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STUDIES OF DISSOLUTION PHENOMENA IN MICROLITHOGRAPHY  
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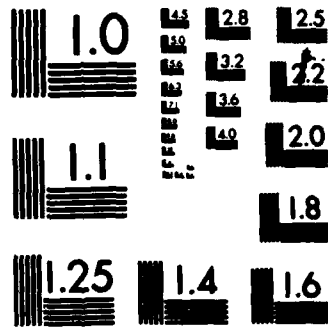
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below a polymer number-average molecular weight of about 30,000. The layer becomes more pronounced as molecular weight of polymer increases.

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STUDIES OF DISSOLUTION PHENOMENA  
IN MICROLITHOGRAPHY

by

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## STUDIES OF DISSOLUTION PHENOMENA IN MICROLITHOGRAPHY

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### ABSTRACT

During the dissolution process, polymer in the glassy state is transported into a dilute solution. In some cases, a transition layer can be measured using laser interferometry. This layer is seen as a difference in reflected light intensity between the bare substrate and the maximum during dissolution. When PMMA dissolves in methyl ethyl ketone, the layer is not detectable below a polymer  $M_n$  of about 30,000. The layer becomes more pronounced as molecular weight of polymer increases.

### INTRODUCTION

Laser interferometry is useful for measuring the dissolution rate of thin polymer films. When the film dissolves without swelling and without the formation of a surface transition layer, the reflected light intensity is easily interpreted. A sinusoidal trace is obtained which yields the rate of dissolution as well as the index of refraction of the polymer film. It has been shown that, when unpolarized light is used, the trace will have the same appearance whether the incident light is normal to the surface or at an angle of up to 30° from the normal.

One phenomenon of particular interest in the pattern of reflected light intensity is the slight change in signal caused by the formation of a thin transition layer at the boundary between solvent and the polymer film. Although such a layer is optically inhomogeneous, its refractive index varies only in the direction normal to the surface of the polymer film. The effective reflection coefficient for the combination of the transition layer and the unpenetrated film can be related to the assuming concentration profiles within the transition layer. In terms of laser interferometry, the existence of the layer can be seen as an offset between the maximum in the light intensity reflected during dissolution and the final intensity from the bare substrate surface.

### EFFECT OF TRANSITION LAYER ON INTERFEROMETRY

In order to understand the manner in which the presence of a transition region influences the reflected intensity oscillations, a review of the pertinent optical theory is necessary. The quantity of interest is the reflectance  $R$  of the polymer film coated onto the substrate and immersed in the solvent. The reflectance of an optical system is defined as the ratio of the reflected light intensity to the incident intensity.

In the case where no transition layer is present and the solvent/polymer interface is perfectly sharp (Figure 1), the appropriate expression for the reflectance  $R$  is

$$R = \frac{r_{23}^2 + 2r_{23}r_{12}\cos\phi_2 + r_{12}^2}{1 + 2r_{23}r_{12}\cos\phi_2 + r_{23}^2r_{12}^2} \quad (1)$$

Here  $r_{23}$  and  $r_{12}$  are the Fresnel reflection coefficients for the polymer/substrate and solvent/polymer interfaces, respectively, which for normal incidence, are given by

$$r_{23} = \frac{n_2 - n_3}{n_2 + n_3} \quad (2) \quad \text{and} \quad r_{12} = \frac{n_1 - n_2}{n_1 + n_2} \quad (3)$$

with  $n_1$ ,  $n_2$ , and  $n_3$  being the refractive indices of the solvent, polymer, and substrate, respectively, while the phase angle  $\phi_2$  is given by

$$\phi_2 = \frac{4\pi d\sqrt{n_2^2 - n_1^2\sin^2\theta_1}}{\lambda} \quad (4)$$

with  $d$  being the film thickness,  $\theta_1$  the angle of incidence of the light onto the film from the solvent, and  $\lambda$  the free-space wavelength of the light. It can be shown that the above expression for  $R$  with the normal incidence Fresnel coefficients is remarkably accurate for incidence angles  $\theta_1 \leq 30^\circ$  using unpolarized incident light.

