

# Effects of Aging on Polyimide: A Study of Bulk and Interface Chemistry

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## SYNOPSIS

We are investigating the bulk and interfacial chemistry of polyimide (PI) exposed to heat and relative humidity (RH) stress (85°C/85% RH) over long periods to understand the long-term reliability aspects of PI for microelectronic applications. The PI surface chemistry and the PI-Si interface chemistry was followed with electron spectroscopy for chemical analysis (ESCA). For exposure times greater than 550 h, the PI surface exhibits significant changes in emission structure and atomic concentration. The PI-Si interface indicates little change in the PI chemistry when compared to control samples. The water-contact angle at the PI surface shows no statistically significant change as a function of exposure time. Bulk and surface chemistry were followed with Fourier transform infrared spectroscopy (FTIR) in a grazing incidence reflection configuration. There were measurable differences in FTIR spectra between aged and control samples only for the case of very thin PI layers. These results suggest that for exposure times of less than 1100 h, chemical changes in PI occur primarily at the PI-air interface for samples 1  $\mu\text{m}$  thick and greater. These changes represent a possible rearrangement of the imide structure and may be a form of deimidization of the polymer, but the final state is not polyamic acid. The PI surface chemistry changes observed with ESCA are reversible upon reheating to the cure temperature.

## I. INTRODUCTION

Polyimides (PIs) have received considerable attention due to their wide industrial application. PIs are used extensively in integrated circuit (IC) fabrication as intermetal dielectrics, passivation layers, sacrificial layers, and surface planarizers.<sup>1-5</sup> Solid-state sensing devices and multichip modules (MCMs) also make considerable use of PI.<sup>6</sup> One goal of VLSI technology is to minimize the use of high-temperature processing and wet-etching chemistry. PI can be fully prepared at temperatures of 300–400°C. It can also be plasma-etched. These features avoid both the high temperatures required for other dielectrics and wet-etch processing.

PI has several advantages that make it attractive for microelectronics applications. In its fully cured form, PI is chemically inert in the presence of many

solvents, mechanically tough and flexible, and thermally stable up to 450°C. PI is an excellent planarizer and can effectively planarize irregular surfaces.<sup>5</sup> Electrically, PI is desirable for high-speed applications because it has a low relative permittivity ( $\epsilon_r$  is 3.2–3.4 at audio frequencies<sup>7</sup>) and low loss over a wide frequency range. It also has a high breakdown voltage.<sup>8,9</sup> There are, however, some disadvantages associated with the use of PI in IC fabrication. These include sensitivity to moisture, sensitivity to variation in preparation procedures, and ionic contamination.<sup>7,10-14</sup> The hygroscopic nature of PI can lead to long-term reliability problems in ICs such as increased insulator conductivity, loss of adhesion, and corrosion.<sup>15</sup>

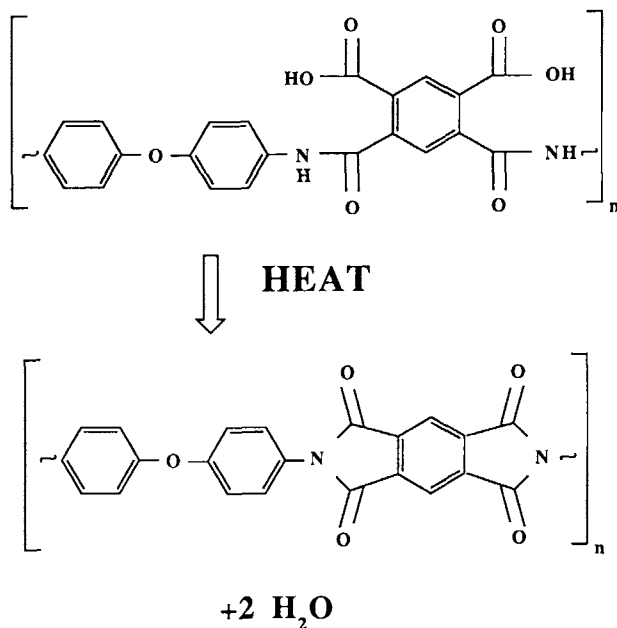
Very little work has been done to examine PI and PI-metal systems exposed to hostile environments over long periods.<sup>16</sup> This is essential to the understanding of the long-term reliability implications of introducing PI into ICs and sensor devices. We report a study of the chemical composition of PI exposed to high temperature and relative humidity

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(RH) stress over long periods. We have used electron spectroscopy for chemical analysis (ESCA), water-contact angle, and Fourier transform infrared (FTIR) spectroscopy to investigate the basic physical mechanisms that influence PI properties when stressed.

