

Laser Interferometric Measurement of Polymer Thin Film Thickness Changes During Processing

KATHERINE L. SAENGER and HO-MING TONG, *IBM Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598*

Synopsis

A simple interferometric technique is described for monitoring thickness changes in solution-cast polymer films as they are dried and cured. This paper follows a freshly spun solution of polyamic acid in NMP as it is converted into a cured polyimide film of 6 μm in thickness. The technique is shown to be nearly quantitative despite the effects of thermal expansion and cure-related refractive index changes.

INTRODUCTION

We describe a simple interferometric technique that can be used to measure the shrinkage of transparent polymer films during drying and curing. Such measurements are of interest for a variety of reasons. For instance, the in situ determination of rates of evaporation from wet films of polymer solution allows comparisons of speed and completeness of drying for different heating schedules. Also, the degree of dry polymer film shrinkage during baking can be usefully related to completeness of cure and thermal stability.

Conventional thickness measurement techniques are not well suited for real-time measurements of rapidly shrinking wet films. Profilometers (e.g., Sloan Dektak and Tencor AlphaStep) relying on physical contact are obviously inappropriate. Film thickness analyzers (e.g., Leitz MPV-SP), which determine thickness from the wavelength dependence of sample reflectance, although noncontact, are slow compared with the rates of thickness change observed during evaporation and are useful only for films thinner than 15 μm (wet films are often much thicker). Thickness range is not an issue with β backscattering techniques (e.g., Twin Cities TC-2000 Betascope), but speed is, since those devices are substantially slower than the film thickness analyzers.

By contrast, laser interferometry is well suited for diagnostic applications in thin film polymer processing. It is noncontact and nonperturbative. As used here, changes in the polymer film thickness and/or refractive index are detected from changes in the film reflectivity. Polymer characteristics related to changes in thickness and/or refractive index include solvent uptake, swelling, or dissolution, thermal expansion coefficient, and drying or shrinkage rates. The statement that "the adaptability of [interferometric techniques] to specific situations seems to be largely a function of the ingenuity of the user"¹ is amply supported by the literature. For example, polymer dissolution has

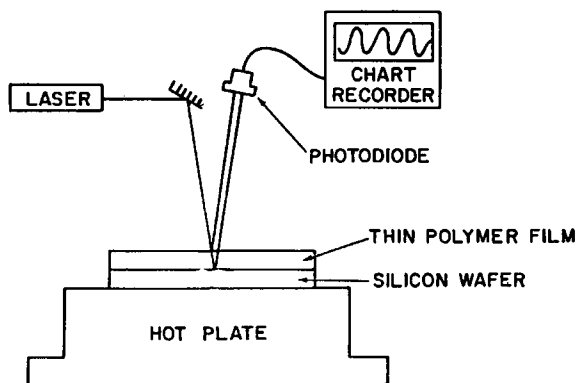


Fig. 1. Apparatus.

been studied by Rodriguez et al.¹ Plasma etch rates of transparent polymer films are routinely determined by laser interferometry.² Other applications not specifically related to polymer thin films include interferometric measurements of cornea thickness,³ refractive indices of liquids,⁴ thermal expansion coefficients,⁵ and temperature (from thermal expansion).⁶

The focus of this paper is a typical experiment, interferometric measurements of thickness changes occurring during the drying and curing of a polyamic acid solution (similar to du Pont's PI-2545) to form polyimide. Polyimide is a thermally stable, low-dielectric-constant material of interest to the electronics industry for device and packaging applications.

EXPERIMENT

A silicon wafer freshly spin coated with an 18.3% solution of polyamic acid (pyromellitic acid dianhydride (PMDA)-oxydianiline (ODA)) in *n*-methyl-2-pyrrolidone (NMP) is heated on a level hot plate (spin conditions: 3000 rpm, 30 s, slow acceleration). The output of a low-power He-Ne laser (≈ 1 mW) is directed at approximately normal incidence toward the sample (Fig. 1). A photodiode monitors the intensity of the reflected light. Interference between reflections from the top and bottom surface of the film causes the reflected light intensity to oscillate as film shrinkage reduces the optical path length difference between the two reflections.

