

# Formation of Polyimide/Substrate Interfaces: Investigation of Interfacial Chemistry of Polyamic Acid with Surfaces of Silicon, Copper, and Chromium

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Received April 21, 1989

We report the results of a spectroscopic study of the initial interface formation between polyimide and a variety of surfaces. Soft X-ray photoemission spectroscopy and near-edge X-ray absorption fine-structure measurements were performed on thin layers of in situ deposited polyamic acid on clean surfaces of Si, Cu, and Cr. The results show a range of reactivity at the interface. Polyamic acid on Cr exhibited the greatest reactivity, which was further enhanced by heating, resulting in molecular fragmentation. The Si 2p core-level spectrum from a polyamic acid/Si(111) interface suggested a complex structure containing three oxidation states of Si with +1 and +2 being dominant, while the carbonyl feature in the C 1s spectrum was totally absent. Copper exhibited the least reactivity of the three substrates investigated; there is spectroscopic evidence for a carboxylate complex being formed at the interface. Similar to previous results for metals deposited onto polyimide surfaces, the main reactive moiety in these systems is initially the carbonyl group. The results for polyamic acid on Cr show striking similarity to previous results for Cr deposited on polyimide surfaces. The terminal step in the polymer/Cr reaction pathway results in molecular dissociation and compound formation at the interface.

## Introduction

There recently has been great interest in the interfacial chemistry of polymer-metal systems because of their relevance to microelectronic fabrication. Polyimide has attracted the most attention because of its favorable dielectric constant and processibility. A number of important fundamental studies have been carried out to understand the interfacial interaction of metals deposited on polyimide substrates<sup>1-6</sup> with the aim of providing a basis for the improvement of metal-polymer adhesion. However, the interfacial chemistry of polyimide deposited onto surfaces (metals, ceramics, etc.) is also important since these interfaces are not necessarily equivalent to those produced by the reverse growth sequence.<sup>7</sup> Chemical interactions may make an important contribution to the adhesion at these interfaces. In this paper we report on the initial steps of interaction of the polyimide precursor, poly(amic acid) (PAA), with clean surfaces of Si, Cu, and Cr. These systems were studied by using soft X-ray core-level photoemission spectroscopy (XPS) and near-edge X-ray absorption fine-structure (NEXAFS) spectroscopy.

Polyimide films are typically formed by the heating of a poly(amic acid) solution that has been applied to a substrate. Such a solution for one commonly used polyimide is made from the monomers pyromellitic dianhydride (PMDA) and oxydianiline (ODA) in a polar organic solvent (e.g., *N*-methylpyrrolidone) (Figure 1). The resulting solution of poly(amic acid) is usually applied by spinning onto the desired substrate and drying at low temperatures (~80 °C) to evaporate the solvent. The spun film is then cured by annealing up to 400 °C, which drives

off two water molecules per protomer and produces ring closure at the nitrogen atoms. In contrast to metals evaporated onto cured polyimide, the polyimide-on-substrate interaction is really a poly(amic acid)-substrate interaction (i.e., an acid-base interaction) and not a polyimide-metal interaction. The experiments reported here were designed to study the initial stages of reaction of poly(amic acid) with several important substrate materials. It should be emphasized that these studies were done without solvent, since solvents have important effects of their own.<sup>7</sup> The polymer overlayers were produced by use of a molecular beam deposition technique instead of by the standard solution-casting technique described above.

## Experimental Section

These experiments were performed at the National Synchrotron Light Source with a 10-m grazing incidence toroidal grating monochromator in combination with an ellipsoidal mirror analyzer.<sup>8</sup> Incident radiation struck the sample surfaces at an angle of approximately 5°, and the acceptance of the electron analyzer was 1.8 sr about the surface normal. Photon energies in the range 100-1000 eV were used to optimize the surface sensitivity of photoelectrons emitted from the samples. Instrumental resolution near the carbon K-edge was approximately 0.45 eV.

