

Depth-profiling analysis of polyimide films on copper substrates

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(Received 14 December 1989; accepted 17 May 1990)

In understanding the degradation of polyimide films on copper substrates at elevated temperatures, it is important to know where in the film degradation is initiated. This study uses Fourier-transform infra-red spectroscopy in combination with a chemical depth-profiling technique to investigate the interaction of various layers of a polyimide film cast on a copper substrate. The films will be analysed under as-cast, partially cured and severely degraded conditions.

(Keywords: polyimide; copper; FT-i.r.)

INTRODUCTION

The catalytic effect of copper on the degradation of polyimide at elevated temperatures has been documented¹. Thermal degradation studies have been carried out using Fourier-transform infra-red reflection-absorption spectroscopy (FTi.r.-r.a.s.). The reflection spectra of the polymer film deposited on copper will represent various molecular structures and orientations from all areas of the film. The molecular changes that occur due to degradation by copper or oxidative effects will be a function of the distance from the copper surface. Thus, the interaction of polyimide and copper at higher temperatures will demonstrate different molecular changes depending on which layer of the film is analysed. If the layer is the interfacial layer nearest the copper, the changes will be different than if the intermediate or outer layer that has the greatest exposure to the atmosphere is studied. It is therefore important to look at what occurs at different depths of the film in order to understand the interaction of the copper and polyimide. A depth-profiling analysis of the polyimide film can provide the information needed to understand these interactions.

A depth profiling analysis can be accomplished by several different techniques. For example, the most common technique used is sputtering associated with electron spectroscopy for chemical analysis (e.s.c.a), secondary-ion mass spectrometry and ion scattering spectroscopy. By this approach, the structural changes as a function of film thickness may be studied. The process requires a bombardment of the sample surface with a beam of argon or xenon ions in order to sputter-etch the specimen surface. This is done while simultaneously probing the specimen with an electron or X-ray beam. The problem with this technique is that the ultra-high vacuum, ion bombardment or heat generation by the energy source may actually cause a molecular or orientation change in the polymer structure^{2,3}. Cupric and cuprous ions, for example, may be reduced or oxidized by the X-rays used for e.s.c.a.

The technique chosen in this paper for depth-profile analysis is the chemical depth profile^{4,5}. This method

involves repeated etching of the polymer film on copper with increasingly concentrated aqueous solutions of acid or alkali for a constant period of time. The film is examined after each etch with FTi.r.-r.a.s. For this study, an etch using a basic solution was used in order to duplicate etching techniques used in industry for microchip fabrication⁶.

The samples used in this study were both cured and uncured. The uncured sample will allow the study of films that are formed at an ambient temperature. The cured samples will demonstrate that the degree of degradation and oxidation of the copper will be dependent on the temperature and time period of polyimide exposure. It is essential to know in which layer the degradation reaction occurs in order to understand the interaction between the polyimide and the copper.

EXPERIMENTAL

Copper plates (2.5 × 5.0 × 0.2 cm, ASTM B 152, type ETP) were mechanically polished with No. 5 chrome oxide. The plates were then ultrasonically washed with acetone, a 1% solution of hydrochloric acid, three baths of distilled water, and finally acetone. The plates were then dried with a stream of nitrogen gas.

Polyimides were dissolved in dimethylformamide (DMF) and solution-cast on copper substrates with a microsyringe. The average thickness of the films was 100 nm as calculated by the concentration of the solution, the quantity used, the area of the substrate and the density of the sample. The film was air dried in a near-saturated DMF environment and then dried for 24 h under a vacuum.

After drying, the polymer sample was exposed to various thermal treatments and then etched. Potassium hydroxide (KOH) solution was used for etching. The sample was etched with different concentrations of KOH for 1 min at room temperature and then rinsed with distilled water. The sample was not moved during the etching period. Samples were etched consecutively, unless otherwise noted, in order of increasing concentration

from dilute to concentrated KOH. The concentration used was based on a percentage by volume of a 0.2 M KOH solution. Reflection-absorption spectra were recorded after each chemical etching.

A reflection-absorption attachment (Harrick Scientific) was used along with a gold-wire grid polarizer (Perkin Elmer). A Digilab FTS-14 Fourier-transform infra-red spectrometer equipped with a triglycine sulphate detector was used to record the spectra. The spectrometer was purged with dry air. The spectra collected were the average of 200 scans at a 4 cm^{-1} resolution with an angle of incidence of 75° . Spectra of samples with the polymer film were subtracted from a reference spectrum of bare copper. The ΔA shown in all spectra indicates the difference between the maximum and minimum absorbance of the spectra.