RESULTS

The reflectance signal during the first step in our polyimide dry-cure cycle, that is, the 10-min "soft" bake on an 85°C hot plate used to remove NMP from the wet film, is shown in Figure 2. One fringe corresponds to a thickness decrease of approximately $0.216 \mu\text{m}$ ($= \lambda/2n$ where λ is the $0.6328\text{-}\mu\text{m}$ laser wavelength, and $n = 1.4684$ is the index of refraction of the evaporating NMP⁷). The initial shrinkage rate is around $200 \text{ fringes min}^{-1}$. As the sample starts to dry out, the amplitude of the interference fringes dramatically increases; at the same time the shrinkage rate rapidly decreases. After 2 min on the hot plate, the rate has dropped to about $5 \text{ fringes min}^{-1}$.

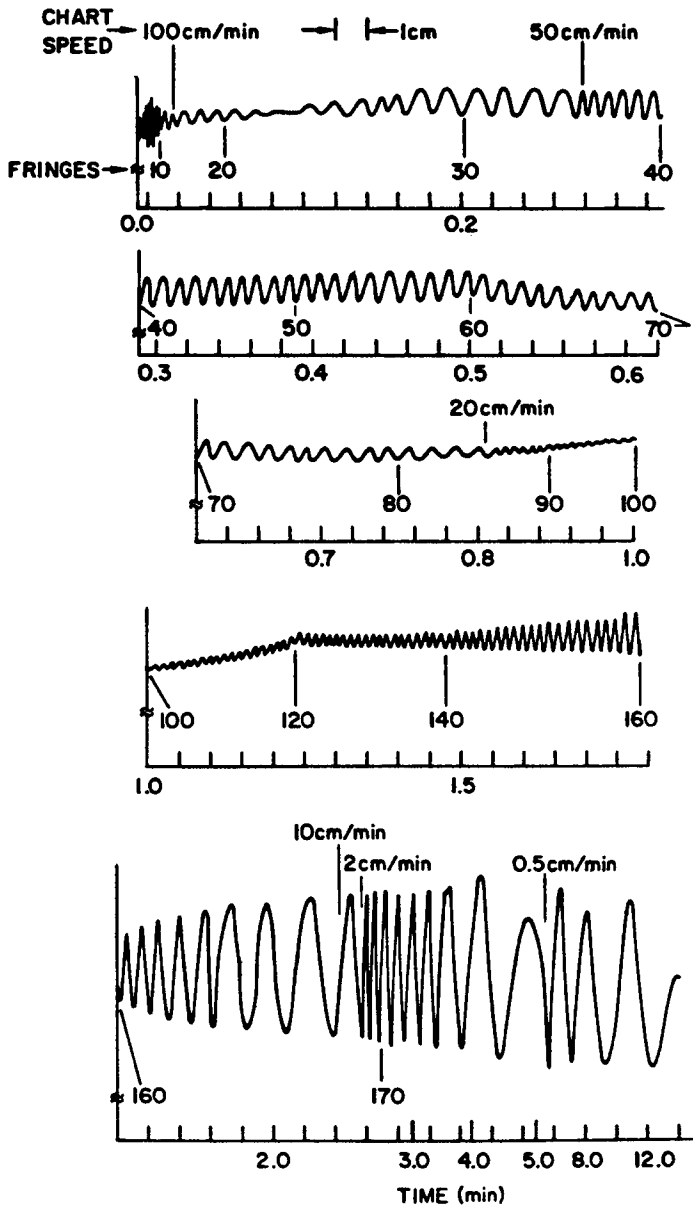


Fig. 2. Reflectance as a function of time during the 10-min, 85°C soft bake. Elapsed fringes, chart speed, and time as marked.

By the completion of the 85°C bake, ≈ 176 fringes have been detected, corresponding to an integrated NMP thickness of $38.0 \pm 1.3 \mu\text{m}$ ($0.216 \mu\text{m}$ per fringe $\times 176 \pm 6$ fringes). At this point the remaining “dry” film is $10.0 \mu\text{m}$ thick, as measured with a Dektak profilometer.

A plot of shrinkage rate (in fringes min^{-1}) versus shrinkage (in fringes) yields a signature characteristic of the drying cycle (Fig. 3). Trace a is for the fixed 85°C baked sample of Fig. 2, and trace b is for a sample prepared under