## II. EXPERIMENTAL

The PI under investigation is DuPont 2545, formed from the polyamic acid precursor of pyromellitic dianhydride (PMDA) and oxydianiline (ODA) as shown in Figure 1. The solvent is *N*-methyl pyrrolidone (NMP). The polyamic acid (PAA) was spun onto 2 or 3 in. Si wafers. The wafers were either clean bare silicon or sputter-coated with a 300 nm layer of chromium. The PAA was diluted and the spin speed was adjusted to give PI film thicknesses from 29 nm to 1  $\mu\text{m}$ . The wafers were baked at 120°C for 15 min to drive off excess solvent and then cured in a Lindbergh furnace at 300°C in a high-purity nitrogen flow at 5 SCFH for 5 h to imidize the PI. The final thicknesses were measured using either a surface profilometer (Tencor Instrument model Alpha-Step 200) or ellipsometry. Wafers were sectioned and some pieces were exposed to heat and humidity (85°C, 85% RH) while others remained



**Figure 1** Synthesis of PMDA-ODA polyimide from polyamic acid. Curing is accomplished by heating at 250–400°C.

in the laboratory environment (22°C, 60% RH) to act as control samples.

A Parameter Generation and Controls environmental chamber provides the exposure environment. This chamber can provide a wide range of temperatures and relative humidities. Its operation is extremely stable. The water for the chamber is triply distilled, IC grade water. The chamber was set for 85°C/85% RH for our study.

ESCA measurements are performed using a Perkin-Elmer 5400 ESCA machine with a nonmonochromatic MgK-alpha source ( $E = 1253.7 \text{ eV}$ ). Data are typically acquired with the wafer normal at 45° to the entrance of the analyzer. Typical operating pressure for the chamber is  $3 \times 10^{-9}$  Torr. The analyzer pass energy for the data presented is 17.9 eV with a scan area is  $1 \times 3 \text{ mm}$ . The data are smoothed and fitted, and the relative atomic concentrations are calculated using the data analysis software of the PE 5400. Low-energy photoemission from the X-ray source minimizes charging at the sample surface. Emission peak shifts due to sample charging can be referenced to the carbon 1s peak position at 285 eV.<sup>17</sup> Peak shifts for these data were less than 0.5 eV.

Contact-angle measurements are obtained with a Rame-Hart telescopic goniometer with the sample immersed in distilled water. Static contact-angle measurements are made by depositing a small air bubble on the surface of the inverted sample with a microliter syringe.

FTIR measurements are made with a Nicolet SX-740 spectrometer using a custom grazing incidence reflection apparatus. The angle of incidence is approximately 78°. All spectra are collected using a resolution of 2 wave numbers and 512 scans. The sample compartment is purged for 5 min with dry nitrogen prior to data collection.

