

In-Plane Solvent Diffusion in a Photosensitive Polyimide

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SYNOPSIS

The diffusion of an organic solvent, *N*-methylpyrrolidinone (NMP), in a fully imidized photosensitive polyimide, 4,4'-benzophenone tetracarboxylic dianhydride (BTDA-*t*MDA), was investigated. The polyimide (PI) films were prepared by spin-coating, soft-bake, deep UV exposure, and final-baked to a peak temperature ranging from 230 to 375°C. The thickness of the final films is approximately 5.0 μm. Patterned metal was then electron-beam-evaporated through a molybdenum shadow mask over the PI surface. The rate of lateral (in-plane) diffusion of NMP in the PI covered with metal follows Fick's \sqrt{t} relationship over a temperature range of 40–85°C. The rate of diffusion was shown to increase with increasing NMP temperatures, typical of a thermal-activated process. The diffusion coefficients, as measured by the solvent penetration distance as a function of the square root of time, were found to obey the Arrhenius equation: $D = D_0 \times \exp(-Q/RT)$ cm²/s, where the frequency factor, D_0 , ranges from 0.0015 to 0.0045 cm²/s, and the activation energy, Q , ranges from 5.52–6.34 kcal/mol. Both D_0 and Q decrease with increasing PI baking temperatures. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

The use of photosensitive polyimide in the fabrication of high-density multilevel wiring schemes in the integrated circuit devices and chip-packaging structures is becoming increasingly important.^{1–4} The major advantage of using a photosensitive PI is that it can be exposed and processed like a photoresist and yet is stable enough, chemically and thermally, to be incorporated as a permanent interlevel dielectric in devices and packaging structures. Thus, the potential of reducing the number of processing steps to reduce the fabrication time and achieve low-cost production has stimulated extensive interest in the development of new formulations of photosensitive PI in various applications.^{1,5–8} Since these applications often require exposure of thin PI films (< 10 μm in thickness) to casting solvent, such as NMP, during processing, a thorough understanding of the mechanisms and kinetics of solvent diffusion in thin PI films can have a signif-

icant impact on the development of processing strategies in microfabrication.

The diffusion of low molecular weight organic solvents into a polymer matrix, which may or may not be swollen by the diffusant, has been the subject of extensive studies.^{9–18} To the best of our knowledge, most of the studies were performed on bare polymers, in which solvent diffusion and film swelling were measured in the same direction, which is perpendicular to the film surface, or in the out-of-plane direction. In these out-of-plane diffusion studies, the general observations are the following: (1) As solvent penetrates into the polymer matrix, a sharp advancing boundary is observed, which separates a glassy region ahead of the swelling front from the swollen gel behind the front. (2) Several types of diffusion processes, such as Case I (Fickian-type, penetration distance $x \sim \sqrt{t}$), Case II ($x \sim t$), or Super Case II ($x \sim t^n$, with $n > 1$), and anomalous diffusion (non-Fickian, $x \sim t^n$, where $\frac{1}{2} < n < 1$), have been described. (3) The combinations of Case I, Case II, or anomalous diffusion were observed at different time periods during solvent diffusion or when using mixed solvents in the same polymer system.^{19–21}

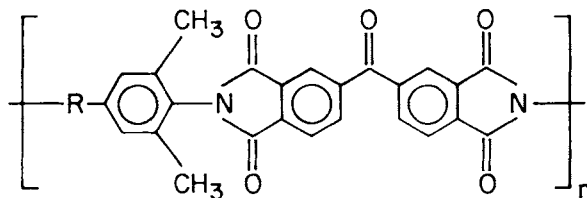
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On the other hand, the case of in-plane (lateral) solvent diffusion has been reported on the PMDA-ODA,²² isoimide,²² and soluble PI films.²³ In the in-plane diffusion studies, solvent penetration always follows Fick's \sqrt{t} relation throughout the diffusion process. The direction of in-plane NMP diffusion is always perpendicular to that of the film swelling due to the containment of the PI film by the silicon substrate. Thus, swelling is only allowed in the out-of-plane direction. In addition, the diffusion front, which separates the swollen gel from the undiffused glassy core, was shown as a low-angle boundary, as opposed to the sharp boundary generally reported in the out-of-plane diffusion studies. It seems that when the solvent is diffusing into a fresh PI in the in-plane direction, the diffusion kinetics follows Fick's $t^{1/2}$ rule where a constant diffusion coefficient is assumed.^{11,24,25}