It is easy to see that the thickness period  $D$ , which is the change in film thickness corresponding to a period in the reflectance oscillations, is given by

$$D = \frac{\lambda}{2\sqrt{n_2^2 - n_1^2 \sin^2 \theta_1}} \quad (5)$$

The extreme values  $R_{\pm}$  of the reflectance are given by

$$R_{\pm} = \frac{r_{23}^2 \pm 2r_{23}r_{12} + r_{12}^2}{1 \pm 2r_{23}r_{12} + r_{23}^2 r_{12}^2} \quad (6)$$

which can be shown to reduce to

$$R_{+} = \left( \frac{n_1 - n_3}{n_1 + n_3} \right)^2 \quad (7) \quad \text{and} \quad R_{-} = \left( \frac{n_1 n_3 - n_2^2}{n_1 n_3 + n_2^2} \right)^2 \quad (8)$$

It is important to note that  $R_{+}$  occurs when  $d$  is an integral multiple of  $D$ , including  $d=0$  which corresponds to a bare substrate in the solvent.

For typical materials employed in dissolution studies using the laser interferometer,  $|r_{12}|$  is generally much smaller than  $|r_{23}|$ . Under these conditions, a sufficiently accurate approximation to  $R$  may be obtained as a power series expansion in  $r_{12}$ , namely

$$R = r_{23}^2 + 2r_{12}r_{23}(1-r_{23}^2)\cos\phi_2 \quad (9), \quad \text{and} \quad R_{\pm} = r_{23}^2 \pm 2r_{12}r_{23}(1-r_{23}^2) \quad (10)$$

In practice, the observed reflectance oscillations typically are purely sinusoidal, which further supports the validity of this approximation.

If the solvent/polymer interface is not sharp but expanded into a continuous transition layer of non-zero thickness, (Figure 2), it can be shown that the appropriate expression for  $R$  is now



$$R = \frac{r_{23}^2 + 2r_{23}fr_{12}\cos\phi + f^2r_{12}^2}{1 + 2r_{23}fr_{12}\cos\phi + r_{23}^2f^2r_{12}^2} \quad (11)$$

Here  $f$  is a positive factor less than unity, and  $\phi = \phi_2 + \phi_t$ , where  $\phi_t$  is a phase angle which, along with  $f$ , depends on the thickness and concentration profile of the transition layer. The approximation for  $R$  which is linear in  $r_{12}$  now becomes

$$R = r_{23}^2 + 2fr_{12}r_{23}(1-r_{23}^2)\cos\phi \quad (12) \quad \text{and} \quad R_{\pm} = r_{23}^2 \pm 2fr_{12}r_{23}(1-r_{23}^2) \quad (13)$$

The effect of the transition layer is to reduce the amplitude of the reflectance oscillations by the factor  $f$  while preserving the average value of the reflectance, and to shift their phase by  $\phi_t$ . A gap or "offset" is created between the extreme value  $R_+$  in the oscillations and the reflectance of the bare substrate in the solvent observed after the film has completely dissolved (Figure 2). The magnitude of this effect may be used to gauge the thickness of the transition layer between the glassy polymer and the solvent. In practice, it is instructive to compare values of the relative offset,  $\psi$ , which is the absolute offset,  $s$ , normalized by the peak-to-peak amplitude,  $a-b$ , of reflectance oscillations. From the diagrams it can be seen that  $f$  is related to  $\psi$  by

$$f = \frac{1}{1 + 2\psi} \quad (14)$$

As an illustrative example, consider the data for poly(methyl methacrylate) (PMMA) dissolving in methyl ethyl ketone (MEK). Through equations 7 and 8 the refractive index  $n_2$  of the glassy polymer may be determined from a measurement of the reflectance ratio  $x = R_-/R_+$ . Here  $R_{\pm}$  are the extreme values that would be observed in reflectance oscillations for a sharp interface, that is, if the transition layer between the solvent and polymer had zero thickness. Considering the offset correction as just discussed, this means that  $x = (b-s)/(a+s) = (b-s)/c$ , rather than simply  $b/a$ . The resulting formula is

$$n_2 = \left[ n_1 n_3 \frac{\frac{n_3+n_1}{n_3-n_1} - x^{1/2}}{\frac{n_3+n_1}{n_3-n_1} + x^{1/2}} \right]^{1/2} \quad (15)$$

In this example,  $x = 0.762$  from which one obtains  $n_2 = 1.485$ , using known values of  $n_1 = 1.380$  for MEK and  $n_3 = 3.80$  for silicon. An accepted value for the refractive index of "dry" PMMA is 1.489. In contrast if the ratio  $b/a = 0.811$  had been inadvertently used for  $x$ , a value of  $n_2 = 1.462$  would have been obtained. Thus, the offset correction for the transition layer is important in the determination of  $n_2$ .

