophore with the concentration of 12 wt% in PMMA were dissolved in the mixture of chlorobenzene and chloroform (2:1). The resulting solution was filtered through a 0.2 µm millipore filter and spin-coated at the speed of 900 rpm on the glass slides coated with both ITO and silicon nitride. The slides were left in ambient conditions for several minutes, then placed into an oven, heated at a rate of 1 °C per minute to 90 °C under nitrogen flow and left for 5 hours to remove residual solvents.

2.4. Characterization

The glass transition temperature T_g of the chromophore-doped PMMA film was investigated by differential scanning calorimetry measurements using a Du Pont 1090B apparatus with a heating rate of 20 °C/min under the nitrogen atmosphere. The thickness measurements of the spin coated polymer layers were made using an Alpha Step stylus profiler. UV–vis absorption spectra of the polymer film, the ITO coated glass substrate and the substrate coated with both silicon nitride and ITO were recorded using a Perkin Elmer Lambda 45 spectrophotometer. The refractive indices of silicon nitride and E-O polymer films were determined using a Sentech spectroscopic ellipsometer. For the ellipsometric measurements both the nitride and polymer materials were deposited onto the silicon wafers.

The E-O response of poled samples was examined using a reflection technique proposed by Teng and Man [10]. The experimental setup is presented in Fig. 1.

The measurement was performed in a crossed-polarizer configuration for a laser beam at the wavelength of 780 nm. A half-wave plate set the polarization direction of the input beam at 45° with respect to the incidence plane in order to equate
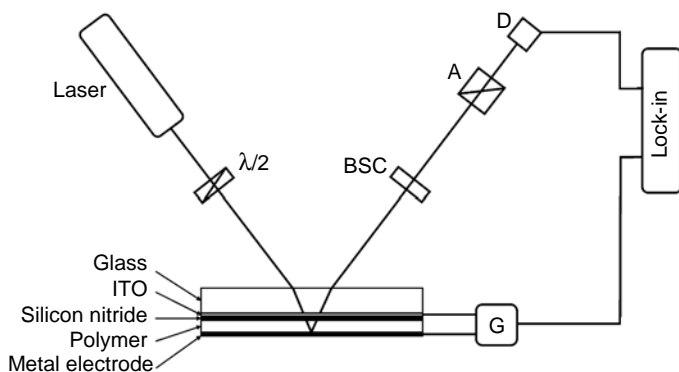
Fig. 1. Experimental setup for E-O coefficient measurement; $\lambda/2$ – half-wave plate, BSC – Babinet–Soleil compensator, A – analyzer, D – detector, G – generator.

the intensities of orthogonal components *s* and *p* of the optical wave. The beam was entering the sandwich structure from the side of the ITO electrode and was leaving it after reflection from the aluminum electrode. The light intensity modulations appearing as a result of a 1 kHz sine voltage signal applied to the poled polymer material were measured by a photodetector and a EG&G lock-in amplifier. To get a maximum effect a Babinet–Soleil compensator was placed in front of the analyzer and set at its quarter wave point. The r_{33} E-O coefficient evaluated from the equation below [11] determined the magnitude of the sample E-O activity:

$$r_{33} = \frac{3\lambda I_m}{4\pi V_m I_c n^2}\frac{(n^2 - \sin^2\theta)^{1/2}}{\sin^2\theta}$$

where: λ is the laser beam wavelength, θ is the angle of incidence, n is the refractive index of the polymer film, I_c is the intensity at the photodetector, V_m is the modulating voltage and I_m is the amplitude of intensity modulation.

Here, one assumes a perfectly transparent ITO electrode, a perfectly reflective metallic electrode, and a negligible absorption of the polymer film. The multiple reflection effects are not taken into account. The r_{33} E-O coefficient is assumed to be $3r_{13}$.

3. Results and discussion

The chemical structure of the synthesized chromophore is shown in the inset of Fig. 2.