In the out-of-plane study, the sorption of penetrant by polymer follows the Fickian-type behavior at the initial stage.^{10,26} As solvent sorption proceeds with time, solvent concentration continues to build up with time at the surface and toward the interior of the film. As a result, the diffusion coefficient is no longer a constant in the already diffused area. It becomes concentration-dependent. At the outer swollen surface, the polymer-solvent mixture contains a high concentration of solvent, which yields a high diffusion coefficient. As solvent concentration is decreased toward the interior of the film, the diffusion coefficient also decreases. It finally reaches the point where the solvent is diffusing into a fresh film. At this point, the boundary condition for the out-of-plane diffusions is analogous to that of in-plane diffusions, except that the former process is perpendicular to and the latter one parallel to the film surface.^{10,27} In the following discussions, the word "solvent" is used interchangeably with penetrant or diffusant and denotes a swelling agent exhibiting partial miscibility with the polymer.

EXPERIMENTAL

The photosensitive polyimide used in this study was prepared from the Ciba-Geigy Probimide 412 solution, which contains about 12% w/v solids and is carried in γ -butyrolactone solvent. Before exposure to deep UV radiation, this preimidized polyimide is solvent-soluble and contains benzophenone and alkyl-substituted biphenylmethane in the main chain.^{6,28} The structure is shown below:



Photocross-linking occurs upon exposure to deep UV radiation through hydrogen abstraction by the triplet benzophenone from the alkyl groups of the aromatic amine and the subsequent coupling of the radicals.⁶ The polyimide films were prepared by coating the Ciba-Geigy 412 solution at a spin-speed of 2200 rpm for 30 s on silicon wafers. Prior to coating, the silicon surface was pretreated with either a mild oxygen plasma ashing or reactive ion etching (RIE), followed by coating a thin layer of A1100, which is a silane-based adhesion promoter, to improve the adhesion of PI to silicon. The initial-coated films were prebaked at 110°C for 30 min in air to remove most of the solvent, then deep-UV-exposed in a Tamarak projection printer with a total exposure energy of 650 mJ/cm². The exposure energy was monitored with an OAI power meter with a 365 nm probe, because the polyimide formulation has maximum sensitivity at 365 nm.²⁸ After the exposure, films were baked in nitrogen at successively higher temperatures of 150 and 230°C, for 30 min each. To compare the effect of baking temperature on the rate of NMP diffusion in these films, some

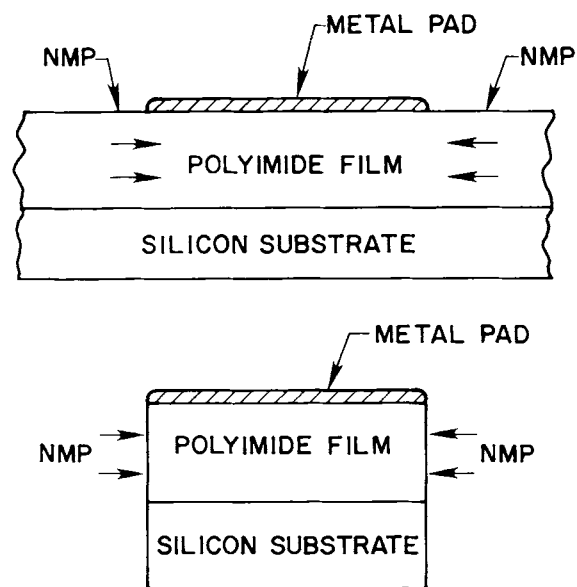


Figure 1 Two configurations of the PI/metal structures were used for the (a) out-of-plane swelling and (b) in-plane solvent diffusion studies.