The polyamic acid films were deposited in situ under ultrahigh vacuum (UHV) conditions using the technique of Salem et al.<sup>9</sup> This technique involves the codeposition of PMDA and ODA from separate monomer sources onto room-temperature substrates. Grunze and Lamb have demonstrated the applicability of this technique to UHV surface studies.<sup>10</sup> The characterization by X-ray photoelectron spectroscopy of thick films (>100 Å) grown by this method<sup>7,9-11</sup> has shown that this technique produces good films of PAA which, upon curing, dehydrate and cyclize to films of polyimide. Therefore, this is a good method to study the initial poly(amic acid)-substrate interaction and the effects that occur upon subsequent curing, without the added complication of solvent effects.

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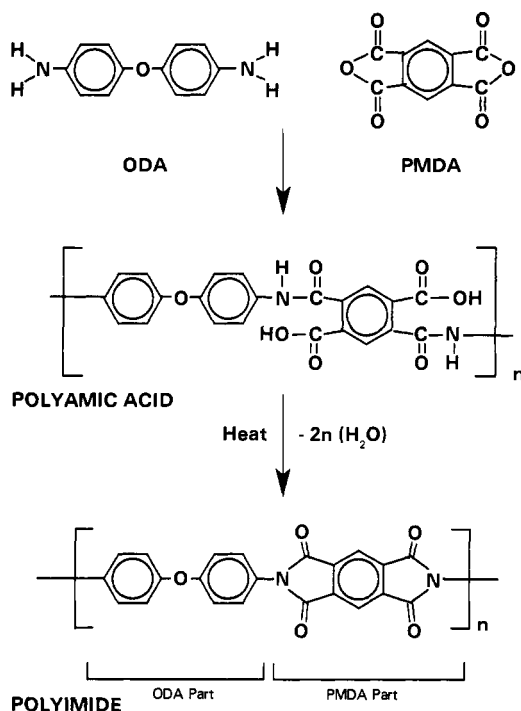
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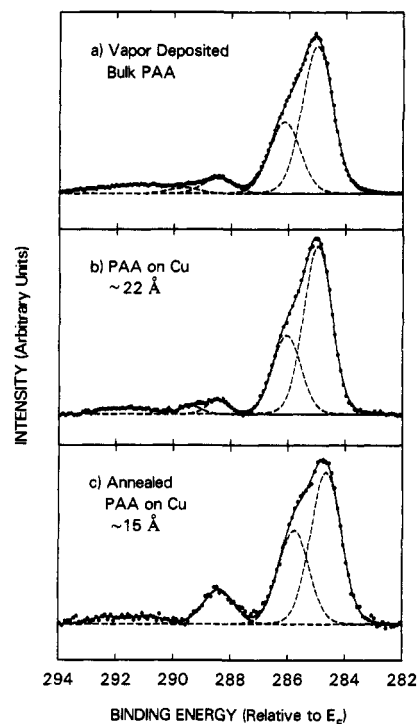
**Figure 1.** Reaction pathway for imidization of PMDA and ODA to polyimide via poly(amic acid) (PAA).

The substrates for the Si experiments were Si(111) wafers cleaned by flashing to  $\sim 1000^\circ\text{C}$ , with cleanliness judged by the appearance of a surface core-level peak and lack of O 1s and C 1s core-level peaks. This treatment produces the Si (111)  $7 \times 7$  surface. Clean Cu and Cr surfaces for PAA deposition were made by deposition of Cu and Cr from resistively heated tungsten wire baskets onto room-temperature substrates of thermally oxidized (to 5000 Å) Si wafers. The cleanliness of the metal films was assessed by O 1s and C 1s core-level spectra. The metal depositions were done in situ in a preparation chamber with a base pressure of  $8 \times 10^{-10}$  Torr. The metal and poly(amic acid) depositions were carried out in different chambers, while the XPS and NEXAFS measurements were taken in a third chamber. The chambers were connected by gate valves through which the samples were transferred by motor-controlled manipulators. The film thicknesses were estimated by the attenuation of the spectroscopic signal of a substrate core level.

