Piezoelectricity and electrostriction of dye-doped polymer electrets

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An interferometric measurement technique is reported by which the piezoelectric and electrostrictive properties of thin films of electrets can be determined. The frozen-in polarization can be determined from the ratio between piezoelectric and electrostriction constants of the electret film. The method is applied to a poled-polymer guest-host system consisting of a polycarbonate host and 4-dimethylamino-4′-nitrostilbene dye. The frozen in polarization measured as a function of poling field agrees well with the predictions for dilute dipolar systems if an affine motion contribution is added to the established theory of the piezoelectric effect of electrets.

Poled polymers with nonlinear optical (NLO) properties are promising candidates for application in optical data processing devices using the Pockels effect.[1] To observe a Pockels effect it is necessary for the material to contain nonlinear polarizable units in a noncentrosymmetric distribution. This can be achieved by poling the materials at elevated temperatures. Materials which have undergone a poling procedure, generally called electrets, possess a large induced polarization[2] and therefore show a piezoelectric (and pyroelectric) effect,[3] that will interfere with the pure electro-optic response. However, it is not possible to separate the piezo- and dielectric contributions in an experiment that measures only the field induced changes in optical path length through the material.[4] The more sophisticated method of attenuated total reflection (ATR) can separate these two contributions[5,6] but the evaluation of the ATR spectra requires a lengthy fitting procedure and the method is limited to a film thickness of between 1 and 5 μm. The aim of our work was to develop a method which can directly determine the thickness changes of a poled polymer film of about 1 μm thickness.

We have chosen an interferometric setup based on the Nomarski principle.[7,8] The experimental setup is shown in Fig. 1. One of two orthogonal polarized beams, s and p, which are separated by a distance of 4 mm, is reflected by a reference mirror, the other one is reflected off the top gold electrode of the sample. The reference mirror is glued to the top of a piezoelectric PZT ceramic, which is used to fix the working point of the interferometer to the fringe position with the highest sensitivity. The sample consists of a glass plate of 1 mm thickness, vacuum evaporated bottom and top gold electrodes and the spin coated polymer film of about 2 μm thickness. After reflection the beam is directed to the detection unit, where a Wollaston-type prism splits the beam into two beams s' and p'. The intensities A and B of these two beams are measured by two photodiodes. When the optical axis of the Wollaston prism is rotated by 45° with respect to the optical axis of the calcite prism, the difference of the intensities A and B is proportional to the phase difference Φ between beams s and p;[8]

$$\frac{A-B}{A+B}=V\sin(\Phi)\simeq V\Phi=V\frac{2\pi}{\lambda}\,2\Delta h. \tag{1}$$

In the above formula, Δh is the thickness change and V is a dimensionless contrast factor, which has to be determined before each measurement. The difference between the two intensities, $A-B$, is measured directly by a lock-in amplifier while the absolute intensities A and B are recorded by an AD converter built into the controlling computer. The dc part of $A-B$ is used to fix the working point of the interferometer.

To a first approximation the poled samples can be treated as parallel plate capacitors, whose plate separation h is changed by an applied electric field. The field induced thickness changes are generally written as follows:

$$h(E)=h_0(1+dE+aE^2+\ldots), \tag{2}$$

where d is the piezoelectric constant and a is the electrostriction constant of the polymer electret. (We assume that the film is fixed in the plane parallel to the electrodes and suppress the tensor notation for d and a.) For an alternating electric field $E=E_0\cos\omega t$, Eq. (2) gives

$$\frac{\Delta h(E)}{h_0}=\frac{1}{2}\,aE_0+dE_0\cos\omega t+\frac{1}{2}\,aE_0^2\cos 2\omega t. \tag{3}$$

Therefore, the piezoelectric and the electrostriction effects can be separated by the lock-in detection. The capacitor is filled with a dielectric of the dielectric strength ϵ. Due to the poling procedure, a polarization P

$$P=\frac{\epsilon+2}{3}\,P_0 \quad \text{with} \quad P_0=\frac{N}{V}\,\mu_0\langle\cos\theta\rangle, \tag{4}$$

has been induced in the material.[9] Here N/V is the chromophore number density, μ_0 is the static dipole moment and $\langle\cos\theta\rangle$ is the average tilt of the chromophores.

