EFFECTS OF THE MULTIPLE INTERNAL REFLECTION AND SAMPLE THICKNESS CHANGES ON DETERMINATION OF ELECTRO-OPTIC COEFFICIENT VALUES OF A POLYMER FILM

E. Nitiss a, M. Rutkus b, and M. Sivilans b

a Institute of Solid State Physics, University of Latvia, Kengaraga 8, LV-1063 Riga, Latvia
b Faculty of Material Science and Applied Chemistry, Riga Technical University, Āzenes 14/24, LV-1048 Riga, Latvia
E-mail: edgars.nitiss@cfi.lu.lv

Received 8 September 2011; revised 18 January 2012; accepted 1 March 2012

New nonlinear optical (NLO) active organic materials are appealing candidates for optoelectronic and photonic technologies. For the evaluation of new NLO polymer materials for applicability in the mentioned technologies, the most important criteria are their electro-optic (EO) coefficients. We have implemented the Mach–Zehnder interferometric (MZI) method for the determination of EO coefficients of thin organic films. Despite the fact that other multiple optical methods for the determination of thin film EO coefficients are known, the MZI method has been chosen because this particular technique has high sensitivity to phase and intensity modulations in the sample arm of an interferometer and allows one to determine independently both the film EO coefficients, r_{33} and r_{31}. In addition to the drawbacks described earlier we demonstrate that some other effects like electrostriction and multiple internal reflections in the sample have a considerable influence on light intensity at the MZI output. Taking into account these effects we have performed numerical simulations of the EO effect caused MZI output changes or modulation depth at different incidence angles using the Abeles matrix formalism. We can show that the modulated signal at the MZI output is highly dependent on the sample structure and is mainly governed by the effects mentioned above. For analysis of modulated signal components and determination of EO coefficients a series of experiments was carried out on PMMA + DMAB 10 wt\% samples.

Keywords: electro-optic coefficient, Mach–Zehnder interferometric method, nonlinear optical polymer, multiple internal reflections in polymer films

PACS codes: 81.70.Fy, 82.35.Ej

1. Introduction

Increasing interest has been devoted to new nonlinear optical (NLO) active organic materials due to their low cost, easy processability and potential applications as optical components in electro-optic (EO) devices. Such organic EO materials are possible substitutes for traditional inorganic materials [1]. A high NLO activity is the most important material prerequisite for further successful application in EO devices making the evaluation of this property an important task for new material development.

13

Fig. 1. Experimental set-up of MZI for determination of EO coefficients of a thin organic film: helium-neon laser (632.8 nm) as a light source. Polarisation of incident light can be controlled by a half wave plate. Afterwards, light is split into sample I_s and reference I_r arms of a MZI by a 50/50 beam splitter. By means of a small angle glass wedge and a computer controllable translation stage in the reference arm the interference phase of I_r and I_s and thus the AC signal measurement point can be shifted. To obtain an interference pattern the light of the reference and sample arms is combined by a second 50/50 beam splitter. The acquired interference pattern is detected by a large area Si photodiode. It is important to note that full overlapping of both light beams is necessary to achieve the maximum modulated signal. As the MZI is highly sensitive to any vibrations the elements of the optical set-up must be fixed firmly. An ultra stable beam splitter and mirror holders are suggested. A modulation voltage at 4 kHz was provided by a computer controlled lock-in detector (Stanford Research Systems SR830) and an amplifier (Tek PZD350). The light intensity modulation (AC signal) as well as the average MZI output light intensity (DC signal) was measured with the SR830 and recorded by the PC. It is important to note that the AC signal recovered by the Lock-in amplifier contains a notable fraction of crosstalk. This effect is caused by electromagnetic induction and can be recognised by its presence in the detection system with the laser light turned off. The crosstalk signal has the same frequency as the modulation caused by EO effect and creates an additional offset value in the signal detected by lock-in which is not dependent on MZI phase.