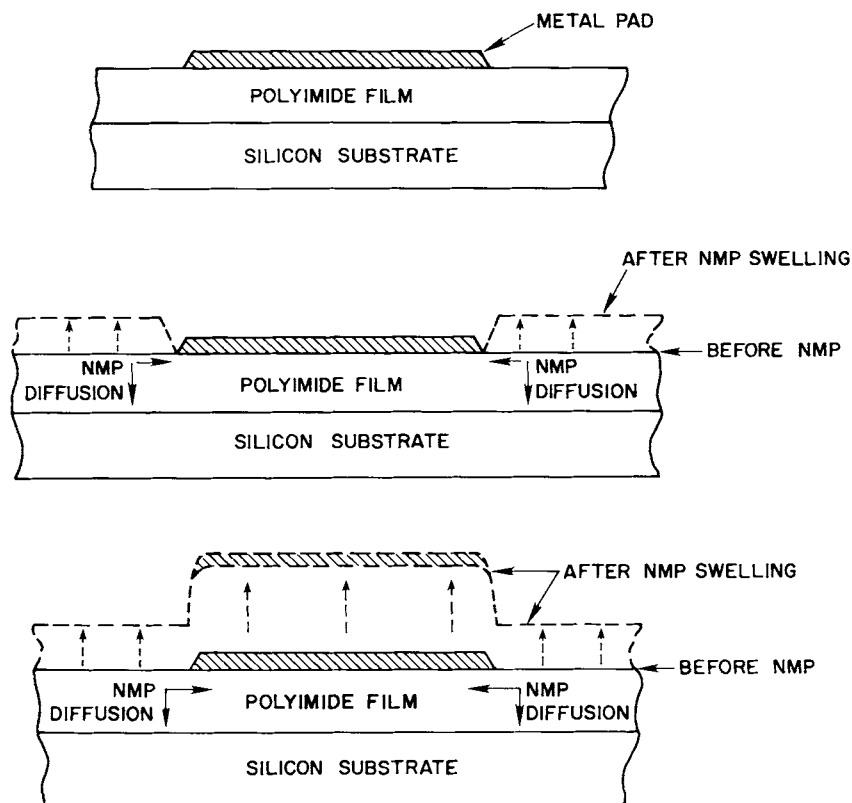


Figure 2 Schematic drawings of the solvent sorption processes in the PI/metal structures: (a) as deposited metal on PI film; (b) shortly after immersion in NMP bath, swelling first occurred in the bare PI film; (c) after prolonged immersion in NMP bath, the in-plane solvent diffusion is followed by film swelling in the out-of-plane direction.

films were heated further to higher temperatures of 300 or 375°C, each for 1 h in nitrogen. The final-baked films were approximately 5.0 microns in thickness, with the higher-temperature baked films slightly thinner than the lower-temperature baked films. After the final bake, a straight-line metal pattern, approximately 5–20 mm in width, consisting of a three-layer Cr/Cu/Cr metallurgy, was electron-beam-evaporated through a molybdenum shadow mask onto the polyimide surface.

The thickness of the Cr/Cu/Cr film was kept thin (ranging from 0.5 to 1.0 micron) such that the mechanical compliance of the metal film is insignificant to affect film swelling. Prior to metal deposition, the surface of the polyimide film was pre-treated with 5 min of argon ion-beam bombardment at the beam current of 200 mA and 800 V to promote metal-to-polyimide adhesion.²⁹ The structure of Figure 1(a) was used for the out-of-plane swelling studies. With this structure, solvent first diffused and swelled the bare PI. It then proceeded laterally into the PI covered by metal. The metal layer, serving primarily as a solvent-diffusion barrier, allowed

observation of in-plane diffusions. The structure of Figure 1(b) was designed for the in-plane diffusion studies. It was constructed by the cleavage of the silicon wafer along the (100) orientation to form a straight and almost vertical edge, which allows direct NMP access to the edge of the PI film. The solvent penetration distance was measured in reference to the cleaved edge on the silicon substrate on one end and the diffusion front on the other. The diffusion front was measurable because, as solvent diffused laterally (in-plane) into the PI film, swelling was rapidly established in the vertical (out-of-plane) direction to form a boundary profile. The solvent diffusion front and the swelling profile were both clearly replicated on the deformable metal pad that covered them.

The solvent penetration distance was measured with a Unitron optical microscope that was equipped with a traveling stage linked to a Microde II[†] digital readout unit. The swelling as well as diffusion profiles behind the solvent front were measured with a

[†] Trademark of the Boeckeler Instruments.