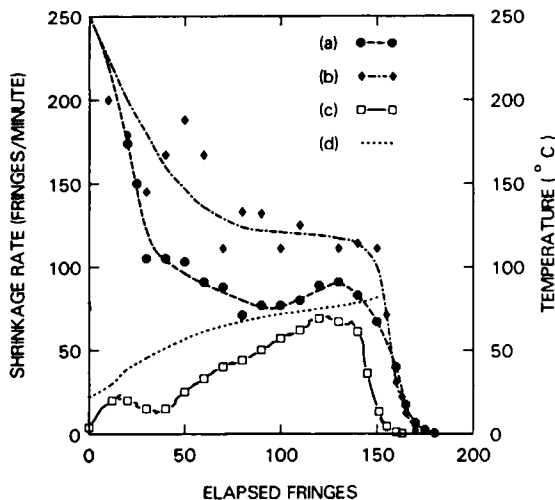


Fig. 3. Shrinkage rate signatures (shrinkage rate in fringes min^{-1} versus elapsed fringes): (a) sample of Figure 2 (fixed 85°C 10-min soft bake); (b) sample prepared under conditions nominally identical to those of a; (c) sample soft baked with ramped ($20\text{--}85^\circ\text{C}$) heating schedule; (d) hot plate temperature during ramped heating schedule.

nominally identical conditions. These signatures begin with a rapidly falling rate, which reaches a plateau by ≈ 30 fringes. This plateau rate holds until ≈ 150 fringes, at which point the rate rapidly drops to zero. A local maximum can be observed in the plateau region of b; its possible significance requires further evaluation.

Should a more uniform shrinkage rate be desired, one can make use of the fact that the evaporation (shrinkage) rate increases with temperature. Figure 3c shows the evaporation signature for a sample dried during a heating cycle ramped from 20 to 85°C (Fig. 3d). In this case, the evaporation rate increases until a maximum is reached at ≈ 130 fringes and then rapidly falls to zero. Note the order of magnitude difference in the initial evaporation rates for the 20 and 85°C films.

The samples were stored in air at room temperature for several days before further processing, during which time they decreased in thickness from 10.0 to $9.6\ \mu\text{m}$. This shrinkage is attributed to continuing solvent loss.

The subsequent "hard" bakes at 150°C (30 min) and 230°C (30 min) led to further shrinkage as the polyimide curing reaction (imidization) proceeded. For sample a in Fig. 3, 12 and 6 fringes of shrinkage were observed, respectively, for the 150 and 230°C bakes, corresponding to thickness changes of $2.3\ \mu\text{m}$ (from 9.6 to $7.3\ \mu\text{m}$) and $1.6\ \mu\text{m}$ (from 7.3 to $5.7\ \mu\text{m}$) (data not shown). As before, the shrinkage rate decreases with time: with 150°C , the initial rate of > 2.5 fringes min^{-1} slows to less than 0.05 fringes min^{-1} ; with 230°C , the initial rate of ≈ 16 fringes min^{-1} slows to < 0.02 fringes min^{-1} .

Profilometer measurements showed negligible shrinkage of the film (about $0.1\ \mu\text{m}$) after the 300°C (30 min) and 400°C (30 min) bakes in dry N_2 .

DISCUSSION

We compare the 9.6 μm pre-hard-bake thickness (sample in Fig. 3b) to the thickness that would be expected from the 18.3% polyamic acid content of the original solution as previously determined from thermogravimetric analysis (TGA; to 450°C). First, we estimate that the wet film had a thickness of $48.0 \pm 1.3 \mu\text{m}$ ($10.0 + 38.0 \pm 1.3 \mu\text{m}$) immediately after spinning. The thickness expected for a dry uncured film would be around $8.8 \pm 0.2 \mu\text{m}$ ($0.183 \times 48.0 \mu\text{m}$). (No imidization occurs during the 85°C bake.⁸) The 0.8 μm discrepancy between 9.6 and 8.8 μm is attributed to the extra volume required to accommodate the residual NMP. This hypothesis is supported by the high NMP content of the 9.6 μm film (31% by weight). (The estimate of 31% is obtained by breaking down the total 37.3% TGA weight loss into NMP desorption plus water evolved during the imidization of polyamic acid (water fraction of TGA weight loss = $[(2 \times 18)/382 \times (0.627/0.373)]$, with 18 the molecular weight of water and 382 the molecular weight of an imidized monomer unit of polyamic acid.)

For the "soft" bake, two potential sources of error merit discussion. First, NMP evaporation goes undetected during the minute or two between spinning and the start of data collection. This error, easily estimated from the room temperature evaporation rates (Fig. 2c at $t = 0$) and elapsed time, is small, usually less than 10 fringes. The NMP selectively lost from the solution during spin has already been accounted for, since our 18.3% polyamic acid content was measured postspin. (This effect is indeed not negligible: the TGA-determined polyamic acid content pre- and postspin (from 16.7 to 18.3%) indicates that after spin the NMP concentration has decreased by about 10%.)