## III. RESULTS

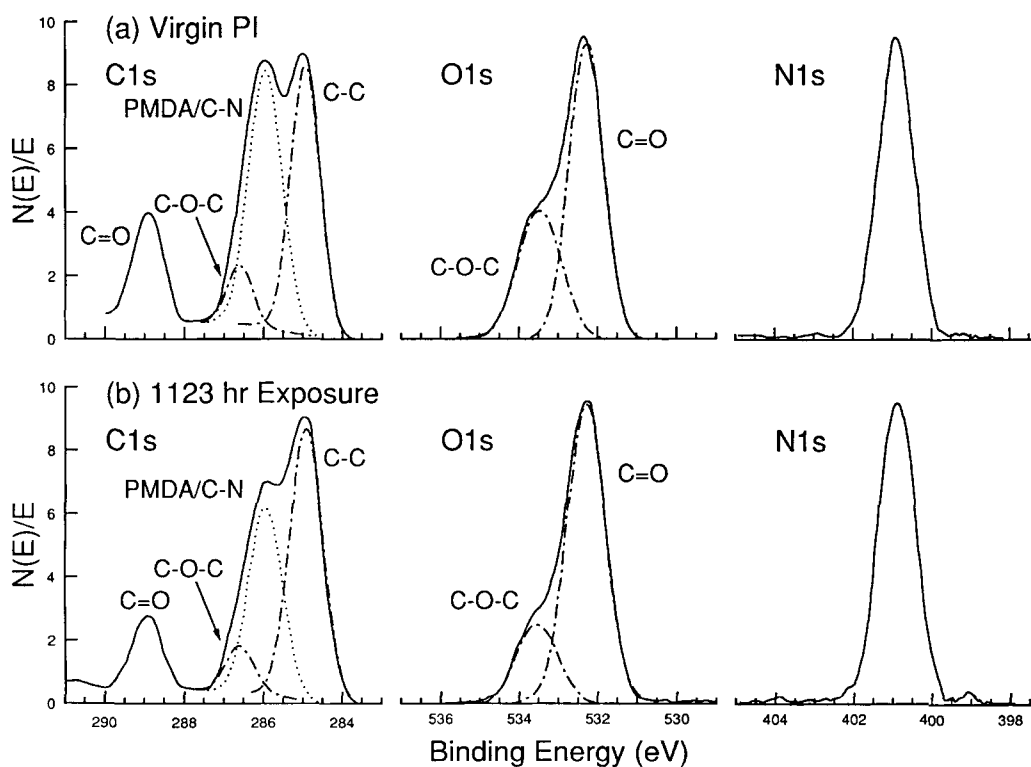
### A. PI Surface

The PI surface chemistry was examined as a function of exposure time by monitoring the carbon, nitrogen, and oxygen 1s core levels with ESCA. Core level line shapes were decomposed using summed Gaussian/Lorentzian curve-fitting software on the PE 5400. In determining the relative atomic concentrations, the PE software uses predetermined sensitivity factors that take into account photoelectric cross section, the electron mean free path, and

the instrumental transmission function.<sup>18</sup> Therefore, for comparison of the PI surface chemistry before and after exposure, the major uncertainty in area calculations for the atomic concentrations is the determination of the base line. With sufficient integration time, the spectral noise is low and the reproducibility of both peak shapes and relative peak areas for multiple measurements on the same sample or measurements on duplicate samples is generally quite high. Figure 2(a) shows high-resolution ESCA spectra for C1s, O1s, and N1s for PI control samples. The components from the curve fit for each type of bond are shown. The C—C peak in the C1s data is attributed to the two phenyl rings of the ODA part. The peak labeled PMDA/C—N is assigned to emission from the phenyl ring in the PMDA part plus emission from the carbon atoms bonded to nitrogen.<sup>19</sup> Our fit agrees well with the results of previous studies of cured PI films.<sup>19–23</sup> Area ratios are in approximate agreement with the ratios obtained by counting the number of atoms that should contribute to each peak if the intensity loss due to shake-up peaks is considered.<sup>19,21,23</sup> As with other studies, our data show a carbonyl deficiency at the PI surface. These carbonyl deficiencies have been attributed to

side reactions other than imidization. Commonly proposed side reactions include anhydride and isoimide formation and the formation of interchain imide linkages.<sup>24</sup> The intensity profiles show no significant changes between PI control samples and PI aged in the environmental chamber for up to 500 h.

When the exposure time at 85°C/85% RH exceeds about 550 h, we begin to see significant changes in bond emission. The changes become more pronounced between 550 and 750 h. For exposure times longer than 750 h, there is little additional change in the peak shapes. Table I shows mean atomic concentrations and uncertainties for several PI control samples and several samples after a 1100 h exposure. There is an increase in oxygen and a decrease in nitrogen after exposure. Figure 2(b) is the ESCA results for C1s, O1s, and N1s for a PI sample aged 1100 h. The C1s data clearly show a decrease in the peak intensity for the PMDA/C—N bond, suggesting a change in the PMDA moiety. There is a reduction in carbonyl emission and broadening of all peaks. However, the O1s data, also in Figure 2(b), show a small increase in the C=O/C—O—C ratio. Relative peak positions referenced to the C—C (285.0 eV) emission peak remain con-



**Figure 2** ESCA spectra for (a) fully cured polyimide prepared as discussed in the text and (b) polyimide after a 1100 h exposure to 85°C/85% RH. Peak assignments are discussed in the text.

**Table I** PI Surface Atomic Concentrations

Element	Concentration (%)	
	PI Unexposed	PI Exposed
C1s	74.2 ± .45	74.0 ± .23
O1s	18.4 ± .64	20.5 ± .62
N1s	7.4 ± .30	5.6 ± .66

