



Determining the out-of-plane thermal expansion coefficient by analyzing the temperature dependence of thin-film interference fringes

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Abstract: We analyze a new method for determining the out-of-plane coefficient of thermal expansion for thin films of transparent materials. The method is based on the measurement of interference peaks recorded in transmission spectra as a function of sample temperature. The locations of interference peaks depend on the optical path. We show how a consideration of Lorentz-Lorenz equation, in addition to the transmission peak equation, can separate the different contributions of index and physical pathlength to the optical path. The analysis is generalized to include the effects of uniaxial material properties (such as anisotropic linear thermal expansion and birefringence). By applying this method of analysis to recent data, we demonstrate the importance of including the effect of the thermo-optic coefficient in interpreting observed data.

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1. Introduction

Polyimides are of interest in optical, photonic, and electronic applications because they can be lightweight, resilient, and have high optical transparency. They often have mechanical toughness, flexibility, good dielectric properties and a high thermal stability. For optical and photonic applications, the coefficients of thermal expansion (CTE) and the thermo-optic coefficients (dn/dT) are of interest. These material properties have an important influence on the response of an optical device to temperature changes.

Polyimide films, synthesized in the laboratory and prepared using the doctor-blade or spin-coating techniques on a substrate, often possess some molecular order that can influence their optical and mechanical properties. X-Ray and spectroscopic evidence show that although these films are amorphous, the polyimide chains are preferentially aligned in the film plane, and the more rigid aromatic moieties are preferentially aligned parallel to the film surface. [1] The optical and thermal expansion properties of such amorphous polyimide films are typically uniaxial, with the unique axis perpendicular to the film surface.

Measurements of the in-plane coefficient of thermal expansion, $CTE_x = CTE_y \equiv CTE_{\parallel}$, is straightforward with a commercial thermomechanical analyzer. This has been reported for a large number of polyimides. In contrast, there are few measurements of the out-of-plane (or thickness-direction) thermal expansion, $CTE_z \equiv CTE_{\perp}$. This is a difficult measurement because the changes in thickness with temperature are quite small. For example, a relatively large CTE_{\perp} , on the order of 200 ppm/°C, gives a thickness change of only 2 nm/°C in a 10 micron thick film.

In a series of recent papers, measurements of CTE_{\perp} are reported for a number of polyimide films, approximately 10 microns thick, based on the temperature dependence of infrared interference fringes measured in thin-film transmission spectra [2–4]. Having recently published an analysis of the interference fringe spectra of poly(methyl-methacrylate) (PMMA) film, where we carefully examined the sources of experimental uncertainty in such measurements [5, 6], we read these recent papers with interest. Based on our experience with interference fringe spectroscopy, combined with insights gleaned from the study of polyimides for optical applications [7], we

offer an alternative analysis of the relationship between temperature-dependent fringe spectra and CTE_{\perp} . In particular, we consider the implications of the Lorentz-Lorenz equation [8, 9], which expresses the thermo-optic coefficient in terms of the volume coefficient of thermal expansion. Temperature-dependent fringe data provide information on the temperature dependence of the optical path nd , the product of refractive index n and physical pathlength d , but not on the individual contributions from dn/dT or the CTE . The Lorentz-Lorenz equation, however, provides an independent relationship between dn/dT and the volume coefficient of thermal expansion. That extra information can be used to separate the two contributions to $d(nd)/dT$. We also generalize the analysis to include the treatment of uniaxial materials.

Interest in the anisotropic thermal expansion of polyimide films is not new [10, 11]. Among the techniques available for measuring CTE_{\perp} for thin films [12], the ones used for polyimides have included capacitance methods [11, 13], surface interferometric methods [10], and laser-induced ultrasonic methods [14]. The method of using through-film interference fringes appears to have been introduced by [2–4], though a closely related method appears in [13]. Given the recent interest in this topic, we present a systematic analysis of the technique used in [2–4]. To the best of our knowledge, this represents the first attempt to analyze temperature-dependent interference fringe data based on the temperature-dependent Lorentz-Lorenz equation, in order to identify the separate contributions from refractive index and physical pathlength to the observed optical path, nd .

2. Temperature dependence of interference fringes in uniaxial films

The theory behind the formation of interference fringes in thin film transmission spectra is well known. A particularly good treatment is presented in Yeh's book [15]. It is also treated in Born and Wolf's classic book on optics [16], well known textbooks [17], and many other monographs. For comparison to an experimental spectrum, the full transmission spectrum through a thin film can be calculated from any of these references. A paper which presents an excellent outline of the calculation of these spectra for birefringent layers (and multilayers) is Ref. [18].

