Novel Poling and Electro-Optic Measurement Methods of Cladded Nonlinear-Optical Polymer Films

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ABSTRACT

We use high temperature liquid-contact poling as a method to pole efficiently cladded nonlinear optical polymer films. Poling voltage as high as 400 volts is applied to planar waveguides which have a nonlinear optical film of 1.2 μm thick. The lack of a quick method to characterize the poled cladded nonlinear optical films inspires us to devise a new electro-optic measurement method. This method can determine r_{33} and r_{13} separately because it uses light of single polarization state to probe the nonlinear optical film. The interference between the modulated light and the unmodulated light in the reflected beam is used to extract electro-optic coefficients. Theoretical analysis of the relationship between the reflected light intensity and the electro-optically modulated signal is consistent with the experimental results. Formulae to calculate electro-optic coefficients are deduced. This method uses an even simpler experimental setup than that of the widely used ellipsometric method.

Keywords: Poling, electro-optic measurement, electro-optic polymers

1. INTRODUCTION

Almost all the applications of nonlinear-optical (NLO) polymers requires one to form the polymers into some kind of a waveguide. Such waveguides usually use an NLO polymer as the core material and use other materials with lower refractive index as the top and bottom cladding layers. Therefore, poling efficiently cladded NLO polymer films and being able to measure quickly the electro-optic (EO) coefficients are very important for development of NLO polymer devices. Using electrode-contact poling to induce nonlinearity in cladded NLO films[1,2] has been studied by some researchers. However, the newly developed poling method known as high temperature liquid contact poling (HTLCP) has not yet been applied to pole cladded NLO films.

To study the poling effect of this new poling scheme, a method that can quickly and reliably measure the EO coefficient is needed. A widely used method of EO measurement of NLO polymers is an ellipsometric method[3,4]. This ellipsometric method may be not applicable to a cladded NLO polymer film because the assumption made in deducing the formula for relating the EO coefficient to the measured quantity of measurement is not necessarily applicable to a cladded NLO film owing to the multiple reflections from all the interfaces. New methods have been reported in recent years[5-8]. These methods either require special design of modulation or poling electrodes or are just an extension of the ellipsometric method and are not suitable to measure the EO coefficients of a cladded NLO polymer film. As a result, the amount of work needed to measure the EO coefficient of a cladded NLO film is almost the same as that of preparing and characterizing an EO device by interferometric means which requires the time consuming processes of polishing and coupling.

In the first part of this paper, we report the primary result of using the HTLCP method to pole efficiently cladded NLO polymer films. In the second part, we at first demonstrate the inapplicability of the ellipsometric methods to cladded NLO polymer films experimentally, and then present both a theoretical analysis and some experimental results on this new EO-measurement method.

2. HIGH TEMPERAURE LIQUID-CONTACT POLING AND ITS APPLICATION TO POLING CLADDED WAVEGUIDES

Poling is a critically important processing step in preparing nonlinear optical polymer devices. The value of the electro-optic coefficient r_{33} of an NLO-polymer film depends on the polarization density achieved after the electric-poling process. To date, two common methods of electric-field poling are contact poling and corona poling. In contact poling, a strong electric field is applied to the cladded NLO polymer film by two parallelplate electrodes. These poling electrodes cover large areas and provide a path of high lateral conductivity. Such an arrangement frequently generates a localized destructive current at certain location with pinhole defects. A single defect created during film processing may introduce a catastrophic short circuit, and thereby destroying the device. As a result, contact poling in most cases can only be performed at a field strength much lower than the dielectric strength of the NLO polymer. In corona poling, a high electric field is produced by the charge deposited on the film surface through the corona discharge process. A poling electric field close to dielectric breakdown can easily be obtained[9]. Larger poling fields activate larger nonlinearities compared with contact poling; however, surface damage is a major concern in corona poling.[10] To overcome the problems with these two methods, we have developed a high temperature liquid-contact poling method[11] that avoids the disadvantages of the other two methods and, hence, makes it possible to apply very high poling electric fields, while keeping the surface damage density low.