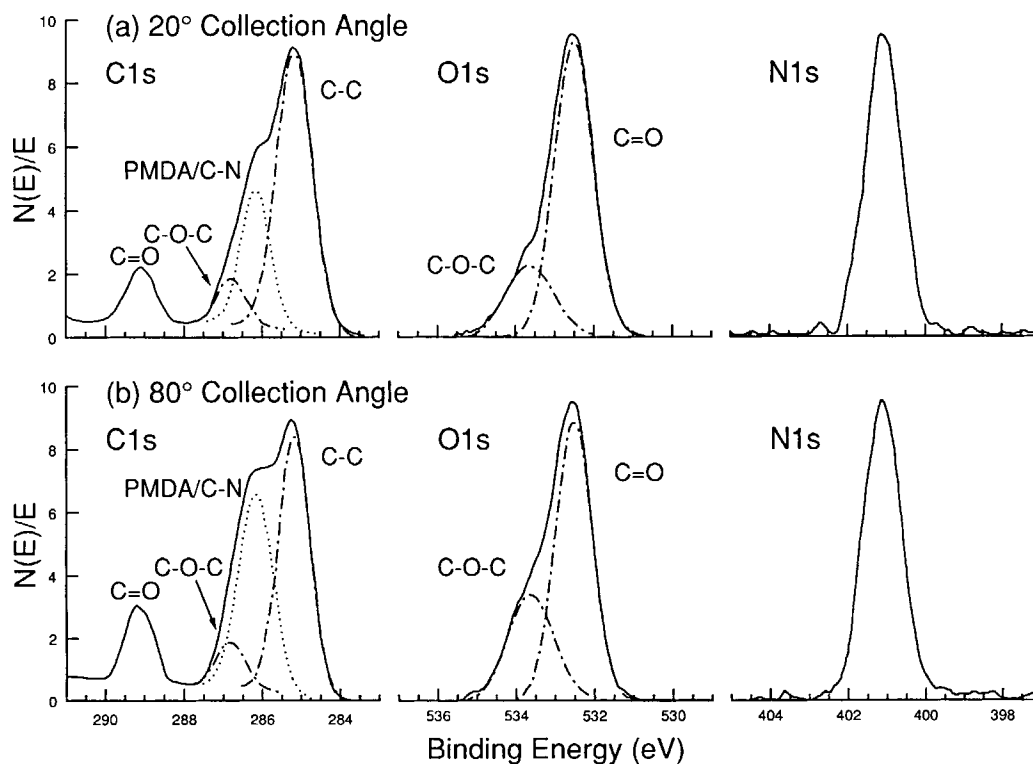
stant to within 0.15 eV. The ESCA results for aged samples are the same for PI spin deposited on either bare silicon or a chromium-coated wafer.

By changing the collection angle of the electron analyzer, ESCA can provide depth-profile information to approximately 10 nm into the PI.<sup>25</sup> Collection angles were varied from 20° to 80° with respect to the sample surface. ESCA spectra are shown in Figure 3 with analyzer angles of 20° and 80°. The degree of change in peak structure increases with a reduced collection angle showing that the changes are greater near the surface of the PI. To the depth of the ESCA probe, the PI is altered by exposure to

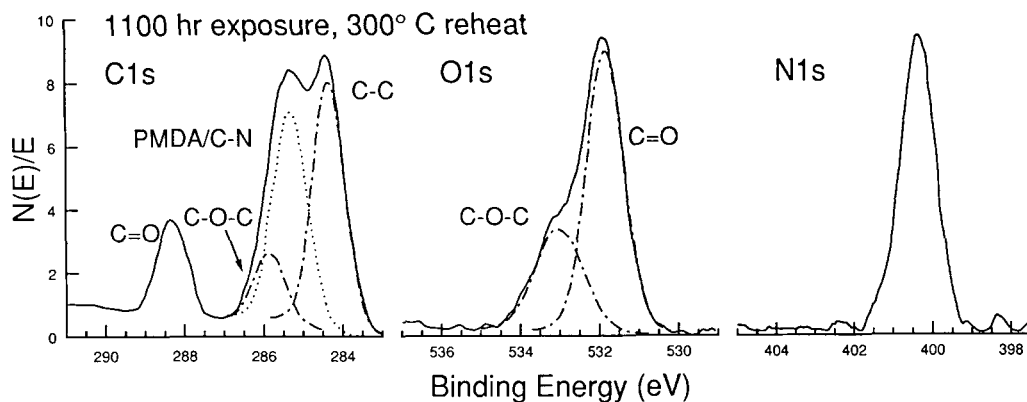
heat and humidity. However, the magnitude of the changes is greatest near the surface.

To learn if the observed changes in the PI are reversible, the aged samples were returned to the Lindbergh furnace and baked at 300°C in nitrogen flow at 5 SCFH for 1 h. The ESCA results after the bake are shown in Figure 4. Heating the aged PI samples produces ESCA spectra that are nearly identical to that of the control samples.

To explore the nature of the PI surface energy before and after aging, water-contact angles for PI, aged PI, and, for reference, PAA were measured statically. Several samples of each type were measured at several points on the surface. The results represent the average for approximately 30 measurements each for the control and aged PI. The average water-contact angles increased from 107° for PI control samples to 109° for the aged samples. Uncertainties in the measurements do not allow any conclusion to be made about whether surface energies of the PI has been changed by exposure to heat and humidity. However, similar measurements were made for PAA spin-coated and prebaked at 120°C. On the same apparatus, the average measured con-



**Figure 3** ESCA spectra for polyimide aged for 1100 h to an 85°C/85% RH environment. The data were collected with the energy analyzer (a) at 20° with respect to the PI surface and (b) at 80° with respect to the PI surface.



**Figure 4** ESCA spectra for PI that has been aged to 85°C/85% RH for 1100 h and then reheated to 300°C in a nitrogen environment.

tact angle for PAA was 130°. These results indicate that while the observed surface changes may be a form of deimidization the surface energies are not characteristic of PAA.