Second, the use of $\lambda/2n_{\text{NMP}}$ as the shrinkage per fringe needs explanation, since the absolute optical path length difference N (in units of fringes) for a film of thickness L is $2nL/\lambda$ where n is the index of refraction of the solution, which varies during the course of the experiment. The key assumption is that the film is a binary mixture of polyamic acid and NMP, whose index of refraction is the volume-weighted average of the indices of its components; that is,

$$n = \frac{(L_{\text{NMP}}n_{\text{NMP}} + L_{\text{PI}}n_{\text{PI}})}{(L_{\text{NMP}} + L_{\text{PI}})}$$

where L_{NMP} and L_{PI} are the integrated thicknesses* of the liquid NMP and polyamic acid, respectively. The total film thickness is $L = L_{\text{NMP}} + L_{\text{PI}}$; L_{PI} is fixed after the spin (the polyamic acid is not volatile), and L_{NMP} decreases as the film dries. With the appropriate substitutions, we find $N = (2/\lambda) \times [Ln_{\text{NMP}} + L_{\text{PI}}(n_{\text{PI}} - n_{\text{NMP}})]$, yielding $dN/dL = 2n_{\text{NMP}}/\lambda$. The thickness

*The integrated thickness of a solution component is its (depth-dependent) volume fraction integrated over the (solution's) total film thickness. Equivalently, it is the thickness of the neat layer that would be produced if the solution separated into its component parts (while keeping constant cross-sectional area).

variation per fringe, dL/dN , is thus $\lambda/2n_{\text{NMP}}$, a constant, rather than $\lambda/2n$. This intuitively makes sense since only the NMP is evaporating.

During the hard bakes at 150 and 230°C, the film (1) loses NMP solvent, (2) imidizes, (3) releases water (the imidization product), (4) undergoes several temperature cycles (between room temperature and bake temperature), and (5) slightly densifies. The densification is deduced from comparison of the thickness decrease (from 9.6 to 5.7 μm ; 39%) and TGA-determined mass loss (37.3%) until complete imidization. First, we will discuss how the number of fringes observed during a bake cycle can be affected by changes in temperature and cure-related refractive index changes. Then we will describe a graphical approach for relating the interference data to the thickness and index changes in the film.

The effect of temperature on the number of fringes observed is estimated by differentiating the absolute optical path length difference $N = 2nL/\lambda$ with respect to temperature:

$$dN = \frac{dN}{dT} dT = \frac{2nL}{\lambda} \left(\frac{1}{n} \frac{dn}{dT} + \frac{1}{L} \frac{dL}{dT} \right) dT$$

The temperature dependence of the index of refraction is responsible for the first term, and thermal expansion is responsible for the second. Here, $1/L dL/dT$ is the linear coefficient of thermal expansion. Measurements on a fully cured 8- μm PI film show that a temperature increase of 200°C results in a 1.4 fringe increase in optical path length (reversible upon cooling). This datum,[†] with $\approx 40 \times 10^{-6}/^\circ\text{C}$ for the polyimide thermal expansion coefficient,[‡] implies that $1/n dn/dT$ and $1/L dL/dT$ are about equal. Alternatively, if dn/dT is assumed to be zero, this datum would imply that the thermal expansion coefficient for polyimide (in a thin film bonded to a silicon wafer) is $\approx 80 \times 10^{-6}/^\circ\text{C}$. With the usual procedure of placing the sample on a pre-heated, fixed-temperature hot plate, however, the experiment is essentially isothermal. The temperature-related thickness and index changes are initial transients only, since the film heats up to the hot plate temperature (85, 150, or 230°C) on a fast time scale compared with the initial shrinkage rate.

The effect of cure-related index changes on the observed number of fringes is estimated as $dN = (dN/dn) dn = (2L/\lambda) dn$. For an 8- μm film of polyimide, the optical path length difference increases by about 1 fringe for every 0.04 increase in refractive index. The refractive indices for the polyimide film do indeed increase with increasing degree of "cure"; after the 85, 150, and 230°C bakes they are found to be 1.66 ± 0.02 , 1.72 ± 0.02 , and 1.76 ± 0.02 , respectively (Leitz MPV-SP). This implies that the fringe data from the 150 and 230°C bake cycles will each contain a negative contribution of 1 fringe, with the net result that the data will show fewer fringes than would be expected for the same physical thickness change occurring at fixed index.