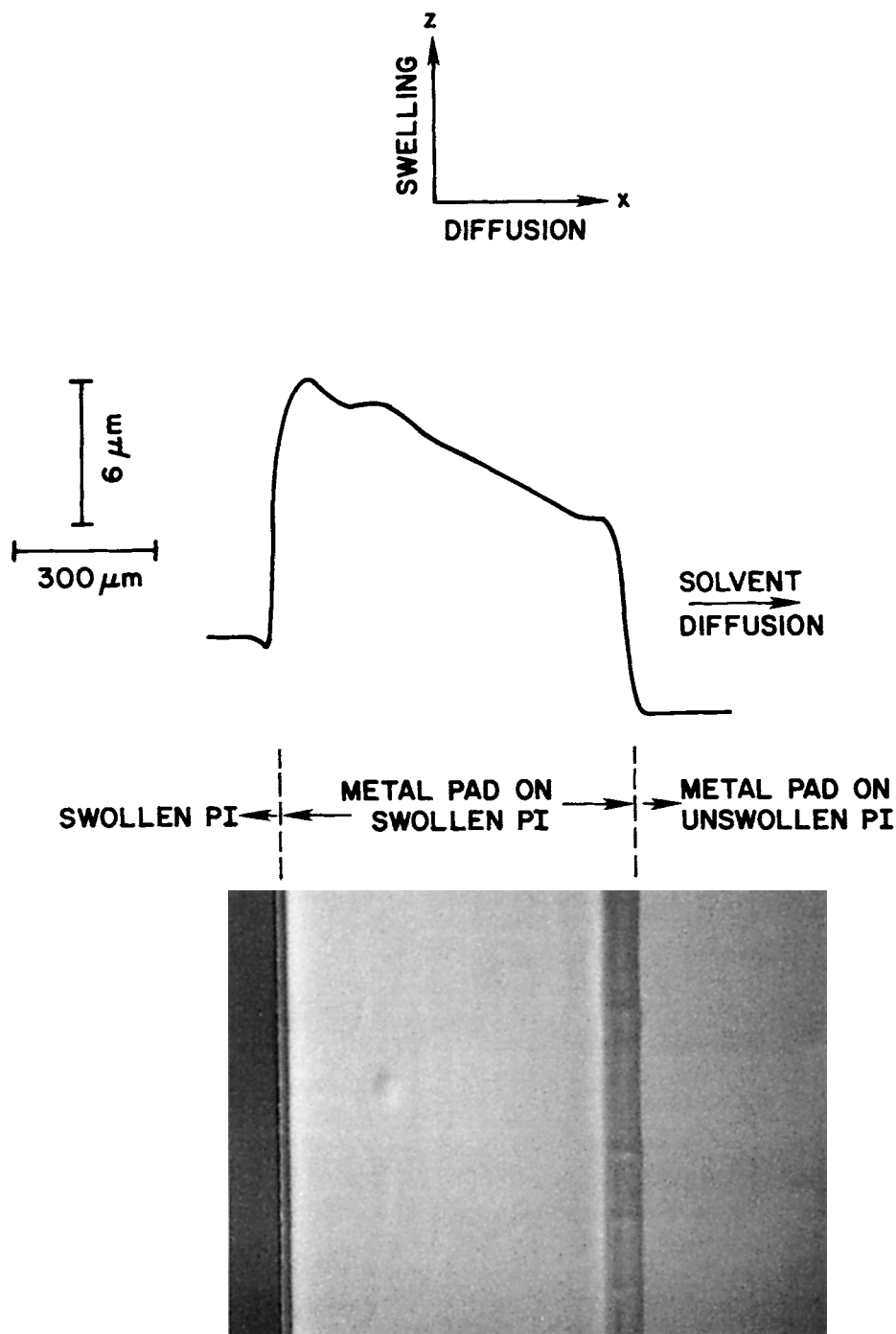


Figure 3 (a) Swelling profile of a $5.0\ \mu\text{m}$ PI film after it had been immersed in a 55°C NMP bath for 45 min. The z -scale in the profile has been significantly expanded ($Z : XY \sim 50 : 1$) as measured by a Dektak surface profilometer. (b) A magnified surface profile of the solvent diffusion front as shown in (a). The profile was measured with a fine-tipped ($2.2\ \mu\text{m}$) Dektak trace.