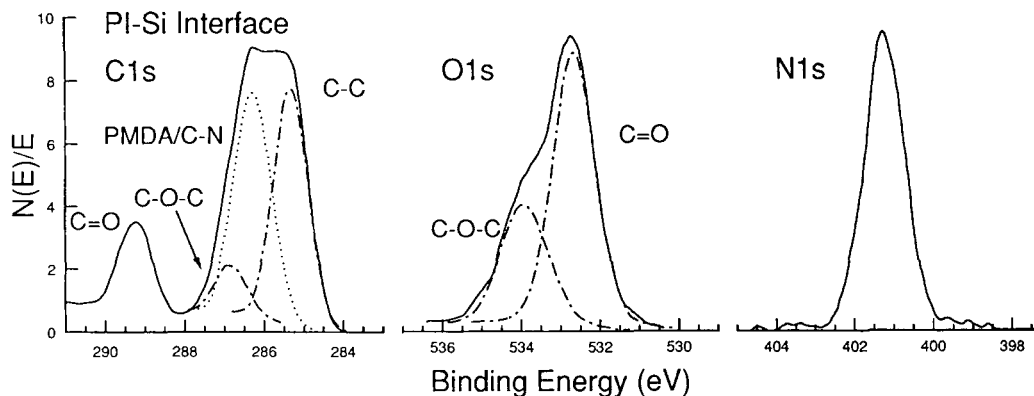
### B. Buried PI-Si Interface

PI-Si adhesion is typically poor and thus it is easy to peel the thicker PI layers from the Si substrate and examine the PI at the Si-PI interface with ESCA. Samples of PI less than approximately 1  $\mu\text{m}$  in thickness would not peel from the wafer surface in sections sufficiently large to examine. Figure 5 shows the data for a 1  $\mu\text{m}$  aged PI layer at the interface after separating it from the Si. There is some slight peak broadening; otherwise, there are no significant changes in the ESCA peak structure from the control PI form after a 1100 h exposure. Table II shows atomic concentrations for PI-Si interface scans of aged and control samples. There is a slight

increase in the relative concentration of oxygen after exposure, although the uncertainties for these measurements are higher than those for the PI surface. Angle of incidence depth profiling with ESCA exhibits no changes in the PI chemical structure to energy-analyzer collection angles within 15° of the surface. ESCA examination of the Si substrate shows that very little PI remains attached to the substrate. These data suggest that except for a small increase in oxygen content the PI chemistry at the PI-Si interface for PI thickness in the 1  $\mu\text{m}$  range is largely unaffected by exposure to heat and humidity for exposure times up to 1100 h.

### C. Bulk PI

Additional chemical characterization of PI was obtained using FTIR spectroscopy. Spectral analysis was accomplished by determining the sizes of rele-



**Figure 5** ESCA spectra for the PI-Si interface after a 1100 h exposure at 85°C/85% RH.

**Table II** PI-Si Interface Atomic Concentrations

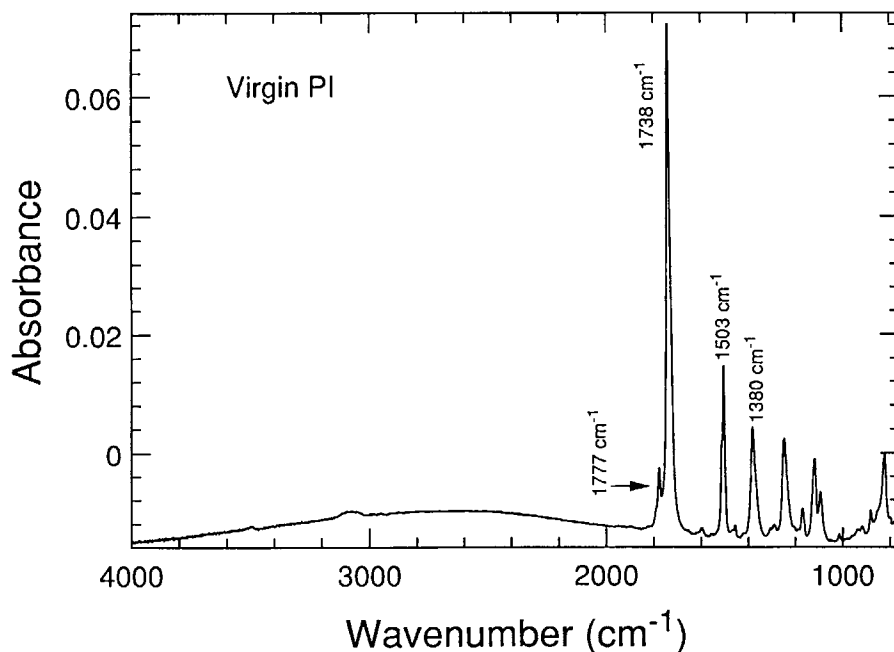
Element	Concentration (%)	
	PI Unexposed	PI Exposed
C1s	73.80 ± 1.9	72.27 ± 1.05
O1s	19.46 ± 1.86	20.56 ± 1.10
N1s	6.73 ± 0.05	7.16 ± 0.09

