Developer-induced debonding of photoresist from copper

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We describe the debonding of a polymeric photoresist film bonded to a thin copper substrate as a result of the diffusion of an organic penetrant into the polymer. The diffusion profile (measured by Rutherford backscattering spectroscopy) consisted of a uniformly swollen layer behind a sharp front which propagated into the polymer at a uniform velocity. Debonding always occurred when the front had penetrated about 12 μm into the polymer (about ⅕ its thickness). The debonding was driven by the release of elastic strain energy created by the swelling.

Introduction

Debonding of a polymeric photoresist film upon exposure to an organic developer is catastrophic until the resist has served its purpose, after which it becomes an efficient way to remove it. In this paper, we describe the debonding of a commercial dry-film photoresist, Riston™*, in various organic environments. The penetration of the organic developer liquid into the polymer causes swelling and hence introduces stress. The swollen layer penetrates into the polymer at a fixed velocity in the steady state by a non-Fickian diffusion process known as Case II diffusion [1–4]. There is an abrupt front ahead of which the penetrant concentration drops sharply to zero. The swollen polymer is rubbery; the penetrant moves rapidly through this swollen region in which the concentration gradient is very small. In this study, the front velocity was measured as a function of time by Rutherford backscattering spectroscopy (RBS). It was found that the debonding time can vary greatly depending on the penetrant, but that debonding occurs when the penetrant front has moved about ⅕ of the thickness of the film [5].

The principal penetrant investigated was 1,1,1,trichloroethane (TCE). The effect of additions of small molecules such as iodomethane was also studied; such additions were found to decrease the debonding time greatly.

Experiments

Riston was obtained from du Pont as 60-μm-thick sheets; it was cross-linked by ultraviolet radiation. Its glass transition temperature was just below 60°C, and its nominal composition was close to that of PMMA. The resist was bonded to a thin Cu foil. When this bilayer was immersed in the penetrant and swelling occurred, deflection of the bilayer composite occurred (the details of the experimental arrangement are given elsewhere) [5]. Temperature was controlled to ±1°C.

The theory of RBS [6] and the techniques used for studying TCE and iodoalkanes are given elsewhere [7].

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*Riston is a trademark of E. I. du Pont de Nemours & Co., Inc., Wilmington, DE 19898.

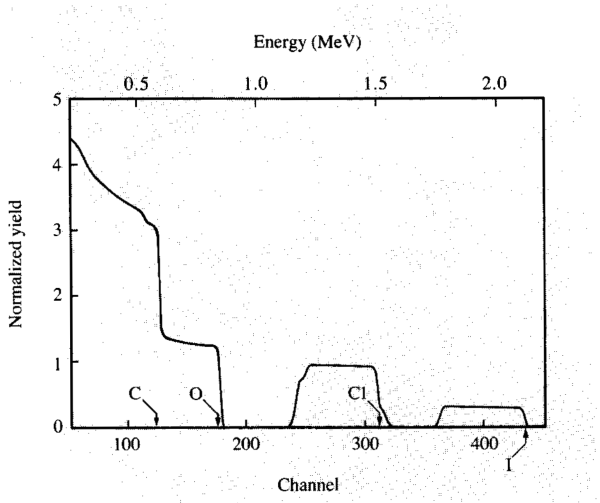

Figure 1

Simulated RBS spectrum from Riston photoresist film after a uniformly swollen surface layer 1 μm thick containing 0.1 weight fraction TCE and 0.01 weight fraction iodomethane has formed by Case II diffusion.

Spectra consisting of the yield of backscattered He^{++} ions versus their energy were obtained using a He^{++} beam of incident energy of 2.4 MeV directed at normal incidence to the sample surface. A simulated spectrum [8, 9] for the case in which the front has advanced to a depth of 1 μm below the surface is shown in **Figure 1.** The swollen layer has been assumed to contain a uniform concentration of the penetrant, in this case 0.1 weight fraction TCE and 0.01 weight fraction iodomethane. The energies of the ions scattered from the surface C, O, Cl, and I nuclei are indicated. Ions reaching the detector from nuclei below the surface experienced a larger energy loss corresponding to a greater depth. If present individually, Cl and I can be probed to a depth of ~2 μm and ~4 μm, respectively, before the spectra from each of these nuclei begin to overlap with that from the oxygen. But what makes the technique so ideal for this study is that the diffusion of an iodine-containing molecule can still be monitored independently in the presence of the chlorine-containing TCE to a depth of ~2 μm.

Results and discussion

- *Pure penetrants*

As long as no debonding occurred, increased swelling caused increased deflection as a function of time. The process is partially analogous to the bending of a bilayer composite under temperature changes where the layers have vastly different thermal expansion coefficients; such stresses (of thermal origin) cause debonding [10, 11]. In the present case swelling creates the bending and the debonding stresses in what is actually a tri-layer composite.