The NLO material used in the experiment is LD-3 and is available commercially. It is a thermally crosslinkable polymer consisting of a poly (methyl methacrylate) (PMMA) backbone and an azobenzene-sulfone chromophore. The cladding material NOA61 is a UV curable optical adhesive which is bought from Norland Products, Inc. The choice of UV curable cladding material was made because the curing process does not need heating. Any heating before poling might partially crosslink the polymer, which would result in limiting the alignment of the chromophores with the poling electric field, the induced optical nonlinearity would thus be reduced. The details of preparing LD-3 polymer waveguides is reported elsewhere[12]. Silicon is used as the substrate with gold deposited on the silicon surface to form a bottom electrode. The bottom cladding, LD-3 film, and top cladding are sequentially deposited by solution spincoating. The thickness of the bottom cladding and LD-3 polymer is measured by an Alpha-Step 200 surface profiler to be 3 μm and 1.2μm respectively. The thickness of the top cladding can be varied for different applications. The process of preparing the liquid-contact-poling cell which contains the cladded LD-3 film is the same as that for a LD-3 single layer[11]. Epoxy spacers are used to maintain a gap between the top cladding and the top electrode. The contact liquid, hexatriacontane, is a solid at room temperature and melts at 75°C. When it melts, its resistivity becomes much lower. Before raising the temperature of the sample, we place this material at the edge of the sample. When the melting point is reached, it becomes a liquid and is sucked into the gap by capillary action with no bubble formation. As a result, an electrically conductive path between the upper electrode and the polymer film is formed through the liquid layer. Most of the voltage applied to the electrodes will drop across the polymer films as long as the resistivity of the contact-liquid layer is much lower than that of the LD-3 polymer film. A high breakdown voltage of the contact liquid is necessary to insure that a high poling field can be applied. If there is any local breakdown in the polymer film, the contact liquid can still prevent a short circuit. Although the poling current might increase, it would not be significant as long as any local breakdown is limited to very small areas.

In the previous report, the samples used in the experiments only had a layer of the nonlinear optical polymer. There were no cladding layers. The poling liquid contacted directly with the top surface of the NLO polymer. Figure. 1(a) shows the configuration of a poling cell for liquid -contact poling where there is only an NLO polymer layer. A poling voltage of 300 volts can be safely applied to this cell. This high voltage drops directly across the 1.2 μm NLO film, so that the applied electric field should be 250 V/μm, which is comparable to the reported value of the corona-poling electric-field strength. For fabrication of any real device, however, a bottom cladding has to be deposited before coating with the NLO polymer. The top cladding can be coated on before or after poling. There are certain advantages placing the top cladding before poling. First, the top cladding separates NLO film from the temporary contact liquid used during the poling step, so less surface damage is expected. Secondly, the buffering effect of the cladding may allow application of even higher poling electric-field strength, which would improve the poling efficiency. Fig. 1(b) shows a poling cell of a cladded NLO film with both the bottom and top claddings.