The chromophore formed a D-π-A type of molecule; the two benzene rings and the azo bond provided the conjugated π-system, the tertiary amine acted as electron donor and both nitro- and cyano-groups acted as electron acceptors. Some characteristics of the host and guest–host materials are collected in Tab. 1.
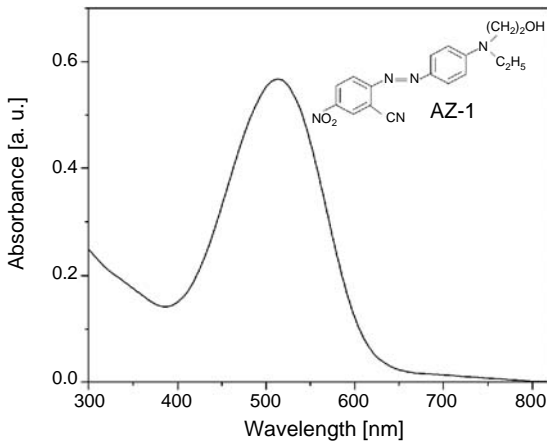
Fig. 2. UV–vis absorption spectrum for PMMA/AZ-1 guest–host film and chemical structure of the AZ-1 chromophore in the inset.

T a b l e 1. Characteristics of host and guest–host materials.

PMMA			PMMA/AZ-1	
M_w [g/mol]	T_g [°C]	n at 632.8 nm [12]	T_g [°C]	n at 632.8 nm
12.4×10^4	126	1.49	103	1.76

As can be seen from the table the glass transition temperature of the PMMA/AZ-1 polymer system under study was lower than the glass transition temperature of PMMA. This is typical of guest–host systems. The PMMA/AZ-1 film refractive index was higher in comparison to pure PMMA.

Figure 2 presents the optical absorption spectrum of the PMMA/AZ-1 polymer film cast onto a glass substrate. The absorption spectrum showed a strong band with the maximum located at 510 nm attributed to the electronic π–π^* and n–π^* transition of the *trans*-azo chromophore.

Silicon nitride was chosen as an additional material separating the polymer from the ITO electrode. Due to excellent properties the silicon nitride films have been widely used in the microelectronics industry as, *e.g.*, dopant diffusion barriers, passivation layers for device packaging or as gate dielectrics in thin film and field effect transistors. The deposition method is dependent on the application requirements. Commonly, the film growth by PECVD is carried out at the temperatures between 250 and 300 °C. We found, however, that one-hour exposure of the 30-nm-thick ITO coated slide to 250 °C had a disadvantageous effect on the ITO electrical properties; the initial surface resistivity increased by more than a 100%. On the other hand, it was checked that the surface resistivity remained unchanged following the exposure at 150 °C. For the above reasons the PECVD process was performed at 150 °C. Since it is known that the deposition temperature of silicon nitride affects the hydrogen content and so

T a b l e 2. The refractive indices (at 632.8 nm) for PECVD silicon nitride films grown at various temperatures.

Temperature	150 °C	300 °C	< 400 °C [13–16]
Refractive index	1.85	1.98	1.8–2.6

the material parameters, a refractive index, chosen as a measure of the material quality, was evaluated and compared with a refractive index of the nitride deposited at 300 °C (Table 2).

As can be seen from Tab. 2 performing the growth at 150 °C leads to silicon nitride of a lower refractive index than that obtained for a 300-degree-process, but within the range reported in the literature.