Dektak 3030 surface profilometer. The temperature of the solvent bath was controlled between 40 and $85 \pm 1^\circ\text{C}$, which is far below the glass transition temperature, $T_g \sim 370^\circ\text{C}$, of the photosensitive PI.²⁸

RESULTS AND DISCUSSION

The swelling behavior of the patterned PI/metal structure, as illustrated in Figure 1 (a), is schemat-

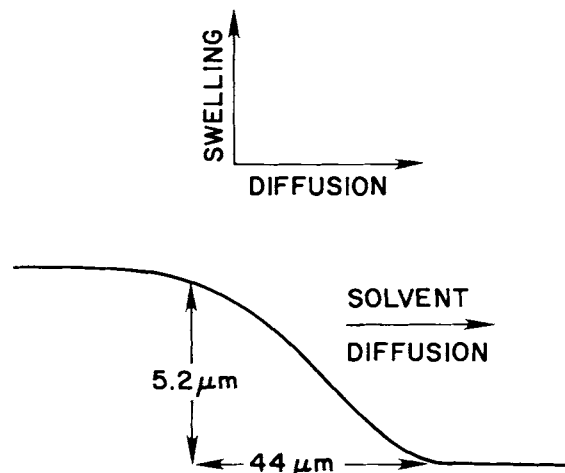


Figure 3 (b) Continued from the previous page.

ically shown in Figure 2, after it had been immersed in a warm NMP bath at 55°C for 45 min. The surface topography of the film changed drastically in the area where solvent had diffused through. The solvent was shown to first diffuse and swell the bare PI area, as shown in Figure 2(b). It then diffused laterally in the in-plane direction into PI covered with metal. Equilibrium swelling in the bare PI area was rapidly established after the films were immersed in the NMP bath, as illustrated in Figure 2(b). As lateral diffusion began to proceed under the metal pad, swelling in the out-of-plane direction, which was perpendicular to the film surface as shown in Figure 2(c), was immediately observed both optically and through a surface profiling trace. The overall profile, as shown in Figure 3(a), contains two boundaries: one due to the differential swelling between the bare PI and the PI covered with metal, and the other boundary representing the solvent diffusion front, which separates the fresh PI ahead of the diffusion front from the swollen gel behind it. A magnified surface trace of the diffusion front is shown in Figure 3(b). The tapered swelling profile indicates that a concentration gradient of the diffusant is set up along the diffusion path, which conforms with the fundamental law of diffusion. It has been reported that in many solvent-polymer systems the diffusion and the subsequent accumulation of the penetrant in an already swollen region can be several orders of magnitude higher than that into a fresh film.^{9,11-13} The concept of a concentration-dependent diffusion coefficient was developed by Crank to explain the sharp boundaries generally reported in the out-of-plane diffusion studies.

Moreover, PI swelling is shown to depend strongly on its peak baking temperatures. Table I summarizes

the values of maximum swelling measured on PI films covered with metal for films baked at temperatures of 230, 300, and 375°C, respectively. For comparison purpose, the data given in Table I were collected from PI films immersed in an NMP bath at 55°C for 45 min and measured with a Dektak surface profilometer. It is seen that PI swelling under metal is significantly higher for the 375°C baked films than that of the 230 and 300°C baked films. To prove that PI has not been lost from the bare PI to the NMP, the swollen PI films were baked at 150°C for 30 min in vacuum. The baked films exhibited no thickness loss, indicating that the possibility of PI dissolving in the NMP bath is minimum. This trend is in good agreement with the results reported previously on the same material.³⁰ It is likely that films baked at 375°C have exceeded the glass transition temperature, causing the polymer to soften and possibly damaging the photocross-linking mechanism. This may result into a more solvent-permeable film. Also noted in the data is that the amount of swelling appears to be independent of the solvent temperatures, which ranged from 40 to 85°C.

The diffusion profiles of the solvent front were traced with a fine-tipped (2.5 μm) surface profilometer. A typical trace is shown in Figure 3(b), which reveals a low-angle boundary, approximately 6.7° between the diffusion front and the film plane. In addition, the profile of the diffusion front appears to have the shape of a Gaussian error function, which is a solution to Fick's diffusion equation with a constant diffusion coefficient. Thus, in the in-plane diffusion, the diffusion coefficient (D) may reasonably be taken as a constant, because in all cases, the diffusant always moves into a fresh PI matrix, which is virtually free of any solvent. This assumption can find proof from the plots of the solvent penetration distance as a function of time, which yield a \sqrt{t} relationship. The solvent diffusion length was measured with the structure of Figure 1(b) as a function of time at four different solvent temperatures: 40,

Table I Dependence of PI Swelling, as Measured by % of Thickness Gains, as a Function of Baking Temperatures

PI Baking Temperature (°C)	% Swelling (Thickness Gain) PI Under Metal
230	91
300	96
375	226

All films were immersed in 55°C NMP for 45 min.