Proceeding with analysis of the transition layer from the example data, the relative offset is found to be  $\psi = s/(a-b) = 0.145$ . This gives a value of  $f = 0.775$  for the oscillation amplitude reduction factor. This factor  $f$  also represents the magnitude of the ratio of the reflection coefficient of the actual transition layer to the reflection coefficient it would have if its thickness were reduced to zero. Although the exact value of  $f$  depends on the shape of the refractive index profile through the transition layer as well as its thickness, in practice this value of  $f$  is somewhat insensitive to the profile shape for a given thickness. For simplicity, a profile which varies linearly between the values  $n_1$  and  $n_2$  with a thickness  $d_t$  may be assumed initially for illustration.

For the linear profile just described, optical theory gives as a good approximation

$$f = \frac{\sin(\alpha/2)}{\alpha/2} \quad (16)$$

where  $\alpha = d_t/\xi$  and  $\xi = \lambda/4\pi n_t \cos\theta_t$ , with  $n_t = (n_1+n_2)/2$  and  $\cos\theta_t = [1 - (\frac{n_1 \sin\theta_1}{n_t})^2]^{1/2}$ . In the example,  $n_t = 1.431$  and  $\cos\theta_t = 0.986$  (using  $\theta_1 = 10^\circ$ ). This gives  $\xi = 0.0357\mu\text{m}$  (using  $\lambda = 0.633\mu\text{m}$ ). Solving for  $\alpha$  in equation 16 (using  $f = 0.775$ ) gives  $\alpha = 2.41$ , from which it follows that  $d_t = \alpha\xi = 0.086\mu\text{m}$ .

The quantity which actually depends linearly upon the mixing fraction of solvent and polymer is the specific electric polarizability rather than the

refractive index. However, in practice the difference between the refractive indices  $n_1$  and  $n_2$  is small enough compared to  $n_1$  and  $n_2$  themselves that the refractive index of the mixture of polymer and solvent is itself approximately a linear function of the mixing fraction. Hence, the refractive index profile also realistically describes the concentration profile in the transition layer. The practical implication for microlithography is that the presence of a transition layer of swollen but not fully dissolved polymer would affect the resolution and lineshape characteristics of a resist material and presumably impose certain corresponding limitations upon its performance. It is hoped that laser interferometry may provide a tool for diagnosing such performance limitations.

More elaborate analysis of transition layers in terms of other refractive index profiles is possible. In particular, a survey of the characteristics of Case II diffusion, which appears to control the rate of dissolution in many polymer systems such as PMMA in MEK, provides some clues as to appropriate profile shapes. Theoretical considerations of Case II diffusion, as well as preliminary results of Rutherford Backscattering Spectroscopy (RBS) performed on typical Case II polymer systems, indicates that an exponential profile or a linear profile combined with a finite step are promising practical candidates. Further work in this area is currently being pursued.

#### SELECTED EXPERIMENTAL RESULTS

Experimental measurements have been made on a variety of systems in which the offset is small (0 to 15% of the total amplitude of oscillation) but easily and reproducibly measured. The variables that are being explored include molecular weight, polydispersity, polymer composition, solvent composition, exposure, history, thermal history, and hydrodynamics of the dissolving system.

A number of molecular weights of PMMA have been synthesized by free radical polymerization and by solvent fractionation. Films of about one  $\mu\text{m}$  were spin coated on 3 inch silicon wafers from solutions of PMMA in chlorobenzene. A standardized bake procedure was used:

1. Bake one hour at 150°C in a convection oven.
2. Cool to about 90°C over a period of 1/2 hour.
3. Hold on vacuum oven for 24 hours at 50°C.

Dissolution rates and offsets on MEK were measured with the laser interferometer. Experimentally, dissolution rate is measured from the amplitude and period of the reflected light intensity, and offset is measured as the difference between the reflected intensity maxima during dissolution and the reflected intensity of the bare substrate after complete dissolution divided by the difference between the maxima and minimum reflected intensities during dissolution (Figure 2).

Of the several variables tested, molecular weight and polymer composition were found to have a noticeable effect on offset. Temperature and solvent had no noticeable effect.

A. Effect of Molecular Weight

At molecular weights ( $M_n$ ) below 30,000, no offset was detected (Figure 3). Despite the experimental uncertainty, there is a distinct pattern of increasing offset with increasing molecular weight. The lower limit at which offset becomes apparent is rather close to the so-called "entanglement" or "critical" molecular weight found in viscous flow. For PMMA, the change in dependence of melt viscosity on molecular weight changes from an exponential value of unity to about 3.5 at a chain length of 208 atoms, corresponding to a  $M_n$  of  $10 \times 10^3$ . In solution, the length is increased. The  $M_n$  of 30,000 is found when the polymer is in a 30% solution of a non-volatile solvent. The inference can be drawn that the occurrence of a transition layer depends on the inability of polymers to disentangle themselves rapidly from the surface of the glassy, unswollen polymer film.