The transmission spectrum of a transparent film contains a series of periodic peaks resulting from constructive interference. The peak locations correspond to wavelengths that are exact multiples of the round-trip path between the film's surfaces. Assuming normal incidence, each interference peak occurs at a wavelength that fits exactly M times within this round trip, thus obeying the relationship:

$$M = \frac{2n(\lambda)d}{\lambda} \quad (1)$$

where d is the film thickness, λ is the wavelength of light and $n(\lambda)$ is the refractive index at λ . Since the physical path length traversed by the light is $2d$ and the wavelength in the film is $\lambda/n(\lambda)$, Eqn. (1) reiterates the condition that the physical path length corresponds to exactly M wavelengths inside the film.

Figure 1 illustrates the spectral behavior of a thin film, calculated using the methods of Ref. [18]. For this simulation, peak locations were chosen to match the peak locations published in Fig. 1 of [2]. Matching the peaks of the low-temperature, solid-line data was achieved with an index of 1.7929 and a film thickness of $5.524 \mu\text{m}$. Note that any thickness and index combination which results in an optical path product nd of $9.904 \mu\text{m}$ generates equivalent peak positions. The peaks of the high-temperature data exhibit an optical path product of $10.084 \mu\text{m}$.

We note that Eqn. (1) makes the implicit assumption that the film material is isotropic, meaning that a single value of n applies to all possible directions of light propagation and is independent of polarization. More generally, however, n depends upon the propagation direction and polarization of light. Materials that exhibit direction-dependent refractive indices are referred

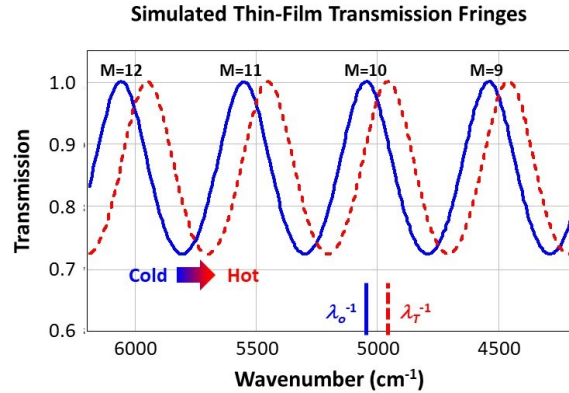


Fig. 1. Simulated transmission fringes for a thin film, with properties as described in the text. The horizontal axis is given in inverse wavelength. The solid curve corresponds to the film at low temperature. At elevated temperatures, fringes from the same film shift to the right (longer wavelengths). Also shown are the peak wavelengths corresponding to Eqn. (8), if the analysis were performed for the $M = 10$ fringe peak.

to as birefringent. For thin-film polymer samples, a common observation is that light polarized along either axis (x, y) in the plane of the film has one index of refraction, while light polarized perpendicular to the film plane (along z) has another, making them uniaxially birefringent. This is illustrated in Fig. 2. For this geometry, one common optics nomenclature denotes $n_x = n_y \equiv n_{TE}$, and $n_z \equiv n_{TM}$. Since the polarization vector is perpendicular to the propagation direction, and Eqn. (1) is written for light that propagates straight into the film surface, the appropriate refractive index for Eqn. (1), in this case, is n_{TE} .

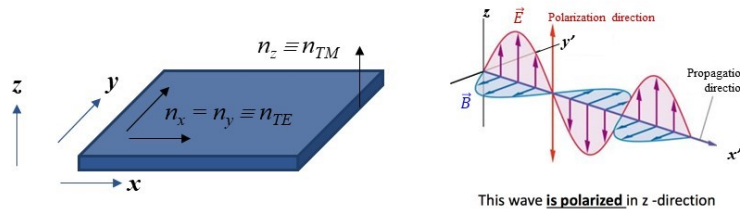


Fig. 2. Illustration of uniaxial birefringence. The refractive index along x or y is denoted n_{TE} , while the refractive index along z is denoted n_{TM} . For light, the refractive index is determined by the direction of its electric field, E . As illustrated on the right, E points perpendicular to the propagation direction. As diagrammed, this light would see the n_{TM} index. Any light propagating normal to the film, along z , will see index n_{TE} , regardless of its polarization. (Illustration on right modified from <https://socratic.org/questions/58f0fd7e7c0149308e221579>)