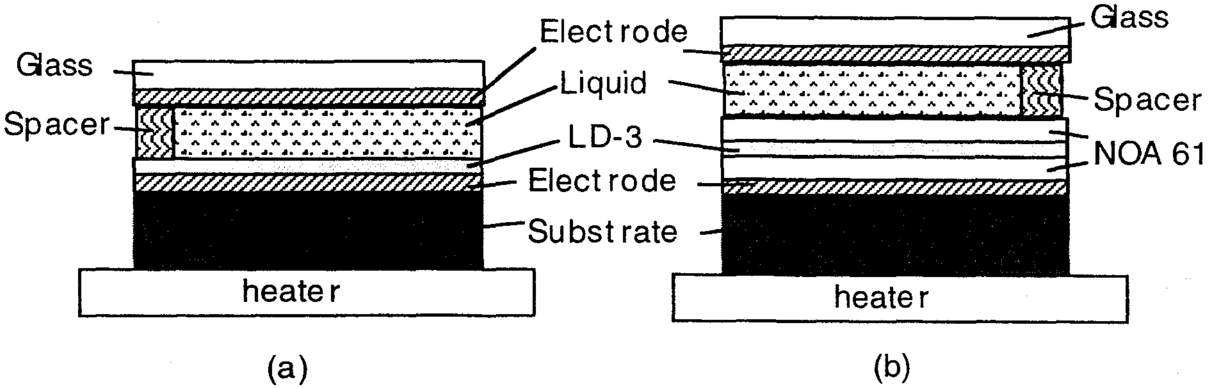


FIGURE 1 The structures of high-temperature liquid-contact poling cells. (a) A cell with only an LD-3 layer and (b)a cell with a cladded LD-3 waveguide.

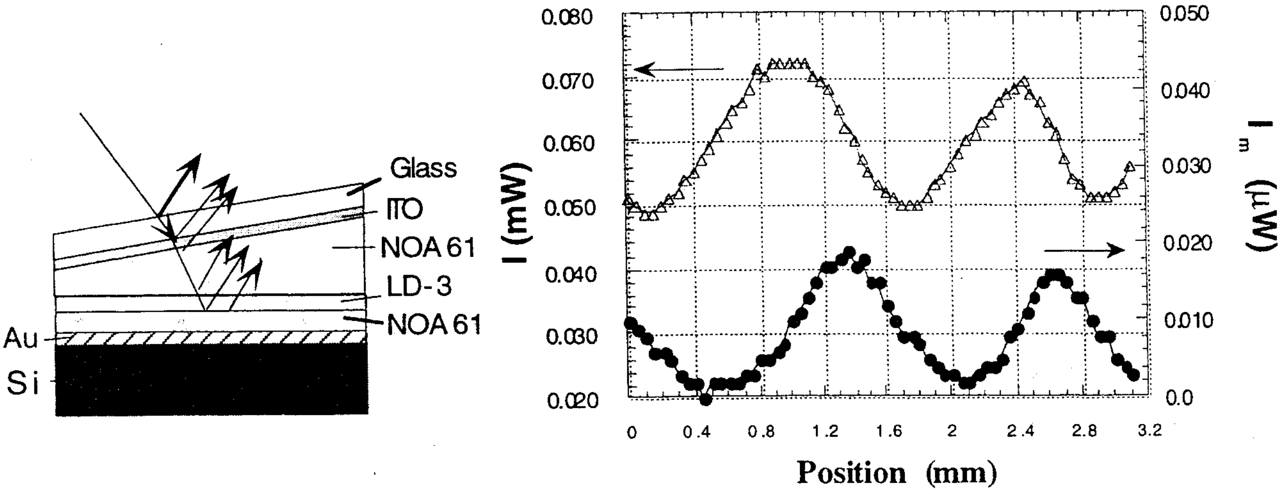
Our experimental results indeed confirm that a poling voltage higher than 300 volts can be applied to a poling cell of a cladded NLO polymer film. Poling voltages of 400 volts have been successfully used to pole several samples. Even higher poling voltages can be applied without causing a short circuit. The highest voltage tested is 500 volts. Although no short circuit occurs at this high voltage, some burn spots do appear on the film.

A high poling voltage applied to a cladded-NLO-film cell is expected to generate a high EO coefficient if the cladding layers have much lower resistivity than the core material at the poling temperature. How effective the poling process is can only be determined by measuring the EO coefficient of the poled film. The ellipsometric method is routinely used to measure the EO coefficient of a single-layer NLO film. However, this method does not give consistent results for cladded NLO waveguide films we have measured. We realize that the error caused by multilayer reflections might be too large and that it could neither be ignored nor removed.

The lack of a reliable method to measure quickly EO coefficients inspires us to search for a new way to do the measurement. It happens that a sample prepared for another purpose has a slightly tilted top electrode. Although this sample is not poled optimally (poled at 190V), it allows us to investigate the effect of the thickness variation of the top cladding on the EO measurement. Further theoretical analysis leads us to propose the following new method of EO measurement.