B. Effect of Polymer Composition

For some other polymers that were investigated their offset was not the same as that of PMMA. The table below lists two other polymers both having offsets less than 0.05. The offsets of comparable molecular weights of PMMA would be much larger.

<u>Polymer</u>	<u>Number Ave. M.W.</u>	<u>Solvent</u>	<u><math>\psi</math></u>	<u><math>\psi</math> for same M.W. PMMA</u>
Poly(dimethyl-itaconate)	400,000	MEK	0.010	0.20
Poly(methyl-itaconate)	400,000	Methyl Cellosolve	0.010	0.20
Poly(dimethyl-itaconate)	400,000	Methyl Cellosolve Acetate	0.012	0.20
Poly(alphamethylstyrene-monomethylmaleate)	130,000	Cyclohexanone	0.031	0.050

### C. Effect of Temperature and Solvent

Of the several variables tested, temperature and solvent were found to have no noticeable effect on offset. For PMMA ( $M_n = 360,000$ ) over the temperature range of 15°C to 30°C  $\psi$  was  $0.13 \pm 0.02$ . There is no noticeable trend in offset even though the dissolution rate increased by a factor of eight over this temperature range. For PMMA in several different solvents,  $\psi$  does not appear to vary, within experimental uncertainty.

Dissolution of PMMA ( $M_n = 360,000$ ) at 22.5°C:

<u>Solvent</u>	<u>Average Dissolution Rate, <math>\mu\text{m}/\text{min}</math> (<math>\pm 15\%</math>)</u>	<u><math>\psi</math></u>
Methyl Isobutyl Ketone (MIBK)	0.007	$0.16 \pm 0.02$
Methyl Cellosolve Acetate	0.09	$0.14 \pm 0.02$
Ethyl Acetate	0.18	$0.14 \pm 0.02$
Methyl Ethyl Ketone (MEK)	0.26	$0.13 \pm 0.02$

### CONCLUSIONS

The transition layer during the dissolution of a glassy polymer increases with the molecular weight of the polymer. It is not directly related to the rate of dissolution since MEK, which dissolves PMMA 35 times faster than MIBK, exhibits about the same optical offset effect. Work on modelling the polymer concentration profiles in the transition layer is in progress.

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Figure 1. Laser interferometry without a transition layer.

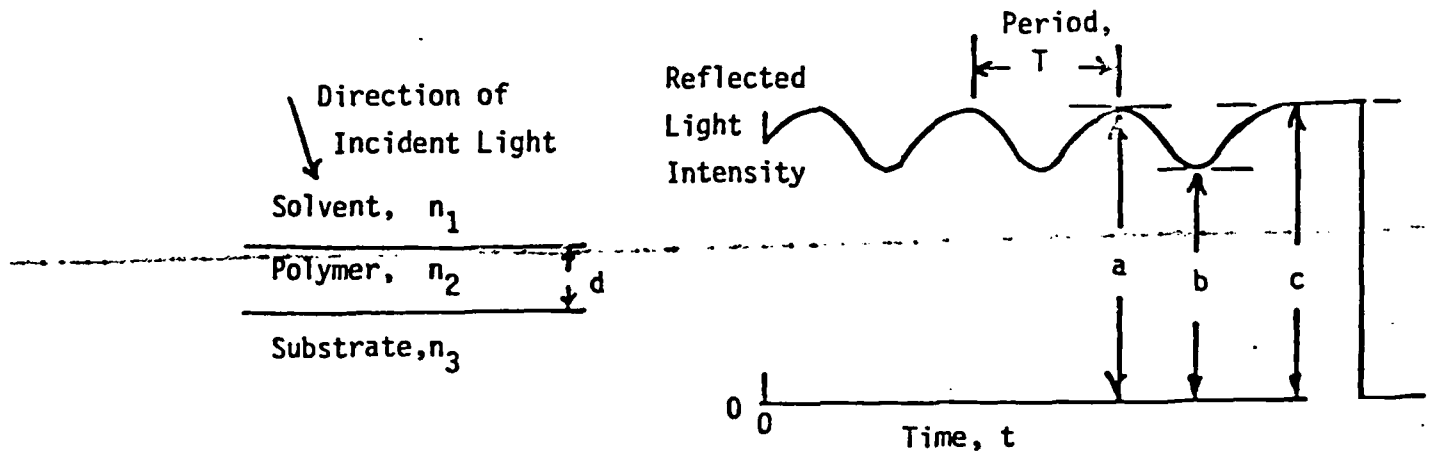


Figure 2. Interferometry with offset due to transition layer.

