Refractive index control in bicomponent polymer films for integrated thermo-optical applications

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1 Introduction
The thermo-optical effect is present in transparent materials, including organic thin films, semiconductors, and dielectric bulks, and has been used for integrated optical devices in the microelectronics industry. Particularly, the effect is characterized by the thermo-optical coefficient (TOC), which is related to refractive index behavior when temperature is modified.

From the Lorentz-Lorenz expression, the Prod’homme relation can be obtained as:

$$TOC = \frac{dn}{dT} = \frac{(n^2 - 1)(n^2 + 2)}{6n} (\Phi - \beta),$$

where $T$ is the temperature, $n$ is the refractive index, and $\Phi$ is the electronic polarizability. Already, the volumetric expansion coefficient ($\beta$) is defined as:

$$\beta = -\frac{1}{\rho} \frac{d\rho}{dT},$$

where $\rho$ is the material density.

Due to its affinity to silicon technology, silica has been used as a material of choice in integrated thermo-optical devices. However, those devices present high fabrication costs, as well as high electrical consumption during operation. Furthermore, due to its low thermo-optic coefficient, the efficiency of refractive index modulation in silica is more than 10 times lower than that for polymers.

In this context, pure polymers, polymeric composites, and hybrid organic/inorganic compounds have been studied as alternative materials to silica-based devices. Among these materials, polymer composites have more flexibility in terms of refractive index, which is achieved by adjustment of their composition. This advantage becomes interesting in stringent applications that require a specific refractive index value.

Abstract. Optical properties of transparent polymer thin films, produced by spin-coating on silicon and constituted of polycarbonate (PC), poly(methyl methacrylate) (PMMA), and PC/PMMA, were investigated with regard to integrated thermo-optical (TO) device applications. Refractive index dependences on wavelength, temperature, and film composition were measured by spectroscopic ellipsometry with a dedicated autocontrolled heater setup, in the ranges of 400 to 800 nm, 25 to 85 °C and 0 to 100 wt % PC, respectively, with determination of Cauchy and Lorentz-Lorenz parameters. Within these intervals, thermomechanical compatibility and pronounced index contrast of around 0.12 between PC and PMMA, as well as their TO coefficients one order of magnitude higher than that of silica, allow convenient tailoring for specific TO requirements. In addition, wide-range fine-tuning of refractive index variation is found to be facilitated by the weak dependence of isothermal dispersion curves and TO coefficients on film composition.

Subject terms: poly(methyl methacrylate); polycarbonate; polymer; ellipsometry; thermo-optic.

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of the prepared films in the 25 to 85 °C temperature range will be presented.

2 Experiment

Films of PC/PMMA (PC from Bayer and PMMA from Aldrich) in concentrations of 20, 40, 50, and 80 wt % of PC, as well as the PC and PMMA pure polymers, were prepared via solution blending at room temperature, using tetrahydrofuran (THF) as solvent. The polymer concentration was 4 wt % in solvent, and the solutions were filtered through a 0.2-μm polytetrafluoroethylene (PTFE) micropore membrane. The solutions were used to prepare thin films on polished silicon substrates (25 mm × 25 mm × 0.5 mm) by the spin-coating process under saturated THF atmosphere. After deposition, the films were dried for complete removal of the solvent.

For measurement comparisons, all films were prepared with physical thicknesses between 300 and 600 nm. This control was achieved by adjusting individually the spinner speed (2500 to 3000 rpm), for each film deposited, and confirmed by ex situ Ambios XP2 mechanical profilometer measurements.

To investigate sample thermo-optic response at different temperatures, a controlled heater device (temperature fluctuation of ±1 °C) was built (see Fig. 1) and integrated into a SOPRA GES-SE spectroscopic ellipsometer, allowing in situ measurements. The ellipsometer uses one rotating polarizer, one analysis polarizer (fixed), and the Hadamard method14 to analyze the output polarization state of light and extract two components, \( \sigma \) and \( \tau \), for each wavelength (\( \lambda \)).