The electrical energy of the charged capacitor with electrode area A is given by

$$W_e=\int_0^Q EhdQ \quad \text{with} \quad E=\frac{Q+Q_P-Q_P^*}{\epsilon_0\epsilon A}. \tag{5}$$

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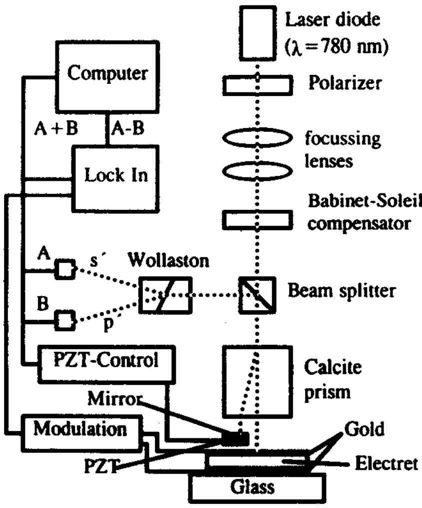

FIG. 1. Experimental setup.

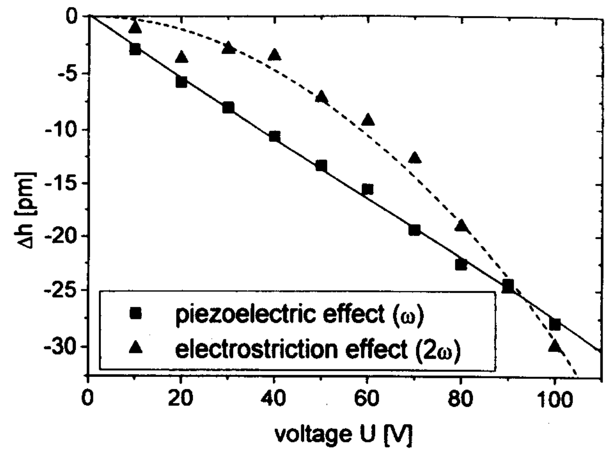

FIG. 2. Fundamental (ω) and first harmonic (2ω) nonlinear electromechanical effects as function of modulation field strength [$d=-0.276$ $(0.005) pm/V$, $a=-6113$ $(275)(pm)^2/V^2$].

The polarization P of the dielectric in the capacitor is replaced by an equivalent charge density $Q_P^*/A=P$. This equivalent charge density is balanced by the compensation charge density Q_P on the capacitor plates. Changing the thickness of the charged capacitor results in an "electrical" force $F_e=-\partial W_e/\partial h$.

$\partial\epsilon/\partial h$ is computed using the Clausius–Mossotti relation. The calculation of $\partial P/\partial h$ follows the procedure given in Ref. 3, but we introduced an additional term describing the affine motion of the dipoles during thickness changes:

$$\frac{\partial P}{\partial h}=P_0\,\frac{\epsilon+2}{3}\left(\frac{\epsilon+2}{3}-\frac{2}{5}-G\right). \tag{6}$$

In the equation for $\partial P/\partial h$, $\partial\langle\cos\theta\rangle/\partial h$ gives two contributions, namely the Grueneisen coefficient G, which will be neglected in the following, and the additional $\frac{2}{5}$, which is due to the affine motion of the dipoles with the deforming matrix.

The mechanical force acting against the deformation of a mechanically isotropic film, which is fixed in the film plane is given by

$$F_m=-\frac{\partial W_m}{\partial h} \quad \text{with} \quad W_m=\frac{1}{2}\,\frac{A}{\beta_{\text{plate}}h}\,\Delta h^2. \tag{7}$$

The apparent plate compressibility of a mechanically isotropic medium is related to its bulk compressibility by the following relation:

$$\beta_{\text{bulk}}=\frac{3(1-2\nu)}{1-\nu^2/(1-\nu)}\;\beta_{\text{plate}}, \tag{8}$$

where ν is the Poisson number of the material. Equilibrium between the mechanical and electrical forces $F_m+F_e=0$ gives an equation for $\Delta h/h$, from which the expressions for d and a can be derived:

$$d=-\beta_{\text{plate}}P_0\,\frac{\epsilon+2}{3}\left(\frac{\epsilon+2}{3}-\frac{2}{5}\right), \tag{9}$$

$$a=-\frac{\beta_{\text{plate}}\epsilon_0}{2}\left(\epsilon+\frac{(\epsilon+2)(\epsilon-1)}{3}\right). \tag{10}$$

Knowing the instantaneous dielectric constant ϵ of the dielectric it is possible to determine the compressibility of the clamped film. From the ratio d/a the frozen in polarization can be determined independently of the mechanical properties of the sample.