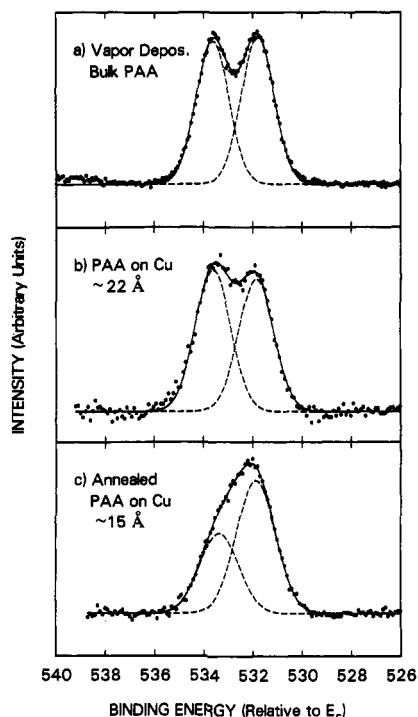
XPS data were analyzed with a least-squares-fitting program that decomposed each spectrum into individual peaks. Secondary electron contributions were treated as part of the subtracted background. O 1s and N 1s peaks were fit by using a Gaussian line shape to represent instrumental and inhomogeneous broadening. Because of the high instrumental resolution in the vicinity of the carbon K-edge, the C 1s peaks were represented by the convolution of a Gaussian with a Lorentzian line shape of full width at half-maximum of 0.1 eV to represent the core-lifetime broadening of the carbon 1s level.

## Results

We first present the results for PAA on a Cu surface. For purposes of comparison, Figure 2a shows the C 1s XPS spectrum for a bulk PAA film.<sup>11</sup> Figure 2b shows the C 1s spectrum for a thin layer ( $\sim 22$  Å) of PAA on clean Cu, which is very similar to that of bulk PAA films. There is a broad feature at  $\sim 289$  eV, which is due to the carbonyl carbon electrons in two different environments, and a more intense doublet at lower binding energy, due to the several different aromatic carbons. We assign the peaks as follows: 289.4 eV for the carboxylic acid functional group, 288.5 eV for the amide functional group, 286 eV for the ODA carbon atoms bonded to N and O, and 285 eV for the remaining arene ring carbon atoms. The O 1s and N 1s spectra (Figures 3b and 4b) are also similar to those for bulk PAA

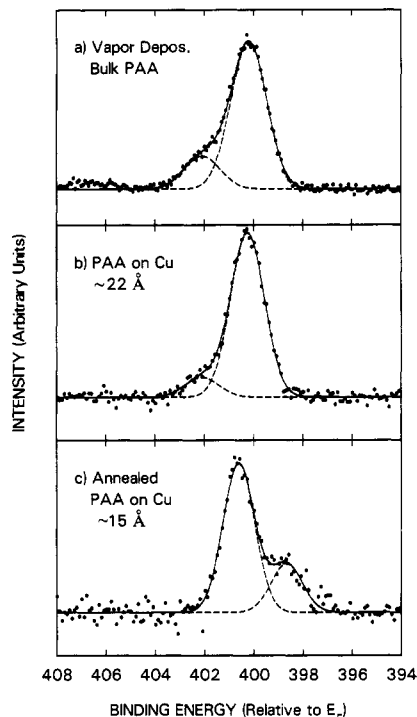


**Figure 2.** Sequence of C 1s core-level spectra for PAA deposited on Cu: (a) spectrum of bulk vapor-deposited PAA for purposes of comparison ( $h\nu = 1486.6$  eV), (b) thin layer ( $\sim 22$  Å) of PAA on Cu ( $h\nu = 345$  eV), and (c) thin layer of PAA on Cu after  $\sim 400^\circ\text{C}$  anneal ( $h\nu = 345$  eV).