3. NOVEL METHOD OF MEASUREING THE ELECTRO-OPTIC COEFFICIENTS OF CLADDED WAVEGUIDES

Our calculation of the amplitudes of the reflected light from each of the different interfaces of our sample shows that error in the EO measurement of a cladded NLO film by the ellipsometric method can come from the interference of the light reflected by all the interfaces. The amplitude and phase of the reflected light are each sensitive to the thickness of each layer of the sample. We confirm this conclusion experimentally by using the sample mentioned at the end of last section. Figure 2(a) shows a schematic of the sample. The tilted top electrode is attached to the top surface of the cladded waveguide by the same material used as the cladding , which is NOA 61. The resulting sample is a waveguide, where the thickness of the top cladding layer varies with position. The incident angle of the light is set at 45 degrees in the measurement. A modulation signal of 50 V (rms) at 1kHz is applied to drive the EO response of the sample. The measured reflected light intensity I and modulated portion I_m vary periodically with position. Every period corresponds to a phase change of the optical path by 2π or 0.18 μm in thickness of the cladding ,which is calculated using n=1.56 for the cladding refractive index at 633 nm.



(a) (b)

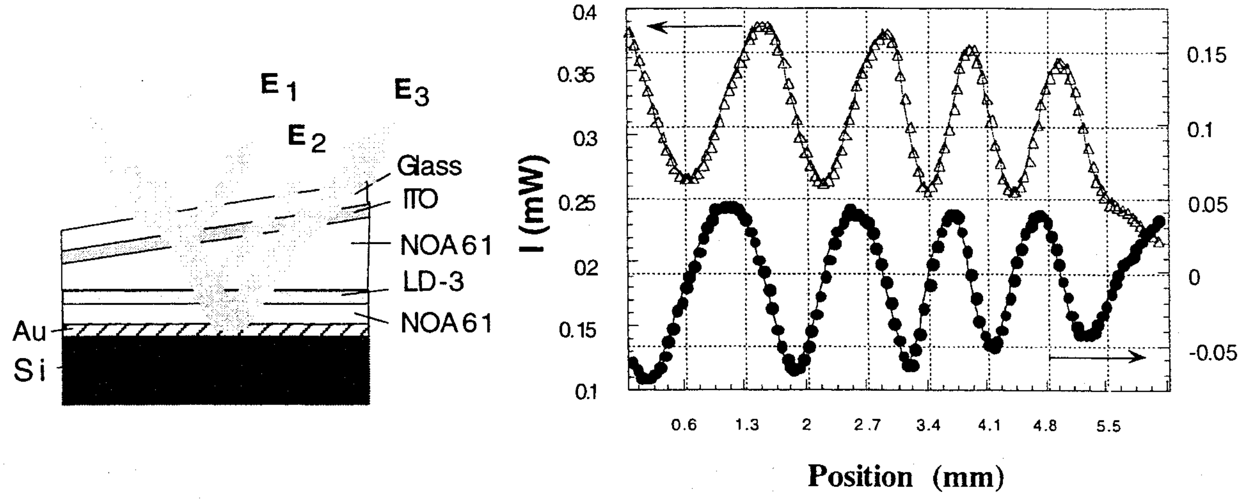
FIGURE 2. The reflected light intensity I and the modulated signal I_m both change in value periodically with increases in the top-cladding thickness. (a) A schematic of the sample with varying top-cladding thickness and (b) measured I and I_m curves

In the ellipsometric method, the change in the phase-difference between the p-wave and the s-wave owing to electro-optic modulation is determined by measuring the ratio of I/I_m. The EO coefficient r is then derived from the change in this phase difference. One important feature of the deduced formula in the references[3,4] is that the phase change is independent of the thickness of the film. We can see from Fig. 2(b) that the ratio of I/I_m is also a periodic function of the top cladding thickness as I and I_m are, so the simple formula used in the ellipsometric method is not applicable to our samples which have a cladded film. To extract EO coefficients from the two curves in Fig. 2 (b) is not an easy job because I and I_m involve the interference effect of many beams.