As soon as debonding began, the deflection decreased, rapidly falling to zero as the elastically bent Cu returned to its original shape. The debonding time, t_{db}, is taken to be the time to reach maximum deflection.

The front depth after various exposure times was determined by matching the observed RBS spectrum with simulated spectra, assuming different-thickness layers of swollen polymer; the front velocity was then obtained by fitting a straight line to the front depth-versus-time data. **Figure 2(a)** shows a plot of the logarithm of the inverse

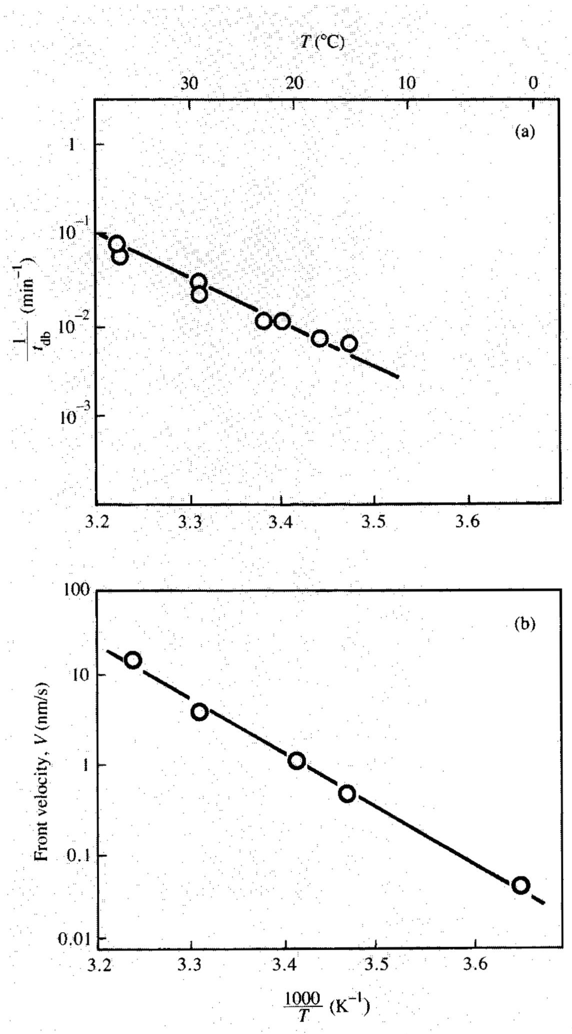

Figure 2

Reciprocal of the debonding time in TCE as a function of reciprocal temperature (a); Case II diffusion front velocity as measured by RBS as a function of reciprocal temperature (b).

debonding time in TCE vs. $1/T$. This slope is nearly the same as (slightly less than) that of the plot of the logarithm of the Case II front velocity vs. $1/T$ shown in **Figure 2(b).**

Since the velocity of the front and the thickness of the film are known, the time, t_f, required for the front to move through the entire thickness can be calculated. In all experiments, it was found that $t_{db} = 0.15$ to $0.25\ t_f$. Thus, debonding is clearly not due to arrival of the front at the interface, but rather to the elastic stresses developed at the interface as a result of the swelling in the penetrated region.

Debonding begins at the ends of the buckled plate where the stress causing debonding is highest. As the debonding progresses, the beam straightens. Prior to the beginning of debonding, the plate is actually a tri-layer composite consisting of copper–unswollen photoresist–swollen photoresist. A detailed analysis would require a knowledge of the elastic constants of all three layers as well as the swelling induced in the outer photoresist layer, which itself may be stress-dependent. Substantial further work is needed first to obtain the required experimental parameters before a thorough mechanics analysis would be quantitatively useful. The analysis of this problem is outlined in [7].

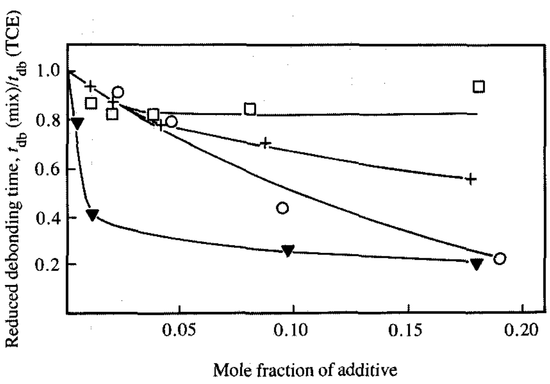

Figure 3

Reduced debonding time versus mole fraction of small-molecule additive to TCE. Additives: methanol (▼), iodomethane (○), iodoethane (+), 1-iodobutane (□).