**Figure 3.** Sequence of O 1s core-level spectra for PAA deposited on Cu: (a) spectrum of bulk vapor-deposited PAA for purposes of comparison ( $h\nu = 1486.6$  eV), (b) thin layer ( $\sim 22$  Å) of PAA on Cu ( $h\nu = 562$  eV), and (c) thin layer of PAA on Cu after  $\sim 400^\circ\text{C}$  anneal ( $h\nu = 562$  eV).

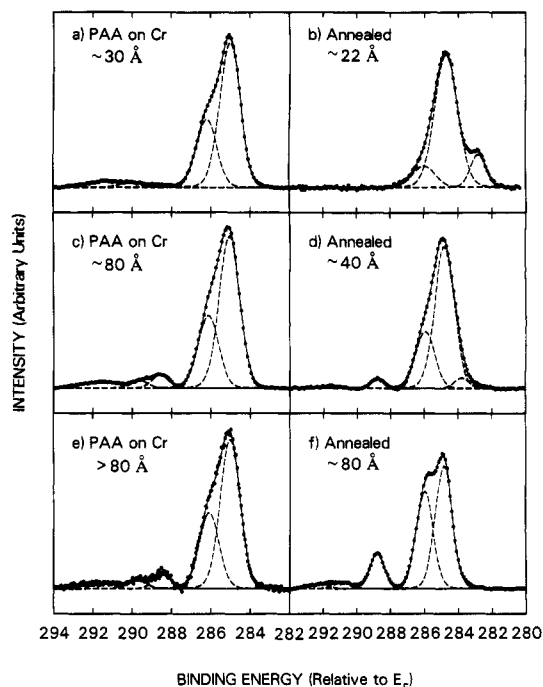
(Figures 3a and 4a). The O 1s spectrum (Figure 3b) is a doublet with a peak at 533.4 eV for the ether and hydroxyl oxygen atoms and one at 531.9 eV for the carbonyl oxygen atoms. It appears that the relative amount of signal from carbonyl oxygen core electrons is less than expected. The N 1s spectrum (Figure 4b) has one peak at 400.2 eV for



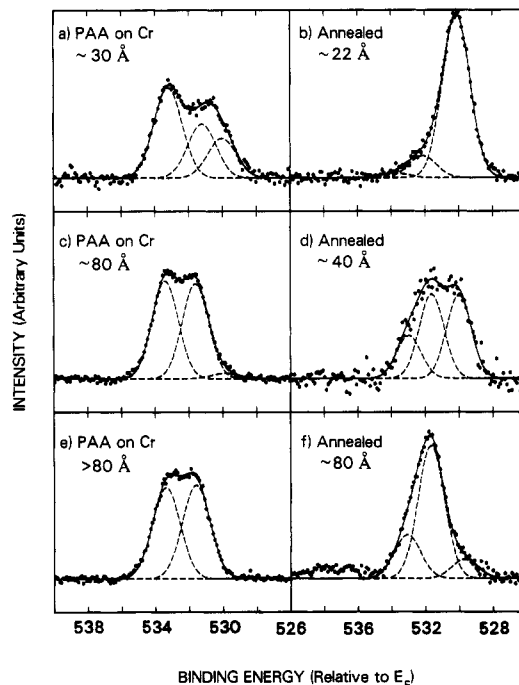
**Figure 4.** Sequence of N 1s core-level spectra for PAA deposited on Cu: (a) spectrum of bulk vapor-deposited PAA for purposes of comparison ( $h\nu = 1486.6$  eV), (b) thin layer ( $\sim 22$  Å) of PAA on Cu ( $h\nu = 460$  eV), and (c) thin layer of PAA on Cu after  $\sim 400$  °C anneal ( $h\nu = 460$  eV).