However, using pure *p*-polarized or *s*-polarized light can simplify the situation. The reflected light from all the interfaces can be sorted into three groups according to their phase properties. The first group is the light reflected from all the interfaces above the top cladding. The phase of this group is not dependent on the cladding or NLO film thickness. The second group only includes the light reflected from the interface between the top cladding and the NLO polymer. The phase retardation of this group is dependent on the top cladding thickness only. The third group includes all the light that passes through the NLO film. The phase retardation of this third group is a function of both the top cladding thickness and the modulation voltage, which induces a change in the refractive index of the EO polymer. The complex amplitude of reflected light can be written as the sum of the three groups

$$E = E_1 e^{i\varphi_1} + E_2 e^{i\varphi_2} + E_3 e^{i\varphi_3}, \tag{1}$$

where E_1, E_2 and E_3 denote the absolute values of the amplitudes of the electric field of the light of the three groups as shown in Fig. 3 (a), and φ_1, φ_2, and φ_3 are the corresponding phases.



(a) (b)

FIGURE 3. The reflected light intensity I and the modulated intensity I_m are functions of the top-cladding thickness owing to interference . (a) Three groups of the reflected light and (b) measured I and I_m curves.

The phase properties of the three groups of light can be expressed mathematically as

$$\varphi_1 = \text{constant}, \tag{2a}$$

$$\varphi_2 = \varphi_2(d_{cl}), \tag{2b}$$

$$\varphi_3 = \varphi_3(d_{cl}, V), \tag{2c}$$

where d_{cl} is the top cladding thickness and V is the modulation voltage. Equation (2) indicates that the reflected light intensity

$$\begin{aligned} I &= EE^* \\ &= E_1^2 + E_2^2 + E_3^2 + 2E_1E_2\cos(\varphi_2 - \varphi_1) + 2E_2E_3\cos(\varphi_3 - \varphi_2) + 2E_3E_1\cos(\varphi_3 - \varphi_1) \end{aligned} \tag{3}$$

is also a function of d_{cl} and V. The top transparent electrode, which is made of indium tin oxide (ITO), has the high refractive index of n=2.0, so the reflectivities of the interfaces between the ITO and the glass or NOA61 are large. The refractive indices of the cladding and the core are quite close, so the E_2 is relatively weak. The ratio of E_3:E_1:E_2 is on the order of 100:10:1, so that the reflected light intensity is approximately

$$I \approx E_1^2 + E_3^2 + 2E_3E_1\cos(\varphi_3 - \varphi_1). \tag{4}$$

Equation (4) gives

$$2E_3E_1 = \frac{1}{2}(I_{\max} - I_{\min}), \tag{5}$$

where $I_{\max}$ and $I_{\min}$ are the maximum and minimum of the reflected light intensity, respectively. The modulated signal is

$$I_m = \frac{dI}{d\varphi_3}\Delta\varphi_3 = -2E_3E_1\sin(\varphi_3 - \varphi_1)\Delta\varphi_3 - 2E_3E_2\sin(\varphi_3 - \varphi_2)\Delta\varphi_3. \tag{6}$$

Changes in top-cladding thickness will not affect the phase difference $(\varphi_3 - \varphi_2)$, so the second term in Eq. (6) can be subtracted out. The maximum and minimum of the modulated signal are

$$I_{m,\max} = 2E_3E_1\Delta\varphi_3 - 2E_3E_2\sin(\varphi_{3\max} - \varphi_2)\Delta\varphi_3, \tag{7}$$

$$I_{m,\min} = -2E_3E_1\Delta\varphi_3 - 2E_3E_2\sin(\varphi_{3\max} - \varphi_2)\Delta\varphi_3. \tag{8}$$

Subtracting Eq. (8) from Eq. (7) gives

$$2E_3E_1\Delta\varphi = \frac{1}{2}(I_{m,\max} - I_{m,\min}). \tag{9}$$

Equation (5) and (9) give

$$\Delta\varphi = |\Delta\varphi_3| = \frac{I_{m,\max} - I_{m,\min}}{I_{\max} - I_{\min}} \tag{10}$$

Using Eq. (10), we can calculate the phase change induced by the drive voltage.