RESULTS AND DISCUSSION

No heat treatment

Figure 1 shows the spectral changes that occur when uncured poly(amic acid) (spectrum A) on copper is exposed to 2×10^{-5} , 2×10^{-4} and 2×10^{-3} M KOH solutions for 1 min at room temperature (spectra B, C and D, respectively). Although changes in the spectra are slight, certain bands are notable.

Shifts in band positions in the $1650\text{--}1546\text{ cm}^{-1}$ area are especially important when comparing the untreated

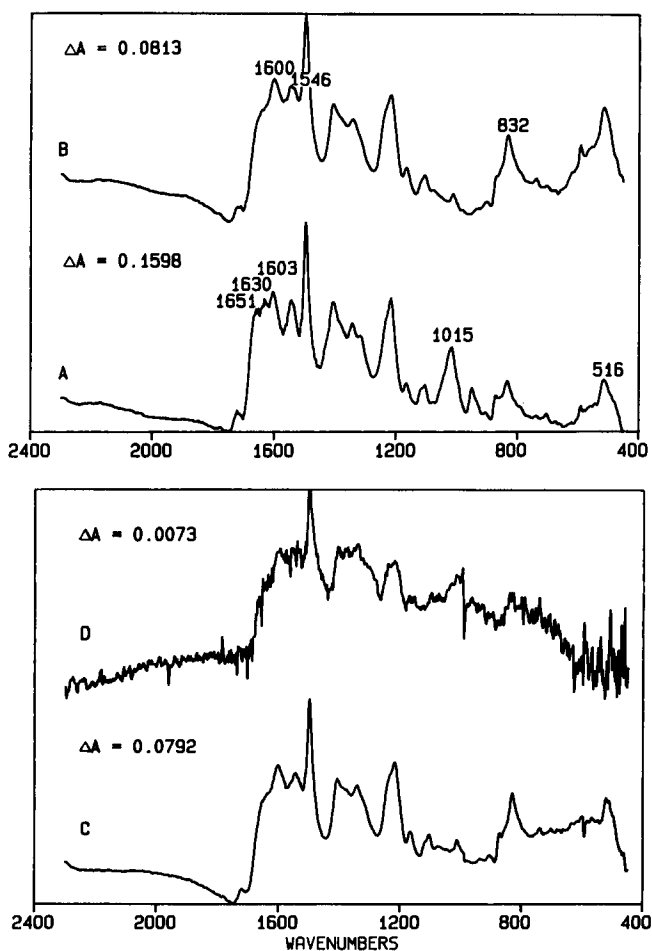


Figure 1 R.a.s. spectra of poly(amic acid) uncured: (A) unetched; (B) etched with 2×10^{-5} M KOH; (C) etched with 2×10^{-4} M KOH; (D) etched with 2×10^{-3} M KOH

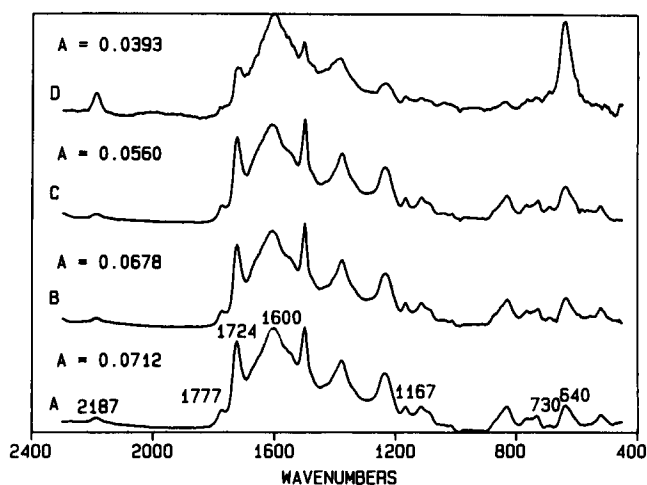


Figure 2 R.a.s. spectra of poly(amic acid) heat-treated for 30 min at 250°C : (A) unetched; (B) etched with 0.001 M KOH; (C) etched with 0.002 M KOH; (D) etched with concentrated KOH

and the 2×10^{-5} M etched samples. When the sample is etched with 2×10^{-5} M KOH, bands at 1651 and 1630 cm^{-1} decrease.