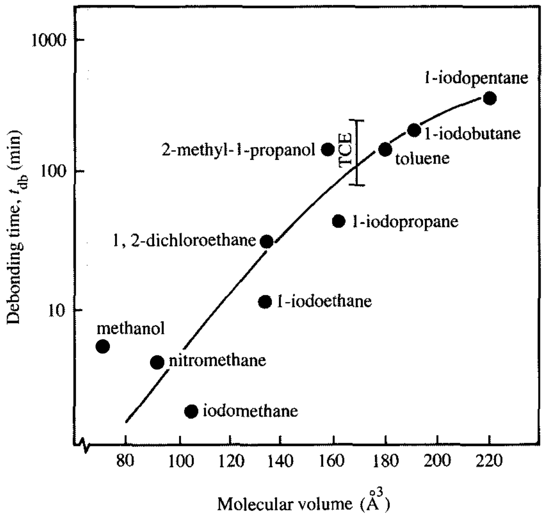

Figure 4

Debonding time as a function of molecular volume for various types of small organic molecules.

- *Small-molecule additive effects*

The addition of small molecules to the TCE decreases the debonding time, as shown in **Figure 3.** The bonding time decreases rapidly when small amounts of methanol are added, less for iodomethane, still less with iodoethane, and only marginally for iodobutane. The debonding time in pure solvents correlates fairly well with the molecular size, as shown in **Figure 4.** It is known that the front velocity in Case II diffusion increases rapidly as the size of the iodoalkane penetrant decreases [10]. This suggests that the decrease in debonding time of the polymer film as small molecules are added to TCE is due to an increase in the Case II diffusion front velocity.

To add to the understanding of the mechanism of the increase in front velocity, RBS was used to follow both the TCE and the iodomethane for the case of a penetrant containing 0.19 mole fraction of iodomethane. The details, given elsewhere [5], are summarized here. It is found that the iodomethane concentration is about three times larger in the 600-nm region *ahead* of the front than in the region behind the front (between the solution and the front). The actual concentration of the iodomethane ahead of the front is quite low (0.007 iodomethane molecules per PMMA mer) compared to the TCE concentration behind the front (0.3 TCE molecules per PMMA mer). Nonetheless, this small concentration of iodomethane ahead of the swollen front substantially increases the front velocity (by a factor of four). By analogy, it is similar to sending some rapidly moving artillery shells into an enemy position (softening it up) to increase the rate at which subsequent penetration by the infantry can be made. The iodomethane diffuses more rapidly into the glassy Riston, resulting in a decrease in the viscosity of the material (i.e., an increase in chain mobility) so that the TCE can subsequently diffuse into this plasticized "softened" region of the front more rapidly.

It is found that regardless of how far the TCE front has advanced, the iodomethane penetration depth is about 600 nm ahead of the front. One interpretation of this is that it is the nature of the region ahead of the front which determines this; thus, in the steady state, the state of stress ahead of the front is constant over time. The triaxial tension ahead of the front may be responsible for the increased solubility of iodomethane there. An alternate possibility is that the decreased concentration of iodomethane immediately behind the front is due to the large concentration of TCE there which might lower the solubility of iodomethane behind the front. Studies of the effect of pressure on iodomethane solubility at fixed iodomethane activity could help to prove or disprove the first of these hypotheses.

The Thomas–Windle model [4] of Case II diffusion has been used to explain the front velocity quantitatively [5]. This results in a front velocity V given by

$$V = \{D(\phi_m)[\partial\phi/\partial t]_{\phi_m}/\phi_m\}^{1/2}, \qquad (1)$$

where ϕ is the volume fraction of penetrant, t is time, D is the diffusion coefficient of the penetrant, and ϕ_m is the volume fraction of the penetrant at the maximum in osmotic pressure ahead of the front. This equation has been shown to predict the front velocities correctly for several iodoalkanes in polystyrene using values of D and $\partial\phi/\partial t$ determined from other experiments [12].

Let us assume that the front velocity for pure TCE is consistent with Equation (1). The effect of the iodomethane ahead of the front is to change each of the quantities for TCE in Equation (1), since the TCE is now moving into the preplasticized Riston. Future measurements are necessary to show whether this model can be extended to include such preplasticizing without further change.

- *Debonding*

Because debonding occurs when the Case II diffusion front has traversed only 1/5 the thickness, we believe that debonding is driven by the release of elastic energy stored in the swollen layer behind the front.

Summary

Debonding of a Riston photoresist film in organic liquid developer environments is caused by the elastic energy stored in the film due to a swollen outer layer which forms by a Case II diffusion mechanism.

The kinetics of debonding are thus determined largely by the velocity of the Case II diffusion front. Factors which increase the front velocity, such as small-molecule additives, also decrease the debonding time by an appropriate factor.

Small-molecule additives can markedly increase the velocity of the Case II diffusion front, apparently by "preplasticizing" the glass ahead of the front.

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