We now consider the effect of temperature changes on the relationship in Eqn. (1). As indicated in Fig. 1, the fringe peak locations shift with temperature. Typically, the peak locations drift towards longer wavelengths with increasing temperature. The two material parameters appearing in Eqn. (1) that are affected by temperature are thickness and the refractive index. The first-order change in film thickness with temperature is governed by the linear coefficient of thermal expansion (CTE) corresponding to the direction normal to the film plane (*i.e.*, along the propagation direction of light), namely CTE_{\perp} , according to:

$$d(T) = d(T_o) [1 + \Delta T \beta_{\perp}] \quad (2)$$

where $d(T)$ is the thickness at temperature T , β_{\perp} is a notationally more efficient variable for CTE_{\perp} , T_o is the initial temperature, and $\Delta T \equiv (T - T_o)$. Note that, for a uniaxial film, the in-plane CTE (β_{\parallel}) can have a different value, meaning that $\beta_{\perp} \neq \beta_{\parallel}$ in general. These relationships are illustrated in Fig. 3.

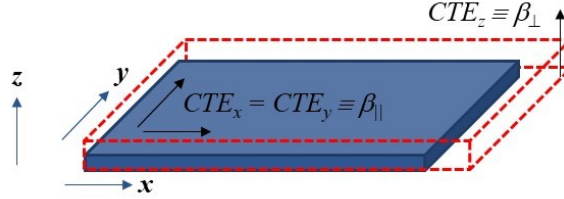


Fig. 3. Schematic of the anisotropic thermal expansion of a uniaxial film, where a film at low temperature expands to a new outline given by the dashed lines. The direction-dependent rate of expansion is given by the linear coefficients of thermal expansion (CTE). The variables used, for convenience, to represent CTE in the equations are β_{\perp} and β_{\parallel} . The volume coefficient of thermal expansion (VCTE) is defined by $2\beta_{\parallel} + \beta_{\perp}$.

Similarly, the first-order effect of temperature change on the refractive index in the direction relevant to the interference peaks described by Eqn. (1), namely n_{TE} , is given by

$$n_{TE}(\lambda, T) = n_{TE}(\lambda, T_o) + \Delta T \dot{n}_{TE}(\lambda) \quad (3)$$

where we define, for convenience, $\dot{n}_{TE}(\lambda) \equiv dn_{TE}(\lambda)/dT$. Again, for a uniaxial film, $dn_{TE}/dT \neq dn_{TM}/dT$ in general.

To determine the wavelength shift of a particular interference peak, corresponding to a specific value of M , we start by rewriting Eqn. (1) explicitly for a uniaxial film at a particular temperature, T_o , as

$$M = \frac{2 n_{TE}(\lambda_o, T_o) d(T_o)}{\lambda_o} \quad (4)$$

Because of the temperature dependence of the parameters $d(T)$ and $n_{TE}(\lambda, T)$ in Eqns. (2) and (3), the wavelength position of peak M is expected to be temperature-dependent. The relationship for peak M upon a temperature change from T_o to T is given by

$$M = \frac{2 [n_{TE}(\lambda_T, T_o) + \Delta T \dot{n}_{TE}(\lambda_T)] d(T_o) [1 + \Delta T \beta_{\perp}]}{\lambda_T} \quad (5)$$

after substitution of Eqns. (2) and (3) into Eqn. (4), and where the new peak wavelength is denoted λ_T . Grouping together terms of ΔT allows us to rewrite this as

$$M = \left(\frac{2 n_{TE}(\lambda_T, T_o) d(T_o)}{\lambda_T} \right) \left\{ 1 + \left[\beta_{\perp} + \frac{\dot{n}_{TE}(\lambda_T)}{n_{TE}(\lambda_T, T_o)} \right] \Delta T + \left[\frac{\beta_{\perp} \dot{n}_{TE}(\lambda_T)}{n_{TE}(\lambda_T, T_o)} \right] \Delta T^2 \right\} \quad (6)$$

In practice, the role of dispersion in Eqns. (4) and (6) is typically negligible, meaning that the difference between $n_{TE}(\lambda_o, T_o)$ and $n_{TE}(\lambda_T, T_o)$, and between their temperature derivatives, can be neglected as long as

$$\left| \left(\frac{\lambda_T}{n_{TE}(\lambda_T)} \right) \left(\frac{d}{d\lambda} n_{TE}(\lambda_T) \right) \right| < 1 \quad (7)$$