A schematic of the experiment setup is shown in Fig. 4. We use p-polarized light with an incident angle of 45° and a modulation voltage of 50 V (rms). A translation stage is used to move the sample. The measured variation of the light intensity I and EO-modulated signal I_m with position is shown in Fig. 3(b). The maxima and minima of these curves are used to calculate the phase modulation $\Delta\varphi$ according to Eq. (10) and the results are plotted in Fig. 5. The scatter of the data points is less than ±10%, so this method gives much more reliable results than the ellipsometric method.

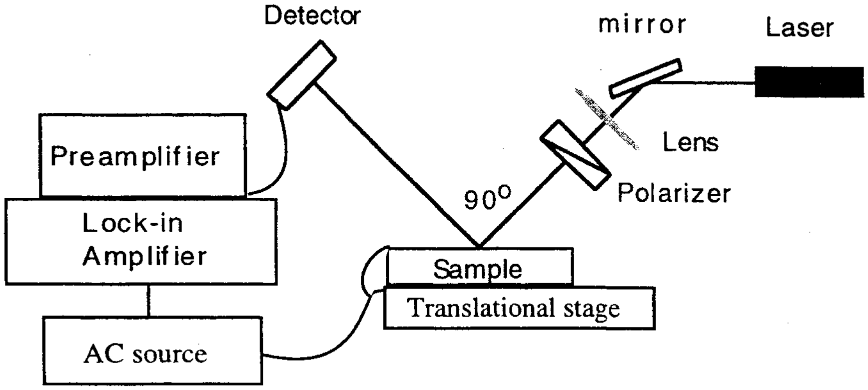


FIGURE 4. Schematic of the experiment setup.

The effective EO coefficient r_{eff} can be calculated from the phase modulation by

$$r_{eff} = \frac{\lambda d\cos\alpha}{\pi n^3 d_{NLO} V}\Delta\varphi, \tag{11}$$

where α is the angle of incidence measured in the NLO polymer, d_{NLO} is the effective thickness of the NLO polymer, and d is the distance between the electrodes, which varies with position. One can see that $\Delta\varphi$ is inversely proportional to the distance between the two electrodes for a uniformly poled film, i.e. $\Delta\varphi$ decreases when d increases. This trend is clear in Fig. 5 . When d is much larger than the wavelength of light in the cladding, r_{eff} can be estimated by the average value of d. The value of r_{eff} is related to r_{33} and r_{13} by

$$r_{eff} = r_{33} \sin^2 \alpha + r_{13} \cos^2 \alpha \tag{12}$$

for p-wave, and

$$r_{eff} = r_{13} \tag{13}$$

for s-wave.

Using Eqs. (10) and (11) we should be able to calculate r_{eff} if the average electrode-to-electrode distance is known. From the data in Fig. 5 we estimate that r_{33}=10.7 pm/V at 633nm assuming $r_{33}=3r_{13}$ and using an average value of d being 8 μm. The 8 μm electrode-to-electrode distance is estimated from the sample fabrication process. More accurate result can be obtained by directly measuring d. Considering the poling voltage of 190V, the r_{33} value is in a reasonable range compared with previously reported data.

However, the assumption that $r_{33}=3r_{13}$ is not necessary for this method according to Eqs. (12) and (13). The values of r_{33} and r_{13} can be determined by applying sequentially a p-wave and a s-wave to probe the EO response. We find the ratio of r_{33} to r_{13} is 3.25, which is larger than but close to 3.0.