### Table 1 Obtained Cauchy coefficients (A, B, and C) of pure polymer solutions and PC/PMMA at different temperatures.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>PMMA A</th>
<th>B (×10(^{-3}))</th>
<th>C (×10(^{-4}))</th>
<th>PC 40 wt % A</th>
<th>B (×10(^{-3}))</th>
<th>C (×10(^{-4}))</th>
<th>PC 80 wt % A</th>
<th>B (×10(^{-3}))</th>
<th>C (×10(^{-4}))</th>
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</thead>
<tbody>
<tr>
<td>25</td>
<td>1.479</td>
<td>5.48</td>
<td>-1.72</td>
<td>1.542</td>
<td>2.21</td>
<td>0.49</td>
<td>1.585</td>
<td>6.59</td>
<td>3.40</td>
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<tr>
<td>40</td>
<td>1.477</td>
<td>5.56</td>
<td>-1.76</td>
<td>1.543</td>
<td>0.22</td>
<td>0.75</td>
<td>1.583</td>
<td>6.29</td>
<td>3.78</td>
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<tr>
<td>55</td>
<td>1.474</td>
<td>5.89</td>
<td>-2.23</td>
<td>1.544</td>
<td>-1.14</td>
<td>0.92</td>
<td>1.581</td>
<td>5.91</td>
<td>4.27</td>
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<tr>
<td>70</td>
<td>1.472</td>
<td>6.04</td>
<td>-2.43</td>
<td>1.543</td>
<td>-1.75</td>
<td>0.99</td>
<td>1.579</td>
<td>5.66</td>
<td>4.58</td>
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<tr>
<td>85</td>
<td>1.469</td>
<td>6.25</td>
<td>-2.71</td>
<td>1.541</td>
<td>-1.93</td>
<td>1.02</td>
<td>1.578</td>
<td>5.48</td>
<td>4.82</td>
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<table>
<thead>
<tr>
<th>T (°C)</th>
<th>PC 20 wt % A</th>
<th>B (×10(^{-4}))</th>
<th>C (×10(^{-4}))</th>
<th>PC 50 wt % A</th>
<th>B (×10(^{-4}))</th>
<th>C (×10(^{-4}))</th>
<th>PC A</th>
<th>B (×10(^{-3}))</th>
<th>C (×10(^{-4}))</th>
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<tr>
<td>25</td>
<td>1.518</td>
<td>8.34</td>
<td>6.16</td>
<td>1.576</td>
<td>-5.05</td>
<td>1.68</td>
<td>1.597</td>
<td>3.96</td>
<td>8.57</td>
</tr>
<tr>
<td>40</td>
<td>1.517</td>
<td>5.47</td>
<td>6.49</td>
<td>1.574</td>
<td>-5.06</td>
<td>1.68</td>
<td>1.592</td>
<td>4.42</td>
<td>7.91</td>
</tr>
<tr>
<td>55</td>
<td>1.515</td>
<td>4.04</td>
<td>6.64</td>
<td>1.571</td>
<td>-4.54</td>
<td>1.61</td>
<td>1.590</td>
<td>4.31</td>
<td>7.99</td>
</tr>
<tr>
<td>70</td>
<td>1.513</td>
<td>3.66</td>
<td>6.67</td>
<td>1.569</td>
<td>-4.50</td>
<td>1.60</td>
<td>1.588</td>
<td>4.20</td>
<td>8.02</td>
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<tr>
<td>85</td>
<td>1.511</td>
<td>6.55</td>
<td>6.27</td>
<td>1.567</td>
<td>-4.11</td>
<td>1.54</td>
<td>1.585</td>
<td>4.52</td>
<td>7.53</td>
</tr>
</tbody>
</table>
where \( A, B, \) and \( C \) are constants. As a result, film physical thicknesses \( h \) and dispersion curves are obtained.

All measurements were performed using a light beam at an incident angle \( \phi \) of 75 deg, in the wavelength range of 400 to 800 nm. To avoid phase transitions in the films, the measurements were performed at temperatures of 25, 40, 55, 70, and 85 °C, which are lower than the glass transition temperatures of PC and PMMA (both higher than 100 °C). Furthermore, to avoid shifts in the refractive index values caused by film water adsorption, room relative humidity was controlled at levels of 40 to 50%.

### 3 Results and Discussion

A total of nine measurements were performed with the spectroscopic ellipsometer for each sample, taken during a down-up-down temperature cycle. From these measurements, film physical thicknesses were obtained and dispersion curves calculated using the Cauchy coefficients (see Table 1).

The dispersion curves obtained for PC, PMMA, and PC/PMMA at temperature 25 °C are presented in Fig. 2(a). As can be seen in the figure, the shape of the dispersion curve is not significantly modified by film composition. However, a great dislocation of the dispersion curves values is observed, around 0.12 from PMMA to PC at wavelength 633 nm. By comparison, when the temperature is modified, the curve shapes remain almost unchanged, and the dislocation observed is less significant than that caused by composition change, as shown in Fig. 2(b) for the PC 40 wt.% film.

![Fig. 2](image_url)

**Fig. 2** (a) Dispersion curves at 25 °C for pure polymers and PC/PMMA films, and (b) dispersion curves of PC 40 wt.% film with PMMA for different temperatures. All dispersion curves were obtained by spectroscopic ellipsometry.

![Fig. 3](image_url)

**Fig. 3** Refractive index and physical thickness variation with standard deviation versus temperature for a pure PC film.

\[
n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4},
\]

where \( A, B, \) and \( C \) are constants. As a result, film physical thicknesses \( h \) and dispersion curves are obtained.

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An interesting result is observed when the physical thickness and refractive index for a single wavelength are plotted versus temperature, as shown in Fig. 3 for the PC 80 wt % film. In all samples measured, behavior of physical thickness and refractive index was linear in the temperature range between 25 and 85 °C.

This behavior is expected, since no phase transitions are
observed in this temperature interval. Therefore, it is possible to write the Lorentz-Lorenz factor \( f_{LL} \) as a linear function of temperature:

\[
f_{LL} = \frac{n^2 + 2}{n^2 - 1} = aT + b,
\]

where \( a \) and \( b \) are constants.