Note that the relationship in Eqn. (7) holds true even in very dispersive spectral regions of materials. For example, consider the well-known polymer polycarbonate. [19] It is very dispersive near a wavelength of 400 nm. Even in this extreme case, the quantity in Eqn. (7) is only 11%. By 550 nm it is <5%, and it drops further to 1% by 1050 nm. In [4], the authors examined polyimide films in the 1500-2200 nm range, wavelengths at which they are expected to be even less dispersive than polycarbonate is near 1050 nm.

Using the approximation in Eqn. (7), we obtain the ratio of the peak wavelengths corresponding to the two temperatures, T and T_o , by equating the right-hand sides of Eqns. (4) and (6) as

$$\frac{\lambda_T}{\lambda_o} = 1 + \left[\beta_{\perp} + \frac{\dot{n}_{TE}(\lambda_o)}{n_{TE}(\lambda_o, T_o)} \right] \Delta T + \left[\frac{\beta_{\perp} \dot{n}_{TE}(\lambda_o)}{n_{TE}(\lambda_o, T_o)} \Delta T^2 \right] \quad (8)$$

Thus, we see in Eqn. (8) that the temperature-induced change in wavelength position of an interference peak depends on *both* the relevant thermal expansion coefficient, β_{\perp} , and the thermo-optic coefficient, \dot{n}_{TE} . This is physically reasonable since the wavelength fundamentally depends on both the thickness and index of the sample, as shown in Eqn. (1).

As long as $\left[\frac{\beta_{\perp} \dot{n}_{TE}(\lambda_o)}{n_{TE}(\lambda_o, T_o)} \right] \Delta T < \left[\beta_{\perp} + \frac{\dot{n}_{TE}(\lambda_o)}{n_{TE}(\lambda_o, T_o)} \right]$, which is often satisfied in practice, a good approximation for Eqn. (8) is

$$\frac{\lambda_T}{\lambda_o} \approx 1 + \left[\beta_{\perp} + \frac{\dot{n}_{TE}(\lambda_o)}{n_{TE}(\lambda_o, T_o)} \right] \Delta T \quad (9)$$

It is interesting to note that, in most polymers, β_{\perp} and \dot{n}_{TE} often have opposite signs. This tendency of the contributions from β_{\perp} and \dot{n}_{TE} to cancel each other can lead to very small temperature-induced shifts in the wavelength positions of interference peaks even in situations where both β_{\perp} and \dot{n}_{TE} are large. Thus, it is important not to misinterpret small, observed wavelength shifts as implying that the material properties are (nearly) independent of temperature.

3. Analysis of thermal dependence based on the Lorentz-Lorenz equation

Equation (8) provides a method for determining β_{\perp} , the linear coefficient of thermal expansion normal to the film plane, from the shift in the interference fringes with temperature. This method requires an independent measurement of the corresponding thermo-optic coefficient, \dot{n}_{TE} , as well as of the room-temperature refractive index, n_{TE} . However, other strategies for obtaining β_{\perp} are possible by recognizing that β_{\perp} and \dot{n}_{TE} are not independent parameters.

The relationship between β_{\perp} and \dot{n}_{TE} can be found by starting with the Lorentz-Lorenz equation [8,9], also known as the Clausius-Mossotti relation, which relates the refractive index n , polarizability α and density ρ of an isotropic material via

$$\frac{n^2 - 1}{n^2 + 2} = \frac{1}{3 \epsilon_o} N \alpha = \frac{\rho \alpha}{3 \epsilon_o} \left(\frac{N_A}{M_W} \right) \quad (10)$$

where N is the number of molecules per volume, N_A is Avogadro's number and M_W is the molecular weight. The equivalence of the second term on the right side, which is proportional to the mass density, follows directly from consideration of the molecular weight of the material. By taking the derivative with respect to temperature of both sides of Eqn. (10), we find

$$\frac{dn}{dT} = \frac{(n^2 - 1)(n^2 + 2)}{6n} \left(\frac{1}{\rho} \frac{d\rho}{dT} + \frac{1}{\alpha} \frac{d\alpha}{dT} \right) \quad (11)$$