It is known that poly(amic acid) (PAA) forms a crust when dried, which prevents solvent loss from the polymer. It would therefore be expected that portions within the polymer would contain more solvent than the outermost portion near the polymer/air interface. This, however, is not the case in this study. The band at 1651 cm^{-1} (amide group) in Figure 1A is due to DMF contained within the polymer. It can be seen in Figure 1B that this band is reduced. When the outer layer of PAA is removed, immediate solvent evaporation and dilution by the etchant will occur, thus decreasing the amount of solvent in the sample. This will also explain the other changes occurring in this region. Loss in intensity of the band attributed to the solvent will also alter the intensity of other bands present in the same area.

Another change in the spectra also occurs with solvent loss. The band at 1015 cm^{-1} (C-N stretch of solvent) drastically decreases from Figure 1A to 1B. Other authors have shown that this band decreases with solvent loss for a polyimide film⁷. No further decrease in this band is seen in Figure 1C.

The increase in the 832 cm^{-1} (C-H out-of-plane bending) and the 516 cm^{-1} (stretch of 1,4- C_6H_4) bands can be seen in Figures 1A and 1B. The changes in these bands could be due to excessive hydrogen bonding that is contributed by the residual water left by etching⁵. In normal curing, both of these bands will eventually decrease in intensity.

Figure 1D represents the interfacial layer between the polymer film and the copper surface. At this point, approximately 96% of the film has been etched away. Further etching with 5% KOH solution completely etches away the remaining film. At no point in the depth profiling is any degradation of the polymer or any signs of copper oxidation seen.

Heat treatment at 250°C for 30 min

Curing at 250°C for 30 min yields much more interesting results, as seen in Figure 2. It has been seen in previous research that the time period between 15 and 30 min is the crucial point between curing and degradation of the polyimide film in air¹. After 30 min of thermal treatment,

partial curing and degradation of the film are seen in Figure 2. The bands at 2187 cm^{-1} (iminonitrile) and 1603 cm^{-1} (fused aromatic ring) have been proposed in past research to be degradation products of the polyimide, while once again 1773 , 1724 , 1380 , 1167 and 730 cm^{-1} are imide bands (Figure 2A)¹. Cuprous oxide (Cu_2O) is seen plainly in all of the spectra at 640 cm^{-1} (ref. 8).

No changes were seen in the depth profiling of the 30 min treatment until a $1 \times 10^{-2}\text{ M}$ KOH etch was used (Figure 2B). A slight increase in the intensity of the imide bands is seen at this point. Also the intensities of the bands assigned to the degradation products decrease and the band assigned to the cuprous oxide increases.

The trend of increasing imide and decreasing degradation products continues in Figure 2C with a 10% KOH etch, though changes are slight. The intensity of the copper oxide band also undergoes an increase as the film is etched away, demonstrating that more copper oxide is present near the copper/polyimide interface. Data by Tromp *et al.* using TEM has shown that copper diffuses strongly into the polyimide, and that a higher temperature will cause the copper to migrate to greater depths⁹. The increasing amount of copper oxide that is being seen here is therefore a function of the degree of etching that has been performed and the layer of the film being examined. This trend is expected to continue with further etching.

The most dramatic differences in the spectra of the samples cured for 30 min is seen with an etch using concentrated KOH (Figure 2D). At this point, approximately half of the film is etched away. Figure 2D shows a polyimide that has undergone severe degradation. The degradation products at 2187 and 1600 cm^{-1} are quite prominent. A large increase in the intensity of the Cu_2O band (640 cm^{-1}) is also seen as predicted.

Yoshida *et al.* have reported in the case of imidazole derivatives that the more oxidized structures are observed at the outermost layers of the film, whereas the less oxidized or the initial degradation products occur at the interface⁴. The difference in these results and the results seen in this paper are due to the immediate and complete chelation of the copper with the imidazole derivative, when compared with the polyimide/copper system, which limits the reaction to the innermost layers of the film. This system will allow oxygen to diffuse to the copper surface and oxidation of the copper and degradation of the polyimide can occur at this point. The copper will then be trapped within the polymer structure, preventing further migration, unless more stringent conditions allow complete oxidation of the film.