Typically, the polymer sample PMMA + DMA-BI 10 wt\% (for a detailed molecular structure see Ref. [14]) used in this investigation was made by spin-coating (900 rpm speed, 300 rpm/s acceleration) it onto an ITO covered glass slide (SPI Supplies ITO 70–100 Ω) from a chloroform solution (concentration of 100 mg/ml) of appropriate amounts of components. The glass transition temperature of the polymer is approximately 110 °C. There are two main possibilities how to obtain the sandwich sample structure. For sample 1, an ITO glass slide carrying the polymer is covered with another bare ITO glass slide as shown in Fig. 2,
The EO experiment was performed as follows. Modulation voltage (typically 50 V rms for sample 1 and 15 V rms for sample 2) was applied to the electrodes, the output light intensity of MZI (DC signal) and the light modulation amplitude (AC signal) was detected with the Si photodiode and measured by the lock-in detector. Data was collected for 20 s at several MZI interference phase points and then averaged. The measurement series was done with s and p polarised light at several incident angles. Figure 3 shows typical measurement results where the interference phase is scanned with the motor-controlled glass wedge.

From Fig. 3 the maximal modulation depth \( m_{\text{max}} \) is calculated by

\[
m_{\text{max}} = \frac{I_{\text{ac max}} - I_{\text{ac min}}}{I_{\text{ac max}} - I_{\text{DC max}}},
\]

where \( I_{\text{ac max}} \) and \( I_{\text{ac min}} \) are the AC maximal and minimal modulated signal amplitudes, \( I_{\text{DC max}} \) and \( I_{\text{DC min}} \) are the maximal and minimal values of DC signal obtained from the MZI phase scan. The maximal modulation depth is a dimensionless number used to describe the relative AC modulation intensity.

2.1. Description of the MZI output

The EO coefficient tensor \( r_{ij} \) characterises the ability of a material to change its refractive index \( n \) when low frequency electric field \( E \) is applied:

\[
\left( \frac{1}{\Delta \lambda} \right) = \sum_i r_{ij} E_j.
\]

Due to Kleinman symmetry, \( r_{ij} \) can be rewritten as \( r_{ij} \) which is a 6 × 3 tensor. In a poled polymer with point group symmetry of C∞v, the effective EO coefficient can be rewritten for s polarised light as [15]

\[
r_{sd} = r_{13},
\]

and for p polarised light as

\[
r_{pd} = r_{13} \cos^2 \alpha + r_{15} \sin \alpha.
\]

Fig. 3. Typical EO measurement performed at 8° incidence angle and s polarised light: \( I_{\text{DC}}, I_{\text{AC}} \) signal experimental data, \( 2I_{\text{DC}}, I_{\text{AC}} \) signal experimental data, \( 3I_{\text{AC}} \) signal sin approximation, \( 4I_{\text{AC}} \) signal sin approximation; \( \Psi \) is AC and DC signal maxima phase difference.
where \( r_p \) and \( r_s \) are the EO coefficients, and \( \alpha \) is the angle between the sample normal and light propagation direction.

The light intensity at the MZI output can be described by the two beam interference equation:

\[
I_n = \frac{1}{2} \left[ I_s + I_p + 2 \sqrt{I_s I_p} \cos(\phi + \varphi) \right]
\]

where \( I_s \) is light intensity in the reference arm, \( I_p \) is light intensity in the sample arm without the sample, \( \varphi \) is interference phase difference (adjustable by phase shifter), \( T \) is transmission coefficient of the sample, \( \varphi \) is an additional phase difference caused by the sample.

If an AC electric field is applied to the sample the transmission \( T \) and phase \( \varphi \) are also modulated as affected by several parameters, e.g. the refractive index, light polarization, sample thickness etc., with corresponding changes in the detected output light intensity and therefore the AC signal amplitude. Some parameters, e.g. \( \psi \), thicknesses and complex refraction indices for each layer could be obtained from independent experiments. The unknown is the effective coefficient \( r_p \) of EO active layer that we would like to determine from our MZI experiment. To describe the intensity and phase of light transmitted through the sample at a certain applied voltage one can use the Abbe\'s matrix formalism. 

Fig. 4. Experimental set-up of MZI in reflection configuration for determination of a thin organic film thickness changes: helium-neon laser 632.8 nm He-Ne, half wave plate 3/2, beam splitter BS, minors \( M_1 \) and \( M_2 \), phase shifter \( PS \), sample, photodiode \( PD \), lock-in amplifier \( Amp \), computer PC.

Fig. 5. Modulation depth \( m_{max} \) as a function of modulation voltage \( U \) for a MZI in the reflection configuration. Quadratic function regression is applied: 1 modulation depth \( m_{max} \) of poled film, 2 modulation depth \( m_{max} \) of unpoled film, 3 quadratic approximation of modulation depth \( m_{max} \) of poled film, 4 quadratic approximation of modulation depth \( m_{max} \) of unpoled film.