In Ref. [20], Mueller argued that the temperature-induced change in polarizability can be considered proportional to the change in density but has the opposite sign. Physically, this is motivated by the idea that a decrease in density allows for an increase in the free space between atoms, thus allowing for freer motion of electrons in response to an electric field. In this picture, a decrease in density results in an increase in polarizability, and vice versa. To incorporate this concept into Eqn. (12), he introduced the proportionality constant L , later referred to by other authors [21] as the strain polarizability constant:

$$\frac{dn}{dT} = \frac{(n^2 - 1)(n^2 + 2)}{6n} (1 - L) \left(\frac{1}{\rho} \frac{d\rho}{dT} \right) = \frac{(n^2 - 1)(n^2 + 2)}{6n} (1 - L) \left(-\frac{1}{V} \frac{dV}{dT} \right) \quad (12)$$

where the final term on the right is -1 times the volume coefficient of thermal expansion, which is $(\beta_{\perp} + 2\beta_{\parallel})$ for a uniaxial film. While Mueller developed this idea for glasses, existing work [21, 22] supports this approximation for polymers as well. Furthermore, the data suggest that L for polymers is generally small, typically ~ 0.15 .

Equation (12) is written for an isotropic material. To extend this analysis to a uniaxial film, we follow Vuks [23], who relates the refractive indices n_i to the polarizabilities α_i along the different directions $i \in \{x, y, z\}$ via

$$\frac{n_i^2 - 1}{\langle n \rangle^2 + 2} = \frac{1}{3 \epsilon_o} N \alpha_i = \frac{\rho \alpha_i}{3 \epsilon_o} \left(\frac{N_A}{M_W} \right) \quad (13)$$

where $\langle n \rangle$ is the average index, defined as the square root of the average dielectric constant, namely

$$\langle n \rangle = \sqrt{\langle \epsilon \rangle} = \sqrt{(2 \epsilon_{TE} + \epsilon_{TM})/3} = \sqrt{(2 n_{TE}^2 + n_{TM}^2)/3} \quad (14)$$

and $\langle \alpha \rangle$ is the average polarizability defined as

$$\langle \alpha \rangle = (\alpha_{\perp} + 2 \alpha_{\parallel}) / 3 \quad (15)$$

Inspection of Eqn. (13) shows that a sum over all i recovers Eqn. (10) with n replaced by $\langle n \rangle$ and α replaced by $\langle \alpha \rangle$, which also means the same substitutions can be made in Eqn. (11). Therefore, we expect an appropriate generalization of Eqn. (12) to be

$$\frac{d\langle n \rangle}{dT} = \frac{(\langle n \rangle^2 - 1)(\langle n \rangle^2 + 2)}{6 \langle n \rangle} (1 - L) \left(-\frac{1}{V} \frac{dV}{dT} \right) \quad (16)$$

where the meaning of L is now adjusted to reflect the proportionality of changes in the *average* polarizability $\langle \alpha \rangle$ to changes in the density.

To separate the temperature dependence of the TE and TM indices in Eqn. (16) we recall Eqn. (14), define $n_{TE} \equiv n_{TM} + \Delta n$, assume $d(\Delta n)/dT \ll dn_{TE}/dT$, and manipulate Eqn. (16) to find

$$\frac{dn_{TE}}{dT} = \frac{(\langle n \rangle^2 - 1)(\langle n \rangle^2 + 2)}{6(n_{TE} - \Delta n/3)} (1 - L) [-(\beta_{\perp} + 2\beta_{\parallel})] \quad (17)$$

The assumption that $d(\Delta n)/dT \ll dn_{TE}/dT$ is not meant to imply $d(\Delta n)/dT = 0$. Rather, this assumption is used to simplify Eqn. (17) based on the physically reasonable assertion that its magnitude contributes very little to numerical calculations of the quantities in (17) for most materials.

4. Discussion

Section 2 related the temperature-dependent wavelength shift of transmission fringes to physical properties of a film. If one already knows \dot{n}_{TE} and n_{TE} , for example, one can use Eqn. (8) to determine β_{\perp} from measured fringe shifts. Note that this suggests how a series of purely optical measurements of temperature-dependent index values and transmission spectra can result in a determination of the physical property β_{\perp} .