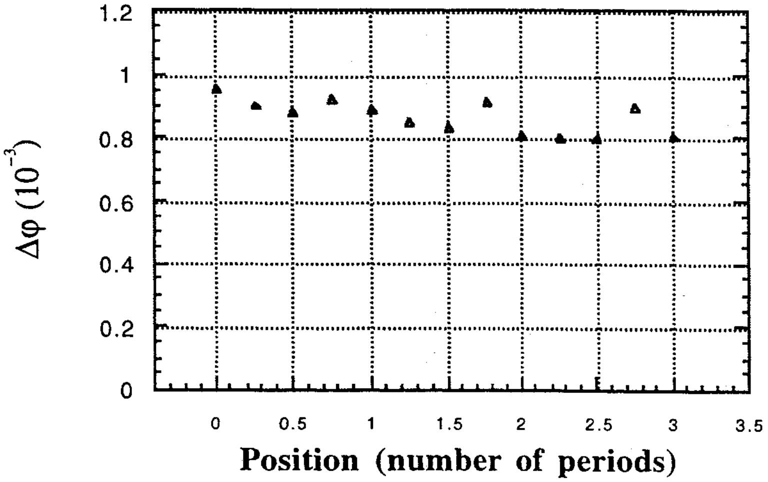


FIGURE 5. Induced phase change s deduced from Figure 3.

4. DISCUSSION

Equations (3) and (6) predict that the I and I_m curves be 90° out of phase with each other, which is consistent with the experimental observation and is clearly shown in Fig. 3. These equations also indicate that the electric field E_2 is an error source in our measuremnt. Its influence on I comes from the 4th term in Eq. (3), which is on the order of E_2/E_3 times $I_{max}-I_{min}$. It affects strongly the curve shape of I_m and is responsible for the asymmetry of the curve with respect to $I_m = 0$. The magnitude of asymmetry caused by E_2 is relatively large and is on the order of E_2/E_1 times $I_{m,max}-I_{m,min}$ (see Eqs. (6)), but the effect of E_2 on the measurement of $I_{m,max}-I_{m,min}$ can be eliminated as shown by Eqs. (7)-(9). So the total error caused by $E2$ in our experiment is proportional to E_2/E_3, which is typically on the order of 1%. The magnitude of E_2 is determined by the index difference between the cladding and the core materials, hence this error can be furthur reduced by reducing this difference.

One important advantage of our method is that the values of r_{33} and r_{13} can be determined separately without knowing the ratio of r_{33}/r_{13}. In the ellipsometric method, a ratio of $r_{33}/r_{13}=3$ is assumed. This assumption is only valid at a low poling electric-field strength. At a high poling electric-field strength, this ratio is larger than 3. This is true for our sample. The ellipsometric EO measurement method can not determine the values of r_{33} and r_{13} if the ratio of r_{33} to r_{13} is not available because it can only measure the difference between r_{33} and r_{13}.

The process to attach the top electrode to the waveguide by UV curable adhesive is simple. It is even simpler than any electrode-deposition method for a trained person. Therefore, our method may allow fast and reliable characterization of NLO polymer films. The measurement setup does not need a phase compensator, so it is also simpler to use than that of the ellipsometric method.

So far we have presented the primary theoretical analysis and experimental results of a new EO measurement method, which is applicable to cladded NLO films. More systematic studies of this method are in progress. Experimental comparison of the result of this method with that of other reliable methods is planned.

5. CONCLUSION

Using high-temperature liquid-contact poling, a poling voltage as high as 400 volts can be applied to a cladded NLO film. The lack of a quick method to characterize the cladded NLO films has inspired us to devise a new EO measurement method. This method makes use of the interference between the modulated light and the unmodulated light in the reflected beam used to probe the electro-optic response of the material. The variation of top cladding thickness required by this method can be achieved simply by using UV-curable optical adhesive to attach a tilted top electrode over the waveguide top cladding layer. Theoretical analysis and experimental results show this method to be promising . Further development of this method is in progress.

6. ACKNOWLEDGE

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