vant peaks by measuring peak areas. The base lines and the peak areas were determined using the software on the Nicolet spectrometer. The imide peaks used for analysis appear sharp and symmetrical. There is an absorbance band at  $1500\text{ cm}^{-1}$  that is the skeletal stretching mode for the aromatic rings in the repeat unit. This band is a reliable internal standard for comparing sizes of relevant peaks.<sup>24,26</sup> The imide structure has absorbance peaks at 1777, 1738, 1380, and  $730\text{ cm}^{-1}$ . Recently, it has been found that both the 1777 and the  $730\text{ cm}^{-1}$  peaks overlap anhydride absorption bands.<sup>24</sup> Thus, changes in the imide concentration can be determined most reliably by following the  $1380\text{ cm}^{-1}$  peak as a function of the internal standard. The 1380, 1738, and  $1777\text{ cm}^{-1}$  peaks were followed to monitor changes in the imide structure as a function of exposure. The  $730\text{ cm}^{-1}$  peak falls outside the operating

range of the detector on the spectrometer. The measurements of peak areas are estimated to be within the following limits:  $1770\text{ cm}^{-1}$ ,  $\pm 2\%$ ;  $1738\text{ cm}^{-1}$ ,  $\pm 3\%$ ;  $1500\text{ cm}^{-1}$ ,  $\pm 2\%$ ; and  $1380\text{ cm}^{-1}$ ,  $\pm 2\%$ . When the peak/internal standard ratio is used, the uncertainties are significantly improved:  $1770\text{ cm}^{-1}$ ,  $\pm 0.3\%$ ;  $1738\text{ cm}^{-1}$ ,  $\pm 1.3\%$ ; and  $1380\text{ cm}^{-1}$ ,  $\pm 0.5\%$ .

Initially, the data were taken in a transmission configuration with sample thicknesses from 300 nm to  $1\text{ }\mu\text{m}$ . There are no measurable differences in the IR transmission absorbance spectra for the aged sample and the unaged sample when normalized using the  $1500\text{ cm}^{-1}$  band. Further, there is no measurable evidence of the formation of hydroxyl groups in the FTIR data. From these data, we conclude that the bulk PI chemistry changes very little after 1100 h of aging time.

To make FTIR more surface-sensitive, a series of samples of PI on Cr was examined in a grazing incidence reflection FTIR configuration. PI thicknesses ranged from 200 nm down to 29 nm. The absorbance structure is generally consistent with the transmission measurements for all the PI samples. Figure 6 shows the absorbance spectrum for a 29 nm-thick control sample of as-prepared PI. There are relative intensity differences in some bands between the transmission and reflection sampling techniques.<sup>27</sup> To eliminate thickness effects, the PI exposed to heat and humidity is always normalized



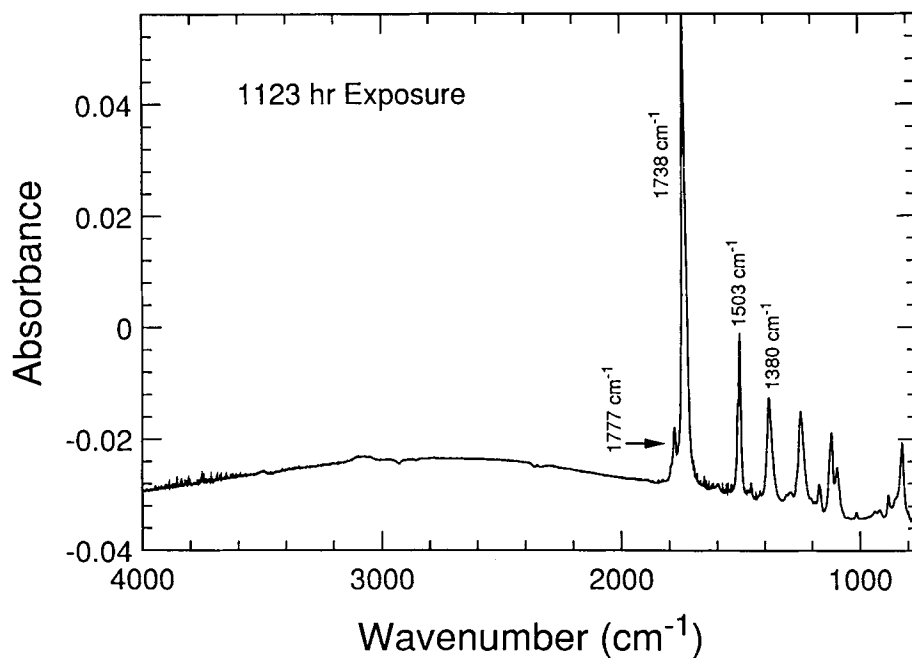
**Figure 6** FTIR grazing incidence reflection absorbance spectrum of fresh polyimide prepared as discussed in the text. The absorbance-band assignments are discussed in the text.

