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Spurious electro-optic coefficients inferred from modulation ellipsometry measurements in the presence of an air cavity

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ABSTRACT

This paper describes how thin air gaps in multilayer polymer thin film structures can lead to unexpectedly large signals in modulation ellipsometry experiments, which can then be misinterpreted as the electro-optic effect. The contributions from the electro-optic effect and polarisation on reflection from the air cavity are indistinguishable and the reflection contribution can be on the order of 100 times that of the electro-optic effect. Caution must thus be exercised in any attempt to measure electro-optic coefficients with modulation ellipsometry in the presence of air gaps, to avoid spuriously high results. Thin film multilayer structures containing air gaps may be suitable for some of the same applications as electro-optic reflectance modulators.

1. Introduction

For the last two decades, modulation ellipsometry has been the experimental measurement of choice for determining the electro-optic effect in poled polymer thin films. This technique was initially promoted as a simpler and quicker method of measuring the r_{33} component of the electro-optic tensor compared to other techniques available at the time [1–3]. Within the following few years several optical effects having a significant contribution to the measured ellipsometric values, most notably the effect of multiple reflections between interfaces, were described which complicate both experiment and analysis [4–7].

In this paper I examine another optical effect, that which air cavities can have on the results inferred from modulation ellipsometry experiments. Experimental results in both reflection and transmission configuration are described which show an anomalously large intensity modulation at the detector and implicate as the cause a thin air gap introduced by the use of monolithic block electrodes. Modulation of the air gap thickness as a potential explanation is examined in detail, through calculations in which the polymer refractive index and the thickness of the polymer and air layers are allowed to vary with applied electric field. The theoretical results potentially explain the experimental observations, and a final case of a blistered film with an evaporated gold electrode is examined.

2. Experimental

Modulation ellipsometry experiments were performed in both reflection and transmission configurations on polymer host-guest films comprised of Bayer APEC DP1-9389/5 amorphous polycarbonate (APC) [8] and the simplest pyridine-donor member of a family of zwitterionic right-hand side merocyanine chromophores [9], commonly designated “PYR3” [10]. The molecular structure of PYR3 is shown in Fig. 1. Films were spin-processed from 1–,1–, 2-trichloroethane solutions on to ITO-coated glass substrates with target thickness 2 µm. Actual film thicknesses and refractive indices were measured with a Metricon 2010 prism coupler at a wavelength of 1300 nm, revealing a typical film thickness of 2.1 µm and a refractive index n=1.558. Metricon measurements also provided the refractive index of the glass substrate n=1.506. The complex refractive index and thickness of the ITO layer were obtained by independent ellipsometry measurements and, at $n = (0.980, 0.12)$ and 15 nm, fell within the range observed in other studies [11–13].

Experimental parameters common to both reflection and transmission measurements were the 1314 nm wavelength of the diode laser source, the 45° external angle of incidence and the host-guest thin films. Typically, modulation ellipsometry measurements are performed at wavelengths in the telecommunications bands centred at 1300 and 1550 nm. The choice of a laser wavelength within the 1300 nm band was made because the absorption of the ITO layer is known to be lower at this wavelength, affecting the modulation ellipsometry experiment to a much lesser degree [11,12]. A Thorlabs DET 10c high-speed InGaAs photo detector was used to measure the light reflected/transmitted from the sample and the modulated light component was measured with a Stanford Research Systems SR830 lock-in amplifier at the reference frequency. The electrical modulation across the sample

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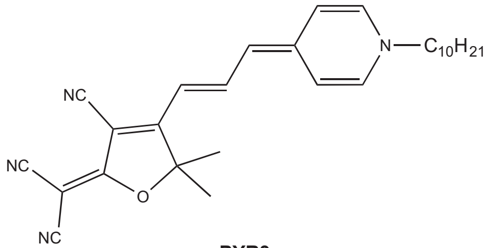

PYR3

Fig. 1. The molecular structure of the pyridine 3-π (PYR3) chromophore [9,10]. The $C_{10}H_{21}$ alkyl group is attached to the pyridine ring to improve chromophore solubility.

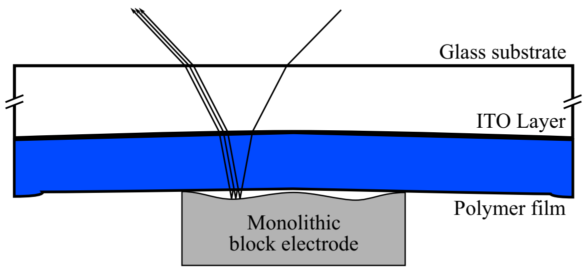

Fig. 2. Schematic of the experimental configuration with the monolithic block electrode. The electro-optic effect contributes a modulated birefringence signal on passage through the polymer film while multiple reflections within the air cavity might be reasonably expected to only introduce a static modification of the reflectance signal.

provided the lock-in reference signal and was typically a 6.6 V peak amplitude sinusoidal waveform at a frequency of 1 kHz.

The experimental parameters specific to each measurement configuration are as follows.