Fig. 6. Modulation depth dependence on the incidence angle in MZI in the transmission configuration for sample 1: 1, 2 experimental data for \( s \) and \( p \) polarised light, respectively; 3, 4 numerical approximation with MatLab performed using functions based on Abbe\'s matrix formalism.

3. Results and discussion

According to our observations, for sample 1 the maximal modulation depth \( m_{max} \) decreases as the incidence angle is increased. This dependence could not be explained just by multiple internal reflection effects. To describe experimental data adequately, sample thickness modulations needed to be included in our model. Thickness change can be caused by electrostriction or piezoelectric effects. To prove the existence of these effects and evaluate the magnitude of sample thickness modulation we used the MZI method in the reflection configuration. In this case the ITO glass slide covered by a spin coated polymer thin film (~1 \( \mu \)m) was not enclosed by another slide, but a reflective 100 nm thick Al layer was deposited on the polymer. Then one of the mirrors (\( M_2 \), see Fig. 1) in our MZI set-up was replaced by the sample with the Al layer facing the incident beam (see Fig. 4). The Al layer was thicker than for sample 2 so that light would not penetrate into the sample. In this configuration, when voltage is applied to electrodes, electric field can cause sample thickness changes, thereby positioning the Al mirror surface and thus mechanically altering the optical path length in the sample arm of the MZI.

To evaluate the actual thickness change of the sample the modulation depth equation is modelled for phase modulation only due to changes in the sample arm path length. In this case the average light intensity at the MZI output, or DC signal, has a phase difference of \( \pi/2 \) with respect to the 4 kHz AC modulation of the light phase and the amplitude are modulated by the sample with the Al layer facing the incident beam. In case of \( s \) polarised light the modulation depth should be dependent only on \( r_p \). However, due to electrostriction and piezoelectric effect the sample thickness changes take place in addition to refractive index changes so that both the light phase and the amplitude are modulated causing the modulation depth decrease for greater incidence angles. The modelling is performed by refining the preliminary experimental results of a thin film and air gap thicknesses and varying the EO coefficients \( r_p \) and \( r_s \), and sample thickness alteration \( \Delta d \) due to electrostriction and piezoelectric effects.

For approximation of sample 1 experimental data we used a simple ITO-polymer-air gap-ITO layer system (Fig. 2 and Table 1) and glass as input and output media. This approach reflects interference effects caused by multiple light reflections within the glass slides and therefore theoretical lines are much smoother than experimental. Of course we could take into account glass slides as additional layers in our approximation. In that case noise-like interference fringes are superposed on the curves. The angular spacing of these fringes is below the experimental incidence angle resolution. After performing the first numerical approximations for sample 1 we found that the modulation depth is a linear combination of NLO active layer thickness and EO modulations. When the EO coefficients were calculated taking into account a thickness modulation amplitude in the range of several tens of pm, the obtained \( r_p \) to \( r_s \) ratio ~10 and \( r_s \) value close to 100 pm/V were obviously too high. Therefore, the final modelling was performed allowing only air gap and sample thickness alteration \( \Delta d \), and the ratio of NLO coefficients \( d_1 \) and \( d_2 \). Both EO and NLO coefficients characterise the material nonlinearity and are proportional to the second order polarisability \( \chi^{(2)} \), but are used to describe the nonlinearity at different interactions and conditions. The NLO coefficient ratio \( d_1/d_2 \) (nominally the same as \( r_p/r_s \)) measurements performed by the second harmonic generation Maker fringe technique on the same sample yielded a value of 1.86. This suggests that the modulation is mainly caused by some effect other than EO variations. As described above the modulations could be caused by thickness changes in the polymer layer. The air gap (Fig. 2) thickness modulations can also take place as shown previously \[18\]. Therefore, the final modelling was performed allowing only air gap and NLO active layer thickness modulations \( \Delta d \) and...
From comparison of data in Tables 1 and 2 one can see that the sample (polymer film) and air gap thicknesses are in good agreement with the preliminary experimental results. As expected, with thickness changes of air gap and NLO active layer, one can have a good approximation of modulation depth values.