to a control sample sectioned from the same wafer. For the thicker PI layers, there are no measurable differences between aged and control samples. The two thinnest PI samples have PI layers approximately 29 and 33 nm and do show changes in FTIR spectra after an 1100 h exposure. Figure 7 is the absorbance spectrum for a 29 nm-thick PI sample aged 1100 h. Using the internal standard, the 1380  $\text{cm}^{-1}$  band shows an average area reduction of approximately 10% for several 29 nm samples and 4% for several 33 nm samples when compared to control samples. In addition, the absorbance band at 1777  $\text{cm}^{-1}$  shows the same percent area reduction for each sample thickness. This band is due to a symmetrical stretch mode of the carbonyls coupled through the imide structure.<sup>28</sup> The presence of hydroxyl groups produces a broad absorbance band at approximately 3500  $\text{cm}^{-1}$ . There is no indication of hydroxyl formation in these data. There is also no observed shift in peak positions in the FTIR spectra after the 85°C/85% RH exposure. The results of the FTIR transmission measurements and the reflection configuration measurements for the thicker samples suggest very little change in the bulk PI chemistry. The observed changes in the FTIR spectra for the thin PI samples support the ESCA data and we therefore conclude that the observed changes in the PI chemistry are confined to a surface layer near the PI-air interface.

#### IV. DISCUSSION

An examination of the bond dissociation energies and bond lengths in the repeat unit reveals that the C—N bond of the imide structure is the most susceptible to dissociation.<sup>29,30</sup> Assuming this bond is broken, the PI reverts to a polyamate or a polyamic acid (PAA). This structure would then be subject to further hydrolysis in the presence of water vapor.

Our spectral data for both ESCA and FTIR show no evidence of the formation of OH groups in the polymer. Although the carbonyl emission peak broadens, it can still be fitted with a single Gaussian, indicating a single, predominate chemical environment for the carbonyl functionality. Hydroxyl emission and carbonyl splitting are distinctive in ESCA studies of PAA cure<sup>31-33</sup> and in the treatment of PI with KOH and NaOH.<sup>27</sup> Our observed changes in carbon emission and the reduction in relative nitrogen emission in ESCA spectra along with the reduction of carbonyl and C—N absorbance in FTIR spectra suggest changes in the imide structure. These changes, however, appear to be something other than a simple deimidization to PAA. The measured water-contact angle for control and aged PI films is 107 to 109°, whereas the measured water-contact angle for PAA is 130°. The difference between these water-contact angles argues strongly against a deimidization to PAA due to aging. The



**Figure 7** FTIR grazing incidence reflection absorbance spectrum of polyimide after exposure to 85°C/85% RH for 1100 h. The absorbance-band assignments are discussed in the text.

increase in oxygen content along with the change in oxygen emission spectra suggest an additional oxygen species of undetermined nature. This species is under investigation.

Our ESCA results agree with other studies of PI immersed in room-temperature water and boiling water and subjected to high heat and humidity.<sup>34,35</sup> In Ref. 34, PMDA-ODA PI samples cured at 325°C were placed in an 85°C/85% RH environment for 280 h and in boiling water for 30 min. The ESCA spectra for each type of treatment show similar changes observed with the PMDA-ODA of the present study including a depletion of nitrogen. In Ref. 35, PMDA-ODA PI was immersed in room-temperature distilled water for 22 days. ESCA spectra show similar changes in the carbon and oxygen emission but no depletion of nitrogen. Neither of these experiments examined the PI with FTIR spectroscopy.

The chemical degradation of PI reported here has been correlated with gravimetric moisture uptake<sup>36</sup> and dielectric permittivity<sup>37</sup> for samples aged in our environmental chamber under the same 85°C/85% RH conditions. PI moisture uptake and PI dielectric sensitivity to moisture increase as a function of exposure time. These results suggest that the aged PI contains additional polar groups or a more polar configuration compared to unaged PI and that the aged PI is more hydrophilic.