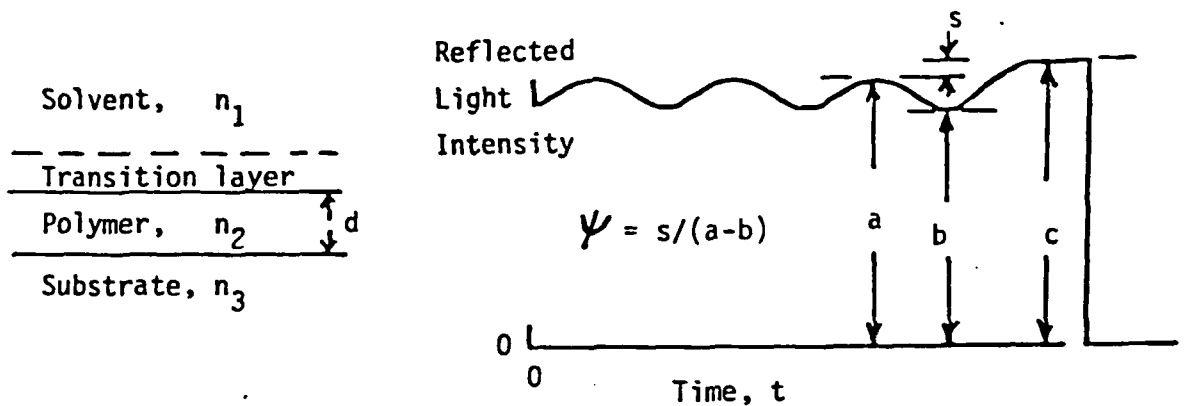
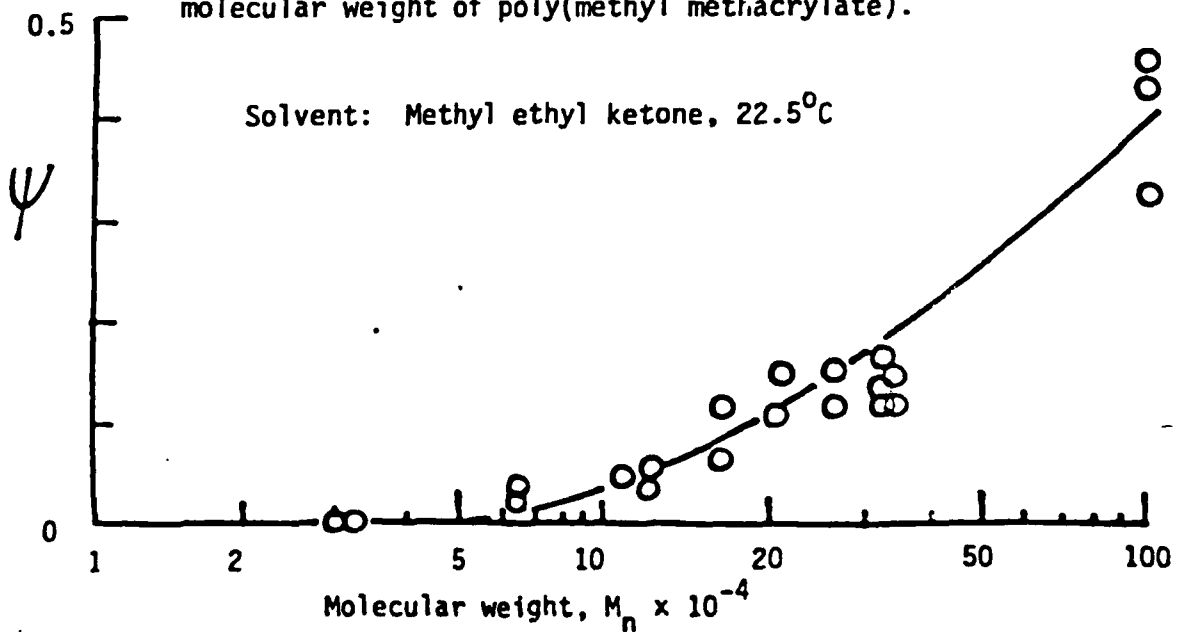


Figure 3. Increase in offset due to transition layer with increasing molecular weight of poly(methyl methacrylate).



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