55, 70, and 85°C. The penetration distance was measured in reference to the cleaved edge on the silicon substrate on one end and the diffusion front on the other. The plots of the solvent penetration distance against the square root of time are shown in Figures 4, 5, and 6, respectively, for the 230, 300, and 375°C baked films. The straight lines indicate that in-plane solvent diffusion follows the \sqrt{t} relationship, characteristic of Fickian-type diffusion with a constant diffusion coefficient.

Also visible in the figures is an induction period established before the diffusion process. It is apparent from the plots that the intercepts of the straight lines when extrapolating back to the time axis are not zero. In the in-plane diffusion system, since our diffusion measurements depend solely on the swelling profiles, the induction time is probably due to the difference between the position of the true diffusion front and the swelling front, and the finite rates at which the polymer structure changes in response to the absorption of solvent molecules. It can be anticipated that the PI will absorb some amount of solvent "interstitially" following solvent diffusion, before a swelling effect begins with further solvent absorptions. The rate of response varies from PI to PI.^{18,22,23} It also depends on the interaction between PI and solvent for different polymer-solvent systems and solvent temperatures. At higher solvent temperatures, the response of film swelling after solvent

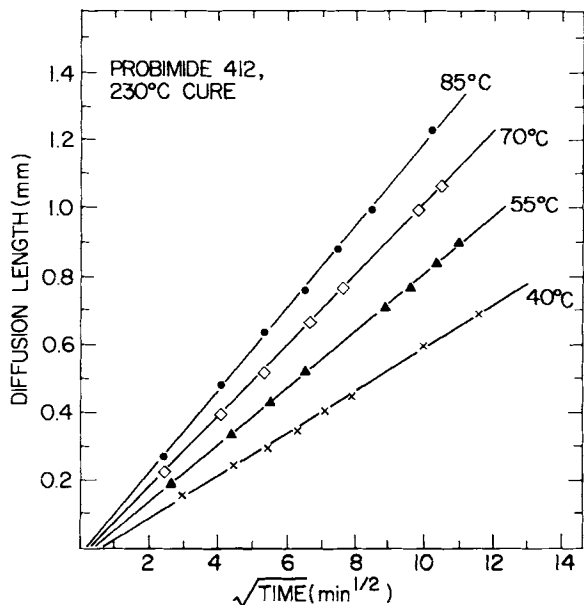


Figure 4 Plots of the solvent penetration distance as a function of the square root of time at NMP temperatures of (x) 40, (▲) 55, (◇) 70, and (●) 85°C, for 230°C baked films.

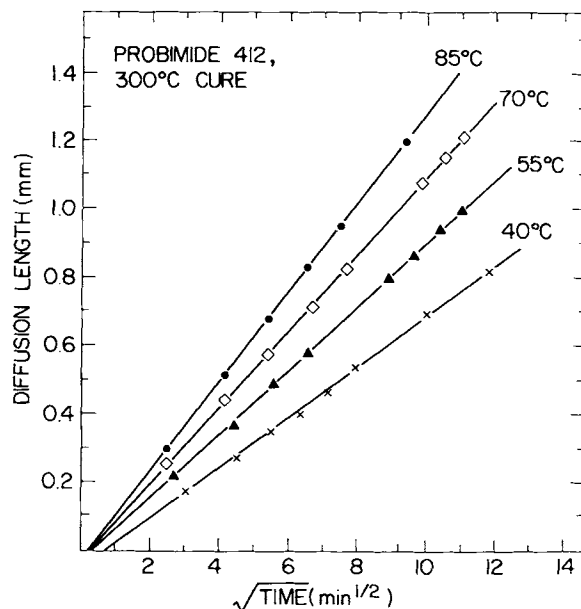


Figure 5 Plots of the solvent penetration distance as a function of \sqrt{t} at NMP temperatures of (x) 40, (▲) 55, (◇) 70, and (●) 85°C, for 300°C baked films.

diffusion is faster than that at lower temperatures. This trend is reflected in the data listed in Table II. Furthermore, the induction time is shown to depend on the measurement structures. A longer induction time was measured with the structure of Figure 1 (a)