Efforts to etch more film after the concentrated etch were unsuccessful, even when the concentrated solution was left on the sample for 1 h. Past literature has noted that it is difficult to etch a fully cured polyimide¹⁰. However, it was found that polyimide on silicon that has been cured for 2 h at 400°C in air can be completely etched with 0.2 M KOH after 30 min. It is possible, therefore, that the catalytic action of copper on the poly(amic acid) has not only interrupted imidization but has also introduced crosslinking into the system. If this is true, then the N–H stretching band at 3300 cm^{-1} , which normally disappears with imidization, will remain intact and crosslinking will produce a structure that is similar to Figure 3^{11,12}. Although the area of the N–H absorption is complicated with noise and overtones from

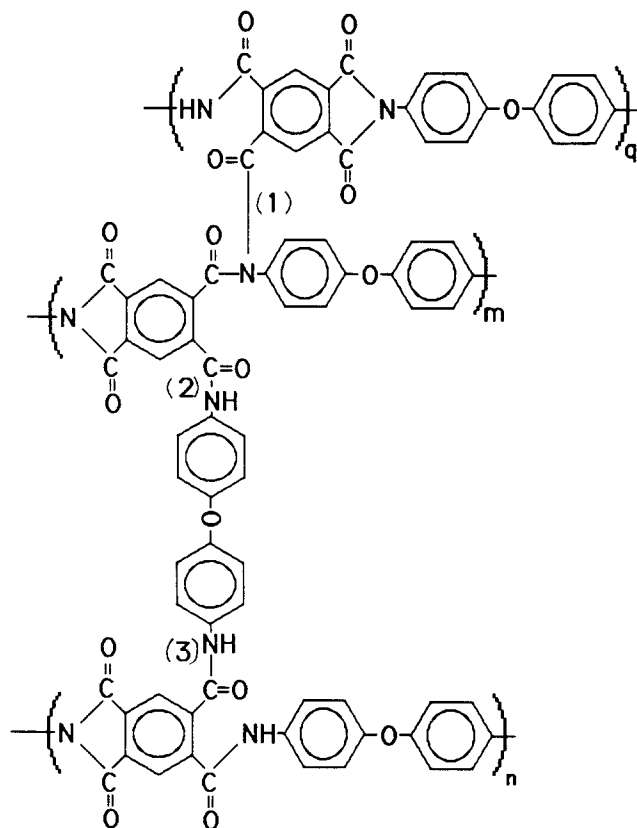


Figure 3 Crosslinking in polyimide

other constituents, it was observed that the N–H and O–H bands in Figure 2D are much stronger (not shown in the figure). At this point further research is needed to substantiate this claim.

Heat treatment at 250°C for 1 h

Figures 4 and 5 show the spectral changes that occur in PAA after 1 h heat treatment at 250°C and various etchings. Figure 4A shows that the PAA film is severely degraded as demonstrated by the appearance of the 2189 cm^{-1} band accompanied by the 2020 cm^{-1} band. Both of these bands are assigned to iminonitriles, with the 2020 cm^{-1} band appearing later in the degradation as the polymer structure changes¹³. There is also a corresponding decrease in the carbonyl bands and an increase in the 1600 cm^{-1} band, which has been shown to be a fused aromatic ring structure that is the final product of this degradation¹.

As the film is etched with a $2 \times 10^{-6}\text{ M}$ solution, all the bands associated with degradation experience a decrease in intensity and a shift of 2 to 6 cm^{-1} (Figure 4B). The hypsochromic shifts in band position are most likely due to excessive hydrogen bonding contributed by excess water left after etching. The copper oxide band at 642 cm^{-1} increases in intensity along with the emergence of the second copper oxide band at 546 cm^{-1} . This band is assigned to cupric oxide (CuO), which is known to exist as a thin layer on top of a thick layer of cuprous oxide¹⁴. This trend continues up to a $2 \times 10^{-4}\text{ M}$ etch (Figures 4B to 4D).