Section 3, however, showed that the properties in Eqn. (8) are not independent of one another. Under the approximation of the Lorentz-Lorenz equation (10) and the proportionality of the temperature dependence of $\langle\alpha\rangle$ to the temperature dependence of ρ , \dot{n}_{TE} is related to β_{\perp} via Eqn. (17). Provided room-temperature values for n_{TE} and Δn are known, along with data on β_{\parallel} , one can use Eqn. (17) to substitute for \dot{n}_{TE} in Eqn. (8), and thus to determine β_{\perp} without measuring the temperature dependence of the refractive index values. This combines optical measurements of temperature-dependent transmission fringe spectra with room-temperature measurements of the refractive index and physical property β_{\parallel} in order to find β_{\perp} .

Note also that the fringe spectra can provide an important check on the validity of Eqn. (16). Independent measurements of all the quantities involved in Eqns. (8) and (17) can determine whether the approximation of a constant L is valid, and allow for a measurement of its value, rather than simply assuming it to be ~ 0.15 .

5. Analysis of reported polymer data

As mentioned in the Introduction, we developed our analysis in response to the work published in Refs. [2–4]. To the best of our knowledge, these papers first introduce the idea of using transmission fringe spectroscopy to measure the transverse coefficient of thermal expansion in uniaxial films. We think this represents an important contribution to the study of thin film thermal expansion. In this section, we demonstrate that our analysis provides new information from their data, \dot{n}_{TE} , which was not reported in the previous work.

However, in all of [2–4] the authors assume the observed fringe shifts result only from changes in sample thickness, thus ignoring any contribution from the temperature dependence of the refractive index. This is a common assumption, and there are situations where the impact of dn/dT is a small perturbation. In this experiment, however, the assumption $\dot{n}_{TE} = 0$ implies that the authors related their reported values of the coefficient of thermal expansion $\beta_{\perp,rep}$ to fringe shifts via

$$\frac{\lambda_T}{\lambda_o} = 1 + \beta_{\perp,rep}\Delta T \quad (18)$$

which is obtained from our Eqn. (8) by setting $\dot{n}_{TE} = 0$. To their credit, the authors also report corresponding values of n , Δn , and β_{\parallel} for many of the polymers. Therefore, we can use the analysis presented here to infer physically consistent values of $\beta_{\perp,inf}$ and $\dot{n}_{TE,inf}$, inferred coefficients of thermal expansion and TE-polarized thermo-optic coefficient, respectively. This calculation is valid to within the approximations made in the derivation of Eqn. (17), as outlined in Section 3.

We now demonstrate the effect of our analysis for the data previously published in [4]. To be clear, we accept all the observed data reported in [4] as accurate. The only difference between [4] and this work is that we account for a non-zero \dot{n}_{TE} when describing the (same) fringe shifts. In that paper, the authors make it clear that they relate fringe shifts to thermal expansion via Eqn. (18). We describe the same data using Eqn. (8). Equating the right-hand sides of each of those equations results in an expression including the unknown parameters $\beta_{\perp,inf}$ and $\dot{n}_{TE,inf}$, along with ΔT and parameters reported in [4]. To reduce the expression to one that involves just $\beta_{\perp,inf}$, we substitute Eqn. (17) for $\dot{n}_{TE,inf}$. Once this (quadratic) equation is solved to find $\beta_{\perp,inf}$, the

solution can be used in Eqn. (17) to compute $\dot{n}_{TE,inf}$. The results of the analysis are shown in Table 1, assuming values of $L = 0.15$ and $\Delta T = 150$ °C.

Table 1. Values in the first 5 columns are reported in [4]. Values in the last two columns are inferred from the same data, but based on the analysis presented in this paper.

Material	n	Δn	n_{TE}	β_{\parallel} ppm/°C	$\beta_{\perp,rep}$ ppm/°C	$\beta_{\perp,inf}$ ppm/°C	$\dot{n}_{TE,inf}$ ppm/°C
sBPDA/PPD-HO	1.7334	0.185	1.7929	7.2	119.6	240.6	-209.3
sBPDA/PPD-LO	1.7188	0.191	1.7801	6.0	139.7	272.8	-227.6
sBPDA/MPD	1.6675	0.015	1.6725	35.7	40.6	128.9	-144.8
aBPDA/PPD	1.6508	0.015	1.6558	49.2	45.7	155.4	-177.6
aBPDA/MPD	1.6456	0.007	1.6479	44.5	48.2	151.5	-166.5
PMDA/MPD	1.6439	0.033	1.6548	33.0	52.6	140.5	-142.5