The calculated \( f_{LL} \) and refractive index values for PC 50 wt % film at different temperatures are shown in Fig. 4.

Furthermore, since \( aT+b \) in this temperature interval, from Eqs (1) and (6), the volumetric expansion coefficient can be obtained from:

\[
\beta = \frac{a}{b}. 
\]

For this result, in the application of Eq. (1) to polymers, for which the contribution of the thermal expansion to refractive index variation is much higher than that of the electrical polarizability, i.e., \( \Phi \ll \beta, \Phi \) was neglected.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( h ) (( \pm 5 \times 10^{-4} )) [( \mu \text{m} )]</th>
<th>( n ) (( \pm 4 \times 10^{-4} )) (25 °C)</th>
<th>TOC (( \times 10^{-4} )) (K(^{-1}))</th>
<th>( \beta ) (( \times 10^{-4} )) (K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC</td>
<td>0.4167</td>
<td>1.6118</td>
<td>-1.72</td>
<td>2.43</td>
</tr>
<tr>
<td>PC 80 wt %</td>
<td>0.6601</td>
<td>1.6031</td>
<td>-1.47</td>
<td>1.99</td>
</tr>
<tr>
<td>PC 50 wt %</td>
<td>0.3909</td>
<td>1.5738</td>
<td>-1.11</td>
<td>1.77</td>
</tr>
<tr>
<td>PC 40 wt %</td>
<td>0.3653</td>
<td>1.5508</td>
<td>-1.25</td>
<td>2.02</td>
</tr>
<tr>
<td>PC 20 wt %</td>
<td>0.4313</td>
<td>1.5239</td>
<td>-1.31</td>
<td>2.18</td>
</tr>
<tr>
<td>PMMA</td>
<td>0.4954</td>
<td>1.4916</td>
<td>-1.41</td>
<td>2.48</td>
</tr>
</tbody>
</table>

Fig. 4 Refractive index and \( f_{LL} \) with standard deviation versus temperature for a PC 50 wt.% film.

Fig. 5 (a) Refractive index isothermal curves as functions of PC concentration, and (b) refractive index variation as function of temperature for PC/PMMA and pure polymers (both at \( \lambda = 633 \) nm).

Taking the slope of \( f_{LL} \) curves and using Eqs. (6) and (7), the expansion coefficients from PC, PMMA, and PC/PMMA films are calculated. Table 2 shows the values obtained for \( \beta \) as well as the refractive index values, film physical thicknesses, and TOCs (\( \lambda = 633 \) nm and 25 °C).

For this result, in the application of Eq. (1) to polymers, for which the contribution of the thermal expansion to refractive index variation is much higher than that of the electrical polarizability, i.e., \( \Phi \ll \beta, \Phi \) was neglected.

### 4 Conclusion

In this paper, fabrication and optical characterization of PC/PMMA films were proposed, as polymeric thermo-optical active film materials, with the benefit of refractive index tunability. The films were fabricated by spin-coating on sili-
con substrates under saturated solvent atmosphere, using rotation speeds that kept physical thicknesses between 300 and 600 nm. In situ spectroscopic ellipsometry measurements were performed with a dedicated autocontrolled heater, during heating cycles and at several temperatures (25, 40, 55, 70, and 80 °C). In this range of temperatures, no phase transitions could be observed in the composites, as expected, and refractive index dispersion curves, as well as Lorentz-Lorenz factors, are linear functions of temperature.

For each PC/PMMA film composition (20, 40, 50, or 80 wt %), resulting film physical thicknesses and Cauchy dispersion coefficients were presented that allow determination of refractive indices and thermo-optical coefficient (TOC) values under a variety of wavelength and temperature ranges. Since the shape of the isothermal dispersion curves and TOC values remain almost unchanged with film composition, even with a pronounced shift of up to 0.12 in refractive index, wide-range fine-tuning of refractive index variation becomes much facilitated for a specific application.

Therefore, transparent PC/PMMA polymer, with TOC values one order of magnitude higher than that of silica, seem to be a viable alternative to this traditional material for integrated TO on Si chip devices that operate within the range of this study, with additional control of refractive index and its variation in a wide temperature and spectral range.

Acknowledgments

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Flavio Horowitz received a PhD in optical sciences from the University of Arizona in 1983, and did postdoctoral work in the Optical and Semiconductor Devices Section, Imperial College, UK, in 1993. Presently, he is a professor of Physics at UFRGS in Porto Alegre and a Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) research leader of the Laser and Film Optics Group. His research activities include seminal contributions in the areas of structure-induced birefringence in thin films, optical properties of materials, and process interferometric monitoring, with application to the first birefringent film retarder at normal light incidence, a tunable visibility device for Smart Interferometry, pioneer development of optopinography and optical monitoring of dip coating, innovative methods for noncontact laser viscometry (patented), poling optical polarimetry, and direct measurement of the near-surface refractive index in inhomogeneous films, also in real time (patented). His present interests include monitored manufacturing of optical coatings, nanocomposite films, superhydrofobicity, and characterization of optical materials with regard to optical devices.