Previous studies have shown that, after heating at 250°C for 1 h, cleavage of the imide rings occurred and led to formation of the iminonitrile compound¹. There is, however, a gradual decrease in absorption of the nitrile bands. Apparently the cleavage of the aromatic rings,

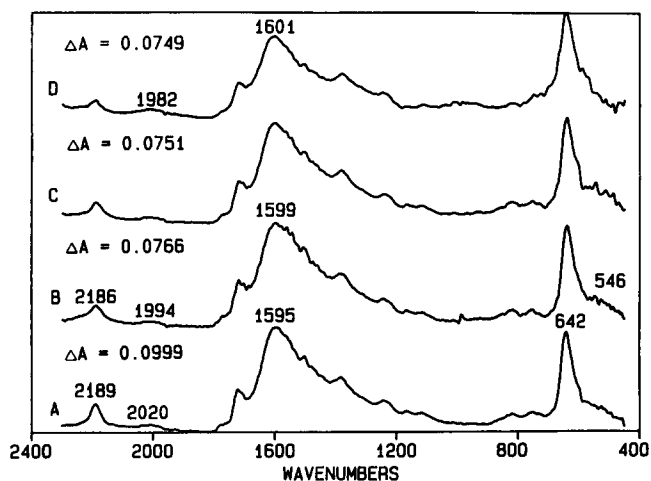


Figure 4 R.a.s. spectra of poly(amic acid) cured for 1 h at 250°C: (A) unetched; (B) etched with 2×10^{-6} M KOH; (C) etched with 2×10^{-5} M KOH; (D) etched with 2×10^{-4} M KOH

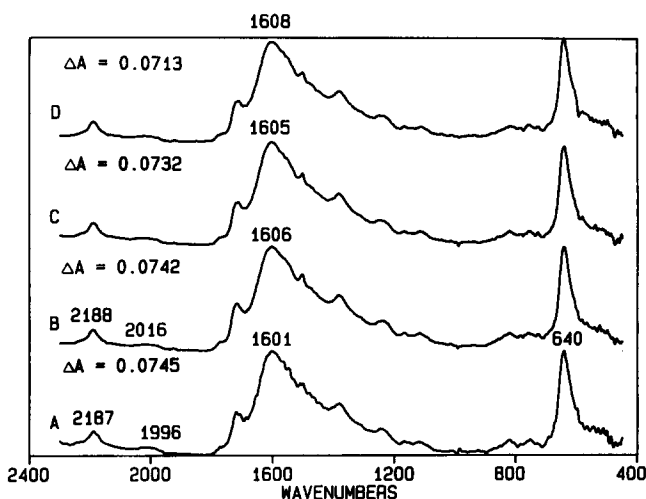


Figure 5 R.a.s. spectra of poly(amic acid) cured for 1 h at 250°C: (A) etched with 2×10^{-3} M KOH; (B) etched with 0.001 M KOH; (C) etched with 0.002 M KOH; (D) etched with concentrated KOH

which leads to the formation of the nitrile, takes place at the outer layer of the film.

However, after a 2×10^{-3} M KOH etch is done, the trend described above changes and an increase in the concentration of the degradation products is seen. The 1600 cm^{-1} band continues to shift up to a maximum of 1608 cm^{-1} . The absorption changes very little between spectrum A and spectrum D of Figure 5. The increase in intensity of these products therefore could once again be due to the greater degree of degradation that occurs at the interface in the presence of copper. No amount of etching could remove this remaining film.

CONCLUSIONS

The depth-profiling analysis of the uncured poly(amic

acid) demonstrated that the outer layer of the film consists of unimidized PAA. As the film is etched, it is found that the etching has allowed solvent escape, which results in the altered appearance of the i.r. spectra.

For the heat-treated samples, excessive hydrogen bonding caused by the residual water left after etching led to hypsochromic shifts of the bands. The nitrile compounds that result from ring cleavage are also found at the outer layer. The middle layer is made up of mixture of partially cured and partially degraded polymer, depending upon the exact site that is monitored.

The greatest degree of degradation is found at the interface, but the exact site for the oxidative degradation is not readily known. This section has shown further proof that the degradation of polyimide at elevated temperatures requires the presence of copper to initiate the degradation process. There is also the possibility of crosslinked structures that will prevent film etching even with extremely stringent conditions.

At this time further experiments are needed to determine how the mechanism of degradation changes in the film. This paper has demonstrated that the combination of chemical etching and FTi.r.-r.a.s. is useful for the study of structural changes occurring in the chemistry of a molecule on a metal as a function of the distance from the metal surface.

ACKNOWLEDGEMENT

The authors are grateful for the financial support of the International Copper Association (ICA).

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