[†]Our data and that of B. Robinson (private communication).

[‡]du Pont literature supported by the measurements of A. Baise (private communication).

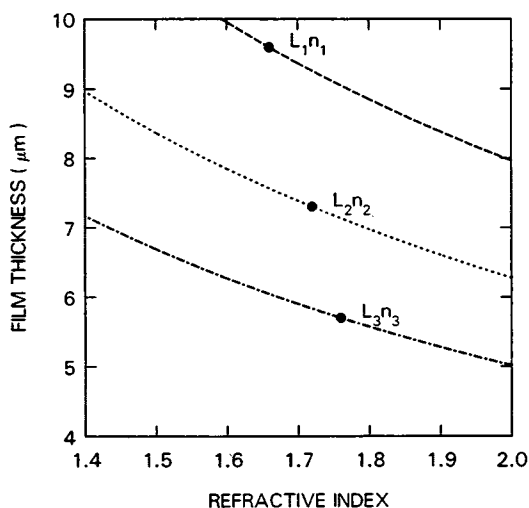


Fig. 4. Polymer film thickness L versus refractive index n during processing: L_1n_1 is prior to the 150°C bake; L_2n_2 is prior to the 230°C bake; L_3n_3 is after the 230°C bake.

In the graphical approach referred to earlier, we plot sample thickness versus index of refraction for the above-measured indices (Fig. 4). These data are in excellent agreement with our fringe data. In going from (L, n) of (9.6 μm, 1.66) to (5.7 μm, 1.76), 18 fringes were observed and 18.7 were expected (cumulative* fringes = $2 \times (L_1n_1 - L_3n_3)/\lambda$). For the intermediate steps, 12 fringes were observed for the transition from (9.6 μm, 1.66) to (7.3 μm, 1.72), compared with 10.7 calculated, and 6 fringes were observed for the transition from (7.3 μm, 1.72) to (5.7 μm, 1.76), compared with 8.0 calculated. The discrepancies can be attributed to inaccuracies in index measurements and imperfect removal from our data of the fringes due to thermal transients.

CONCLUSION

We conclude that the simple technique of laser interferometry can be used to monitor thickness and/or index changes in solution-cast polymer films as they are dried and cured. Depending on one's interest, the interferometric device described in this paper can be used as a process monitor (e.g., to quantitatively compare one film's processing to the next for a well-defined process), or as a research tool (e.g., use a detailed interpretation of the "evaporation signature" to unravel the kinetics of film structure and chemistry changes during curing).

*By cumulative fringes we mean fringes resulting from changes in cumulative phase. The cumulative number of fringes is equal to the observed number of fringes when the optical path length difference, proportional to Ln , monotonically increases or decreases. Under these conditions, the number of fringes observed during transition from any L_1n_1 to L_3n_3 is independent of path in Ln space. Given the placement of the Ln data points (Fig. 4) with respect to the lines of constant Ln , it seems obvious that the Ln product does monotonically decrease. (Note: Thermal cycling is an instance in which multiple fringes appear in spite of the fact that the cumulative phase is zero.)

Future studies will investigate the curing of photosensitive polyimides, the relation of differential shrinkage rates during dry or cure to final film uniformity, and the adsorption-desorption of NMP in polyimide.

The authors thank S. Wiand and G. Hougham for their technical assistance, and acknowledge helpful and enjoyable discussions with M.-J. Brekner, G. Czornyj, and C. Feger.

References

1. F. Rodriguez, P. D. Krasicky, and R. J. Groele, *Solid State Technol.*, **5**, 125 (1985).
2. S. D. Klyce and S. R. Russell, *Rev. Sci. Instrum.*, **49**, 1318 (1978).
3. H. H. Busta, R. E. Lajos, and D. A. Kiewit, *Solid State Technol.*, **2**, 61 (1979).
4. D. Beysens, *Rev. Sci. Instrum.*, **50**, 509 (1979).
5. T. S. Aurora, S. M. Day, and D. O. Pederson, *Rev. Sci. Instrum.*, **55**, 149 (1984).
6. R. A. Bond, S. Dzioba, and H. M. Naguib, *J. Vac. Sci. Technol.*, **18**, 335 (1981).
7. *Handbook of Chemistry and Physics*, CRC, 64th edition (1983-1984).
8. M.-J. Brekner and C. Feger, *J. Polym. Sci., Poly. in Chem. E.*, to appear, 1987.

Received June 24, 1986

Accepted July 28, 1986