Perhaps the most striking result of this re-analysis of the data is the 2-3X greater magnitudes of β_{\perp} (*i.e.*, the differences between $\beta_{\perp,rep}$ and $\beta_{\perp,inf}$) found when incorporating the contribution of the thermo-optic coefficients. An increase is expected because the thermal dependence of density and that of refractive index in polymers tend to cancel each other in shifting transmission fringe peaks, as described at the end of Section 2. It is important to note that the impact on interference fringes remains unchanged. Returning to the simulation parameters of Fig. 1, for example, one computes exactly the same change in optical path using $\beta_{\perp,rep}$ and $\dot{n}_{TE} = 0$ as when using the inferred values in Table 1. Since the authors of [4] assumed $\dot{n}_{TE} = 0$, their value of $\beta_{\perp,rep}$ is unrealistically small. The values of $\beta_{\perp,inf}$ in Table 1 clearly demonstrate that the contribution of physically consistent thermo-optic coefficients is not negligible in the determination of β_{\perp} from interference fringe data.

The newly extracted values of dn/dT provide important information concerning possible optical applications of these materials. We note that the lower dn/dT values in Table 1 are comparable to the higher dn/dT values we measured previously in a set of different polyimide films, where the goal was to synthesize materials with as little dn/dT and CTE as possible. [7]

5.1. Uncertainty analysis

The conclusion that the inferred values of β_{\perp} must be 2-3X higher than the reported values is unchanged after an uncertainty analysis. Uncertainties in the inferred values $\beta_{\perp,inf}$ and $\dot{n}_{TE,inf}$ can be estimated by a Monte Carlo analysis in which randomly perturbed values of the reported values in Table 1 (plus L and ΔT) generate distributions of the inferred values. In the following, "uncertainty" values will refer to standard deviations of parameters selected from a Gaussian distribution.

Looking at variables in isolation, the uncertainty in L has a direct impact on the calculation. As L shrinks, the magnitudes of $\beta_{\perp,inf}$ and $\dot{n}_{TE,inf}$ grow. Starting from its initial value of 0.15, an uncertainty of 0.05 in L results in relative uncertainties of 7% and 10% in the magnitudes of $\beta_{\perp,inf}$ and $\dot{n}_{TE,inf}$, respectively. The analysis leading to Table 1 also depends on ΔT , though the dependence on this value is weak. Even an uncertainty as high as 100°C results in relative uncertainties <10% of the inferred values. Our group has a lot of experience [5] with the instrument used in [4] to measure refractive index. Even a relatively large, for this instrument, uncertainty of 0.001 in the index values in Table 1 results only in sub-1% relative uncertainties in

the computed quantities. The values for $\beta_{\parallel,inf}$ given in [4] are quoted to 0.1 ppm/°C. With that level of uncertainty, the computed quantities again have a sub-1% relative uncertainty. Because the values of $\beta_{\perp,rep}$ are the results of contributions from multiple fringe-based measurements, the uncertainty in these values is difficult to judge. If we start with a 10% uncertainty, then the relative uncertainty of $\beta_{\perp,inf}$ and $\dot{n}_{TE,inf}$ values are no worse than the same 10%. Any other relative uncertainty scales similarly. Lastly, there is the impact of violating the assumption made in the derivation of Eqn. 17 that $d(\Delta n)/dT \ll \dot{n}_{TE}$. Consider a situation where $d(\Delta n)/dT$ is $\sim 10\%$ of $\dot{n}_{TE,inf}$. Then the $\beta_{\perp,inf}$ values increase by $\sim 3\%$ and the $\dot{n}_{TE,inf}$ magnitudes increase by $\sim 5\%$. If the ratio changes sign, so that it becomes -10% , the magnitudes of the inferred quantities decrease, rather than increase, by the same relative amounts as before.

For a more comprehensive uncertainty analysis, a Monte Carlo simulation was run with the following uncertainties (standard deviations) in the independent variables: 0.05 for L , 0.001 for all index values, 1.0 ppm/°C for β_{\parallel} , 100 °C for ΔT , and a 10% relative uncertainty for $\beta_{\perp,rep}$. 10,000 trials were run for each material listed in Table 1. The resulting aggregate, relative uncertainty for each value of $\beta_{\perp,inf}$ and $\dot{n}_{TE,inf}$ is less than 16%, in all cases. In other words, the uncertainty analysis predicts an overall relative uncertainty for $\beta_{\perp,inf}$ of less than 16%, which is substantially less than the 200-300% differences between $\beta_{\perp,inf}$ and the $\beta_{\perp,rep}$ values from [4]. For the actual values of β_{\perp} to be anything other than factors of 2-3X higher than those reported in [4], both standard thin-film theory and the Lorentz-Lorenz model, leading to Eqn. 17, would have to be invalid for polyimide films.