To investigate the reversibility of the aging-induced changes, the PI was heated at the original cure temperature under nitrogen for 1 h. The resultant ESCA spectra are very nearly identical to that of the control PI samples. The reheating temperature approaches the softening temperature of this type of PI.<sup>38,39</sup> In addition, PI is not typically highly cross-linked. The reheating may cause one of two changes in the aged PI. First, the PI surface may be chemically converted back to its original structure by the elevated temperature. Second, there may be a rearrangement of the polymer chains at the elevated temperature so that PI from the bulk is brought to the surface and the PI altered by the 85°C/85% RH exposure is mixed into the bulk. In Ref. 35, a reheat of the PI at 280°C under vacuum-produced ESCA spectra is nearly identical to that of the control sample. The authors suggest that the surface consists of a polymer of lower molecular weight, but suggest no mechanism for recovery of the original chemistry by reheating. The mechanism for chemical recovery of the aged PI by reheating is under investigation.

We have conducted several experiments on PAA to attempt to reproduce a similar chemical structure

to that of aged PI and to examine the sensitivity of ESCA and FTIR to changes in the repeat unit. We have examined partially cured PI with both ESCA and FTIR. Samples cured at 200–210°C show no evidence of OH in ESCA, while the FTIR spectra indicate the presence of a small amount of OH in the polymer. Both types of spectra for these samples show that the 200–210°C cure results in lower percent imidization than do the typical higher cure temperatures.<sup>24</sup> These data show that for this application FTIR is more sensitive to the presence of OH. In ESCA spectra, the binding-energy peak for OH overlaps the binding energy peaks of the other oxygen bonds, while the OH absorbance band in FTIR is well separated from other bands. The overlaps in ESCA make detection of OH more difficult. Samples cured at lower temperatures retain enough solvent so that spectral interpretation of the state of the PI and determination of the degree of cure is questionable.<sup>†</sup> We have also reported the effects of exposure to 85°C/85% RH on PAA.<sup>40</sup> Results show that the 85°C/85% RH environment promotes imidization of the PAA but only to about 80% of that of fully cured PI. ESCA spectra of the 85°C/85% RH-treated PAA are similar to spectra of aged PI except that the PAA spectra do not show a reduced nitrogen content. FTIR spectra of 85°C/85% RH-treated PAA are similar to the spectra for aged PI but show a small absorbance band due to OH not present in the aged PI spectra.

There are several possible explanations for the observed changes in the PI. First, there may be deimidization of the PI but not of sufficient extent so that OH is detectable with either ESCA or FTIR. As mentioned above, PAA treated at 85°C/85% RH exhibits an 80% cure level, while the aged PI shows a cure level of about 90%. OH emission is not evident in the ESCA of PAA exposed to 85°C/85% RH and shows only a small absorbance band in the FTIR spectra. Second, there could be deimidization of the PI, and the result may be a polyamate of unknown composition. Formation of polyamates has been observed in PI treated with KOH and NaOH.<sup>27</sup> Finally, there may not be deimidization but instead the conformation or morphology of the PI near the surface may be changed, leading to the observed spectroscopic results. Comparison of molecular orbital calculations with ESCA results suggest that the PI im-

<sup>†</sup> The NMP solvent provided by DuPont contains constituents in addition to *n*-methyl pyrrolidone. For example, fluorine appears in the ESCA spectra in PAA after the 120°C prebake and to a lesser degree after low-temperature cures. Without a knowledge of the specific chemical composition of the solvent, we cannot be confident of interpretation of the spectra.



ide structure is opening and that cross-linking or isoimide formation is not likely.<sup>41</sup>

The presence of the PI-air interface affects the structure of the polymer and its crystallinity.<sup>42</sup> While moisture permeates the entire volume of the PI, the surface layer is most affected by aging at 85°C/85% RH. The results reported here suggest that the chemistry of the surface of the cured PI differs significantly from that of the bulk in its susceptibility to attack by moisture. Further studies are underway and will be reported subsequently.

## V. CONCLUSIONS

We have made ESCA, water-contact angle, and FTIR measurements to investigate the effects of long-term exposure of PI to heat and humidity stress. For exposure times up to 1100 h, the results show that, except for a small increase in oxygen content, chemical changes are confined to a surface layer at the PI-air interface. ESCA data show significant chemical changes at the PI-air interface. The PI-Si interface remains unchanged except for a small increase in oxygen concentration. The surface chemistry of the aged PI is characterized by a significant reduction in ESCA emission from bonds in the PMDA moiety, reduction in the relative concentration of nitrogen, and changes in the bonding of oxygen. This surface chemistry can be returned to that of original PI by reheating the aged PI to the original cure temperature. Water-contact angle measurements after aging at 85°C/85% RH suggest that the degradation product is not PAA. FTIR results exhibit changes in chemistry only for very thin layers of PI. Within measurement error, FTIR data from layers of PI greater than about 40 nm indicate no change in the bulk chemistry due to heat and humidity exposure. There are changes in the imide structure for the PI surface, but the mechanisms of change require further study. This chemical degradation has reliability implications for microelectronic systems and sensors incorporating PI as a dielectric.

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