2.1. Reflection configuration

A schematic of the reflection configuration is shown in Fig. 2. Instead of the more typical evaporated gold electrode, a detachable monolithic block of gold-coated stainless steel, of dimensions 10 × 10 × 1.5 mm, was used as the rear electrode. This was strongly motivated by materials breakdown issues encountered with the APC host prior to, and particularly during, the contact poling process. These problems were predominantly short-circuits between evaporated electrode and ITO directly after electrode deposition, severe blistering/bubbling of the film under the electrode during the heating to the poling temperature of ~180 °C and catastrophic irreversible short-circuits on the application of electric field during the poling cycle. The block electrode alleviated all of these problems, with the additional advantage that it could be easily reseated in event of a short-circuit and the film would not blister underneath the block electrode.

Despite these advantages, the block electrode introduced a thin air gap between the block and the film due to curvature of both the block electrode and the glass substrate. Both substrate and block were determined to have curvatures of 0.2–1 µm over the 10×10 mm area of contact. One effect of this air gap was readily observable — Newton's rings interference fringes could easily be seen when the electrode was viewed through the glass side of the multilayer structure. At the time experiments were performed in this configuration, it was reasoned that any optical effects from a passive air cavity would be independent of the modulating electric field and contribute only a static factor to the modulated intensity.

High r_{33} values, on the order 100–200 pm/V, for PYR3 and other chromophores measured using the block electrode in reflection configuration have been previously reported in the literature [14–17]. Typical r_{33} values inferred from experiments performed in this configuration on a poled sample which was measured and stored at room temperature are shown in Fig. 3. The sample contained 5 wt% chromophore in APC and was contact poled at 175 °C, where the

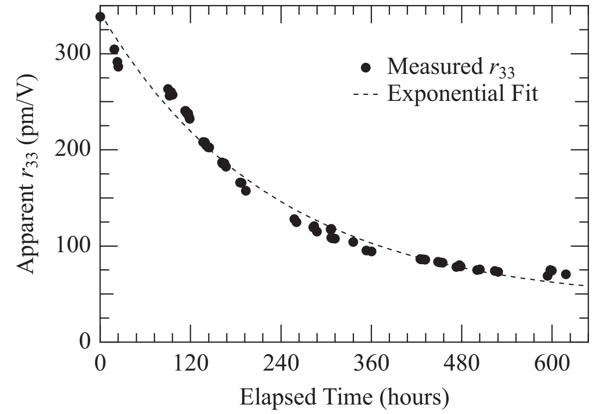

Fig. 3. The experimental electro-optic coefficient r_{33} measured in reflection configuration using the block electrode, as a function of time elapsed after contact poling for a sample stored and measured at room temperature (solid circles). The data exhibited the high r_{33} associated with the use of the block electrode and followed a simple exponential decay (dashed curve). See the text for more detail.

APC T_g = 218 °C [8]. A fit to a simple exponential decay was performed, the dashed curve shown in Fig. 3, yielding reasonable agreement with the r_{33} data and decay constant τ = 230 h. Previous studies of chromophore orientational relaxation in APC with a T_g ~ 150 °C [18–21] show stretched exponential decays with average decay constants $\langle\tau\rangle$ on the order of 1000's of hours at room temperature, decreasing to 100's of hours or less only at elevated temperatures of (80–100 °C (within 70–50 °C of T_g). A stretched exponential fit applied to the data of Fig. 3 produced a poorer fit around t=0 h and $\langle\tau\rangle$ still on the order of 200 h. That the r_{33} decay seen in Fig. 3 is single exponential in character implies that only one decay process is dominant, in contrast to a stretched exponential decay which is conventionally interpreted to imply a distribution of decay processes [18,19]. The expected r_{33} under these experimental conditions should be on the order of 4 ± 1 pm/V [9,10] rather than the 300 pm/V observed. The latter feature, in particular, bore further investigation.

Further investigation produced several empirical observations. The phenomenon: (i) produced a modulated signal at the detector in a modulation ellipsometry experiment — it was either a modulated birefringence or a modulated reflectance, (ii) was strictly related to the poled state — it was not observed in unpoled materials and showed a decay with time at room temperature broadly consistent with a relaxation of the poled state; (iii) scaled with the guest molecules — with their first hyperpolarisability and/or dipole moment, and with their number density; (iv) was strictly related to the application of an electric field — it was not observed when the applied electric field was removed in the modulation ellipsometry experiment; (v) showed a phase relationship with the driving field which was either in-phase (expected) or out-of-phase (unexpected) with the out-of-phase signal larger in magnitude; (vi) was observed at much reduced level in poled host-only (no guest chromophore) thin films; and (vii) was observed only when a monolithic top electrode was used to perform the experiment.

Observations (i)–(iv) were consistent with the electro-optic effect from a nonlinear optical host-guest polymer, but (v)–(vii) were difficult to explain solely in terms of an electro-optic effect contributed by the guest chromophore. In particular, for (v) the experimentally measured intensity modulation often exhibited an inverted phase relationship with applied voltage: out-of-phase at the A point and in-phase at the B point of the experimental compensation curve — the relationship is expected to be in-phase at the A point and out-of-phase at the B point [2,3,5,6]. There was no simple explanation for this phase inversion nor for observation (vii), that the high values were observed only when a block electrode is used. And yet, the first four observations were consistent with expectations.