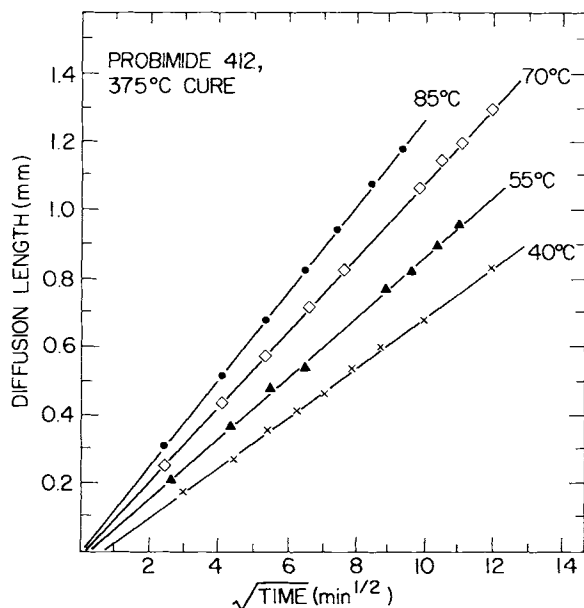


Figure 6 Plots of the solvent penetration distance as a function of \sqrt{t} at temperatures of (x) 40, (▲) 55, (◇) 70, and (●) 85°C, for 375°C baked films.

Table II Diffusion Coefficients Measured at NMP Temperatures Ranging from 40 to 85°C on 230, 300, and 375°C Baked Films

Baking temperature (°C)	NMP Temperature (°C)	Diffusion Coefficient (D, cm ² /s)
230°C	40	1.7 × 10 ⁻⁷
	55	2.9 × 10 ⁻⁷
	70	4.4 × 10 ⁻⁷
	85	6.0 × 10 ⁻⁷
$D_{230^\circ\text{C}} = 0.0045 \times \exp(-6.34 \text{ kcal/RT}) \text{ cm}^2/\text{s}$		
300°C	40	2.3 × 10 ⁻⁷
	55	3.5 × 10 ⁻⁷
	70	5.1 × 10 ⁻⁷
	85	6.9 × 10 ⁻⁷
$D_{300^\circ\text{C}} = 0.0020 \times \exp(-5.69 \text{ kcal/RT}) \text{ cm}^2/\text{s}$		
375°C	40	2.2 × 10 ⁻⁷
	55	3.3 × 10 ⁻⁷
	70	5.1 × 10 ⁻⁷
	85	6.6 × 10 ⁻⁷
$D_{375^\circ\text{C}} = 0.0015 \times \exp(-5.52 \text{ kcal/RT}) \text{ cm}^2/\text{s}$		

as compared to that of Figure 1(b). The extra time is attributed to an additional step required for the solvent to diffuse and swell the bare film in the structure of Figure 1(a), prior to proceeding with the in-plane diffusions. The sequence of diffusion steps, as measured by a Dektak surface profilometer, is illustrated in Figure 2(a)–(c). The other reason for choosing Figure 1(b) over Figure 1(a) for the in-plane diffusion studies is because the diffusion front in Figure 1(b) is always shown as a straight line, which parallels the starting solvent/PI boundary. This allows for a precise measurement of the solvent diffusion length, whereas the diffusion fronts measured in Figure 1(a) were often uneven and therefore could not be measured accurately.

Therefore, by using the structure of Figure 1(b) and assuming that diffusion occurs effectively in one dimension, that is, the gradient of solvent concentration only occurs along the x – axis, Fick's second law of diffusion now reduces to

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) \quad (1)$$

where C is the concentration of the solvent; D , the diffusion coefficient; and x , the space coordinate measured in the direction of diffusion. In the case where D is a constant, Equation (1) may be simplified to