In microsystems fabrication technologies dielectric layers from several nanometers up to a couple of microns are used depending on application. Here, for the first examination of the role of the nitride interlayer in the poling process the ITO surface was covered with the 200-nm-thick nitride. The recorded transmission spectra of ITO coated slides (Fig. 3) showed that after silicon nitride deposition the nominal transmittance did not change. The sinusoidal oscillations in the spectra are due to the interference effects arising from the presence of uniform thin films onto a thick glass substrate.
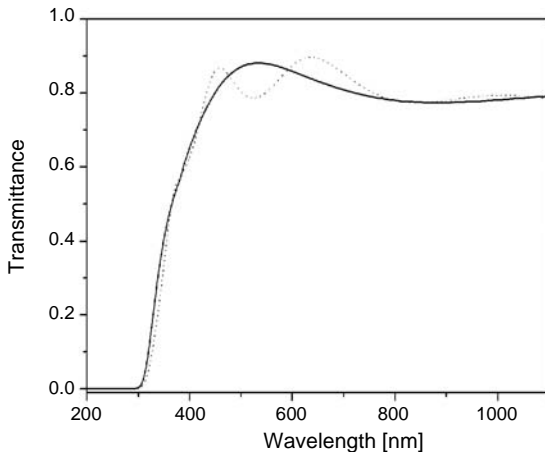

Fig. 3. Transmittance curves of an ITO coated glass slide (solid line) and a glass slide coated with both ITO and silicon nitride (dotted line).

The silicon nitride layer deposited at 150 °C showed a good adhesion for the spin coated polymer solution. Spin coating and drying procedure led to continuous polymer films of a uniform thickness of *ca*. 2.0 μm.

Poling experiments were carried out for 10 minutes at 95 °C and electric field strengths between 100 and 140 V/μm. Electric field strengths were defined as the applied voltages divided by the thickness of the polymer film. Poling tests performed on

several samples showed that a destructive breakdown occurred at *ca.* 135 V/μm. In the case of a sandwich structure without the nitride layer the sample breakdown occurred at the applied field slightly below 100 V/μm. Such a sample could be successfully poled in the electric field of only moderate strength and exhibited poor E-O response. Poling the samples with the additional insulating layer at 100 V/μm was going on without appearance of any singular breakdowns. At 130 V/μm singular breakdown events were detected. The events were responsible for the appearance of few pinholes in aluminum electrode due to metal evaporation. The significant delay in onset of dielectric breakdown for samples with the silicon nitride layers is in agreement with the results obtained by SPRAVE *et al.* [6]. They showed that coating the ITO electrode with an inorganic polymethylsiloxane layer allowed extending the maximum achievable poling field strengths by 27%.

There are various methods of measuring the linear E-O coefficients such as simple reflection technique [10], Mach–Zehnder interferometry [17], Fabry–Perot interferometry [18] or attenuated total reflection [19]. The reflection technique proposed by TENG and MAN is based on the polarization rotation of a laser beam due to the E-O effect. The method has been quite frequently used for the evaluation of E-O coefficients of poled polymer films because of a relatively simple sample preparation and measurement [8, 20–22].

The E-O response was examined directly after cooling down the samples to room temperature. For samples poled at 100 and 130 V/μm, the r_{33} coefficient was 3.3 and 4.1 pm/V, respectively, showing an improved E-O activity with the poling fields. The measurement was performed for a laser beam wavelength of 780 nm, lying outside the chromophore absorption band. At this wavelength the ITO slide transmittance was almost 80%. It has recently been shown that if the operating wavelength is longer than 1 μm Fabry–Perot effects inside the polymer layer are enhanced (due to an increased reflectance of ITO) and the effect is more pronounced for thick (100 nm) ITO films [23]. The thicknesses of the polymer and ITO layers applied in this study corresponded to the ranges identified by PARK *et al.* [23] that allow the accuracy of *ca.* ±20% of E-O coefficient evaluation under assumption of no loss in the polymer film and no multiple reflection effects.

4. Conclusions

A guest–host polymer system containing synthesized azobenzene chromophores and PMMA matrix was formed. For a successful high electric field poling an additional silicon nitride layer was deposited between the polymer material and a transparent conducting plate. The thin insulating layers were obtained on the ITO coated glass substrates at 150 °C, which was a safe temperature for the ITO substrates. The presence of 200-nm silicon nitride layer delayed the onset of dielectric breakdown of the sandwich structure by *ca.* 35% in comparison to the structure without the layer. The poling process was performed at 130 V/μm leading to an electro-optic coefficient of the investigated polymer of 4.1 pm/V.

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