The guest-host polymer was prepared with a number density of 4-dimethylamino-4′-nitrostilbene (DANS) molecules ($\mu_0=7.1D^{10}$) of $N/V=1.86\times10^{(20)}$ cm^{-3}, checked by ultraviolet absorption. The polycarbonate-DANS (PCD) films have been poled with different poling fields at temperature $T_{\text{pol}}=438$ K. Assuming an isotropic potential for the poling process and considering poling conditions $\mu_0E_{\text{pol}}/kT_{\text{pol}}\ll1$, the frozen in polarization is given by

$$P_0=\frac{N}{V}\;\mu_0\langle\cos\theta\rangle \quad \text{with} \quad \langle\cos\theta\rangle=\frac{\mu_0E_{\text{pol}}}{3kT_{\text{pol}}}\;f, \tag{11}$$

where f is an Onsager-type local field factor.[11]

Figure 2 shows the determination of the piezoelectric and electrostriction constants for a sample poled with $E_{\text{pol}}=60$ V/μm. For the piezoelectric effect the modulation frequency was 993 Hz. The electrostriction will lead to a periodic modulation of the film thickness at double the frequency of the applied field. Because the dynamic compressibility is generally frequency dependent, the electrostriction has to be excited with half the measuring frequency of 993 Hz. The quadratic effect was found to be independent of the strength of the poling field. With the assumption $\nu=0.3$ and with $\epsilon=2.92$ and $\epsilon^{\text{st}}=2.96$ (Ref. 12) for the local field factor we calculated the bulk compressibility, the elastic modulus E, and the frozen-in polarization P_0.

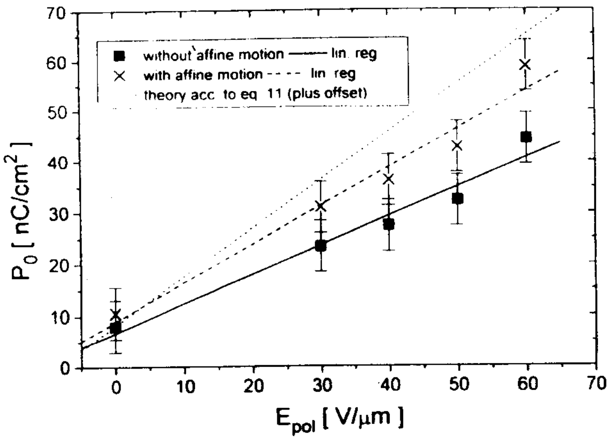

FIG. 3. Frozen-in polarization for different poling fields.

The linear dependence of P_0 on the poling field is shown in Fig. 3 for two different models. In the first case the affine motion contribution to the piezoelectric constant was neglected during the computation of P_0, while in the second case an affine motion contribution was included. These results have been compared to the theoretical predictions of Eq. (11). Very good agreement is obtained only when the affine motion effect is respected in the evaluation. The frozen-in polarization exhibits an offset of about 7.8 nC/cm^2. This offset is added to the theoretical model of Eq. (11) in Fig. 3. The offset may be caused by trapped charges, which are known to contribute to the piezoelectric effect in the case of a noncentrosymmetric distribution of trap sites.[13,14] From the electrostriction constant we determined the elastic modulus of the PCD film to be E=2.88 GPa. For comparison the electrostriction of a pure polycarbonate film of 2 μm thickness yielded a modulus of E_{pc}=3.16 Pa. This value deviates by 10% from the value of E^s_{ps} = 3.51 GPa obtained for polycarbonate using a commercial PVT apparatus (Gnomix Research).

We have demonstrated the application of an interferometric method to the measurement of the piezoelectric and electrostrictive thickness changes of thin electret films. The proposed model allows for the determination of the elastic modulus and the frozen-in polarization of the electret. We have shown that the piezoelectric properties of a dye-doped polymer electret typical for NLO guest-host systems can be described by the theory of Mopsik and Broadhurst, which must take into consideration an affine motion contribution to the thickness dependence of $\langle \cos \theta \rangle$. Further work will be devoted to the influence of the piezoelectric effect on electrooptical light modulators.

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