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (2)$$

Assuming the boundary conditions of $C(0, t) = C_0$ and $C(x, 0) = 0$ apply, the solution to eq. (2) is given by^{11,24}

$$C(x, t) = \frac{1}{2} \left[1 + \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right] \quad (3)$$

where erf is the error function, of which tables are available.²⁴ From the error function table, the position of the diffusion front with $C/C_0 = 0.92$ is given by the relation

$$x = 2\sqrt{Dt} \quad (4)$$

Based on eq. (4), the diffusion coefficients at each solvent temperature were calculated from the slopes obtained on each straight line through linear regression. These data are summarized in Table II for the 230, 300, and 375°C baked films. Since the logarithms of the diffusion coefficients when plotted as a function of the reciprocals of the absolute temperature yield a straight line (Fig. 6), then the data can be fitted to the Arrhenius equation

$$D = D_0 \times \exp(-Q/RT) \quad (5)$$

Equations (4) and (5), together, quantify our diffusion process completely. Thus, the activation energy Q and the preexponential factor (frequency factor) D_0 can be obtained, respectively, from the slopes and intercepts of the experimentally determined straight lines plotted in Figure 7. The diffusion coefficients (D) of NMP in PI films cured at each baking temperature are described by the following expressions:

For 230°C baked films,

$$D_{230^\circ\text{C}} = 0.0045 \times \exp(-6.34 \text{ kcal/RT}) \text{ cm}^2/\text{s} \quad (6)$$

for 300°C baked films,

$$D_{300^\circ\text{C}} = 0.0020 \times \exp(-5.69 \text{ kcal/RT}) \text{ cm}^2/\text{s} \quad (7)$$

and for 375°C baked films,

$$D_{375^\circ\text{C}} = 0.0015 \times \exp(-5.52 \text{ kcal/RT}) \text{ cm}^2/\text{s} \quad (8)$$

From the above expressions and Figure 7, it is seen that both the activation energy (Q) and the preexponential factor (D_0) decrease with increasing baking temperatures, which range from 230 to 375°C. This is similar to a previous study conducted on the PMDA-ODA films,²² where Q and D_0 also decrease with increasing curing temperature. The values of the activation energy obtained in this study for the photosensitive PI are much lower than those

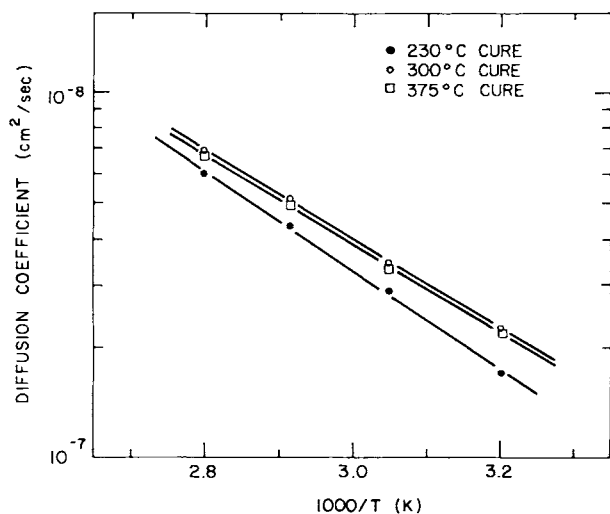


Figure 7 Arrhenius plots of the diffusion coefficients in logarithm scale against $1/T$.

for the PMDA-ODA films,²² but are significantly higher than those of the soluble PI films.²³ In all cases, it appears that the PI baking (curing) temperature may have affected the structure of the film and, consequently, the solvent diffusion process. If we compare the films baked at 230°C versus those baked at 375°C, both the rates of diffusion and the amount of swelling are higher for the 375°C baked films. The correlation between solvent diffusion and film swelling may indicate that the 375°C baked films possess a structure that facilitates both diffusions and swellings, as compared to those of 230°C baked films. It is speculated that the chemical bonds formed by photocross-linking may not be thermally stable at higher temperatures, namely, $\geq 375^\circ\text{C}$, which exceeds the glass transition temperature (370°C) of the polymer film. If this is the case, the transport of solvent molecules in the photosensitive PI would require less energy and diffuse at a faster rate in films baked at higher temperatures.^{31,32} However, the effect of the different degrees of swelling on the rates of in-plane diffusion of NMP needs to be further investigated.

CONCLUSIONS

The in-plane diffusion of the NMP solvent in the photosensitive PI follows Fick's $t^{1/2}$ relation. The diffusion coefficients were determined experimentally. The values ranged between 1.7 and $6.9 \times 10^{-7} \text{ cm}^2/\text{s}$, over the 40 – 85°C temperature range. In all cases, the rate of diffusion increased with increasing NMP temperatures, typical of a thermal-activated process. The diffusion coefficient was shown to increase, along with decreasing activation energy and preexponential factor, as the peak film baking temperature increased from 230 to 375°C .

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