6. Summary

We use standard thin-film optical interference theory and the well-known Lorentz-Lorenz equation (Eqn. 10) to derive relationships between the temperature-dependent wavelength shifts in observed spectral transmission peaks, the optical constants, and the coefficients of thermal expansion in uniaxial thin films of transparent materials. As discussed in Section 4, this allows the use of different combinations of optical measurements and thermo-physical measurements for determining values of properties that aren't measured directly. To the best of our knowledge, this analysis does not appear elsewhere in the literature.

This contribution was motivated by recent work [2–4] which attempts to extract the out-of-plane coefficient of thermal expansion, β_{\perp} , from temperature-dependent interference fringe data for thin films of different polyimide materials. We read those results with interest, as they represent important data. Recognizing, however, that there did not appear to be a published source containing a detailed treatment of the analysis, we prepared this contribution. Our careful interpretation of these measurements allowed us to re-analyze the published data, thereby obtaining new information, namely, values of dn/dT for their set of polyimide films, in addition to new, physically consistent values of β_{\perp} . Notably, there is a substantial difference between the values of β_{\perp} we extract from the published data and those reported in [2–4].

7. Appendix

The authors, having some experience with high-precision measurements of thin-film interference fringes [5, 6], felt it prudent to point out an often-overlooked source of systematic error in attempting to analyze such spectra. Additional sources of error are also treated in [6].

7.1. Sample thickness fluctuations

Fringe-based measurements typically require stringent control of sample thickness uniformity within the illuminated sample area, and of repositioning accuracy between separate measurements. After a brief discussion of the degree of uniformity required, often at the nanometer level, we outline a simple experimental approach to estimating whether it poses a problem for a given

sample in a specific experiment. The observations can be reported along with measurements to guide experimental design and bolster confidence in the results.

Thin-film transmission peaks are often used to extract either refractive index or sample thickness with a high degree of precision. In [5] we attempted to extract index values with uncertainties of $\pm 10^{-4}$ for 50 μm thick films, and in [2–4] the authors attempted to extract CTE values of ~ 100 ppm/ $^{\circ}\text{C}$ from films only 10 μm thick. In each case, the desired values are extracted from observations of optical path (nd). For a constant-thickness 50 μm thick film, a 10^{-4} relative change of the optical path causes a 10^{-4} relative difference in refractive index. On the other hand, an uncertainty in thickness of only 5 nm has just as great an impact on the optical path! Similarly, the optical path of the bottom four materials of Table 1 changes by only ~ 50 nm for a 10 μm thick film even for a 100°C temperature difference. The spectral shift in a fringe due to this temperature change would be indistinguishable from a room-temperature measurement of a portion of the sample just 30 nm thicker. For a high-confidence measurement of CTE_{\perp} , the uncertainty in film thickness between measurements at the two temperatures would have to be substantially less than 30 nm. Given that the expected radius of gyration of polyimide polymers [24] is ~ 20 nm, this level of thickness homogeneity could be challenging to achieve, in practice.

It is straightforward, however, to assess sample quality for the purpose of a specific experiment. One need merely observe the variation of fringe positions as the sample is translated under the optical beam. If the fringe locations stay stable for all reasonable sample positions, then sample uniformity does not play a role in the analysis of fringe data. More commonly, however, and particularly for polymer samples, significant perturbations of the fringe spectra are observed as the sample is translated across the spectrometer light path. It should be straightforward to determine the amount of spectral shift per length of translation of the sample. Reporting a value for this quantity (an average peak shift of 1 wavenumber per 100 microns of travel, for example) provides a concrete measure of sample quality, and a clear indication of how precisely the same spot needs to be located for different measurements to be compared to one another.

Using the $10^{-2} \text{ cm}^{-1}/\mu\text{m}$ value as an example, if a fringe needs to be measured to an accuracy of 0.1 cm^{-1} at two separate times, then it is straightforward to recognize that the sample needs to be held still to well under 10 μm between measurements. This would be particularly important for measurements as a function of temperature, where large temperature swings are anticipated to cause significant thermal expansion of mount hardware, leading to unavoidable translations of mounted samples.

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