The dependence of modulation depth on the incidence angle for sample 2 can be seen in Fig. 7. After measuring the dependence of modulation depth on the applied voltage we found that the dependence was linear. As thickness changes in the sample were expected to be quadratic, we consider that the effect of thickness change in this case has a small influence on the total modulation depth. Therefore, we excluded the sample thickness change effect in approximation by leaving only EO modulations. The approximation can be seen in Fig. 7. The numerical fit values can be seen in Table 3.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness</td>
<td>0.85 ± 0.05 µm</td>
</tr>
<tr>
<td>Air gap</td>
<td>5.85 ± 0.10 µm</td>
</tr>
<tr>
<td>Δl_1</td>
<td>170 ± 5 pm</td>
</tr>
<tr>
<td>Δl_2</td>
<td>76.5 ± 1.0 pm</td>
</tr>
</tbody>
</table>

Table 2. Sample 1 parameters calculated from numerical approximation results.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness</td>
<td>1.34 ± 0.05 µm</td>
</tr>
<tr>
<td>r_1</td>
<td>0.19 ± 0.02 pm/V</td>
</tr>
<tr>
<td>r_2</td>
<td>0.55 ± 0.06 pm/V</td>
</tr>
</tbody>
</table>

Table 3. Sample 2 parameters calculated from numerical approximation results.

4. Conclusions

Both EO coefficients (r_1 and r_2) of poled polymer films can be determined by applying the Abeles matrix formalism for numerical approximation of experimental MZI data at different incidence angles. However, one has to consider the sample structure. If an air gap is formed in the sample, the modulated signal in the MZI is usually generated by the air gap thickness modulations. The thickness modulations in the NLO active layer are also to be taken into account. An experimental procedure and data modelling are demonstrated for determining the EO coefficients of a poled PMMA + DMABI 10 wt% thin film. The obtained values are r_1 = 0.19 ± 0.02 pm/V and r_2 = 0.55 ± 0.06 pm/V.

Acknowledgements

This research was granted by ERDF 2.1.1.1 activity project No. 2010/0308/2DP/2.1.1.1.0/10/APIA/VIAA/051 “Development of Polymer EO Modulator Prototype Device” and Latvian National Research Program “Development of Innovative Multifunctional Materials, Signal Processing and Information Technologies for Competitive Science Intensive Products”.

References

DAUGKARTINIO VIDINIO ATSPINDŽIO IR BANDINIO STORIO Kitimo ĮTAKA POLIMERINIO SLUOKSNIO ELEKTROOPTINIŲ KOEFICIENTŲ Verčių NUSTATYMUI

E. Nitišs a, M. Rutkis a, M. Svilans b

a Latvijos universiteto Kietojo kūno fizikos institutas, Ryga, Latvija
b Rygos technikos universiteto Medžiagotyros ir taikomosios chemijos fakultetas, Ryga, Latvija

Santrauka

Naujos organinės netiesiškai optiškai aktyvios medžiagos yra naudojamos optoelektroniniuose ir fotoniuose taikymuose. Tokių medžiagų tinkamumas minėtiems taikymams gali būti vertinamas pagal jų elektrooptinius (EO) koeficientus. Mes pritaikėme Macho ir Cenderio (Mach–Zehnder, MZ) interferometrų trijos metodą plonų organinių sluoksnių EO koeficientams nustatyti. Nepaisant daugybės kitų EO koeficientų nustatymo ploniems sluoksniams optinių metodų, šį metodą pasirinkome todėl, kad jis pasižymi dideliu jautrumu fazės ir intensyvumo moduliacijoms interferometro bandinio petyje ir leidžia nepriklausomai mautoti abu plonojo sluoksnio EO koeficientus – $r_{13}$ ir $r_{33}$.

Parodėme, kad elektrostrikcija ir daugkartiniai vidiniai atspindžiai bandinyje stipriai veikia šviesos intensyvumą MZ interferometro išėjime. Atsižvelgdamas į šiuos reiškinį, skaitmeniškai naudodami Abelès matricų formalizmą, sumodeliavome EO koeficientų poveikį MZ interferometro signalo kaitai arba moduliacijos gylį esant skirtiems kritimo kampams. Pavyko parodyti, kad moduliuotas signalas MZ interferometro išėjime labai priklauso nuo bandinio sandarios ir yra stipriai lemiamas EO koeficientų. Moduliuoto signalo sandų analizei ir plonų polimerinių sluoksnių EO koeficientų nustatymui atlikome keliolika eksperimentų su PMMA ir 10 svorio % DMABI bandiniais.