the amide nitrogen atoms and a small shoulder at  $\sim 402$  eV. After being annealed at the standard cure temperature ( $400$  °C), the thin PAA layer does not fully imidize to polyimide. There are several changes in the XPS spectra: (1) there is an increase in the intensity of substrate signal to overlayer signal, due to reevaporation or a change in packing of the film; (2) the C 1s spectrum (Figure 2c) is not identical with that of a fully imidized film, as seen in the decreased ratio of the carbonyl carbon to aromatic carbon intensity and in a lower than expected intensity at  $286$  eV; (3) the O 1s and N 1s spectra (Figures 3c and 4c) are also not characteristic of polyimide. The ratio of O 1s peak intensities is far from the ideal ratio of 1:4 expected for polyimide. The N 1s spectrum exhibits a new feature at  $398.5$  eV, which may be due to isoimide formation. This feature has also been found, but is less intense, for thick cured vapor-deposited PAA films.<sup>9</sup> The incomplete imidization at the interface is due to the reactivity of poly(amic acid) with copper, which has been reported before in studies of solution-cast films.<sup>7,12,13</sup> The interaction appears to occur via carbonyl groups, which may bond to the Cu surface, perhaps through the acid as a carboxylic complex. This would inhibit ring closure and keep the PMDA arene ring intensity centered at  $\sim 285$  eV instead of shifting it to  $286$  eV, as in the case of polyimide.

Thin layers of PAA are much more reactive with Cr surfaces. From Figure 5a one can see that the carbonyl feature is entirely missing from the C 1s spectrum. There also is a significant difference in the O 1s spectrum (Figure 6a), with the addition of a third feature at lower binding energy ( $\sim 530$  eV). The N 1s spectrum (Figure 7a) is similar to that of thick PAA films but has a small shoulder at  $\sim 397$  eV. Annealing at the standard temperature ( $\sim$



**Figure 5.** Sequence of C 1s core-level spectra for PAA deposited on Cr ( $h\nu = 345$  eV): (a) thin layer ( $\sim 30$  Å) of PAA deposited on Cr, (b) thin layer after  $\sim 400$  °C anneal, (c) thicker layer ( $\sim 80$  Å) of PAA deposited on Cr, (d) thicker layer after  $\sim 400$  °C anneal, (e) thick layer ( $\gg 80$  Å) of PAA deposited on Cr, and (f) thick layer after  $\sim 400$  °C anneal.

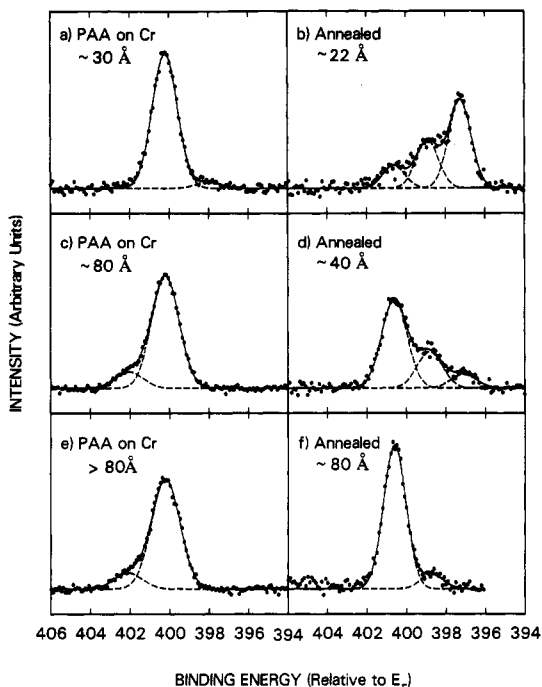


**Figure 6.** Sequence of O 1s core-level spectra for PAA deposited on Cr ( $h\nu = 700$  eV): (a) thin layer ( $\sim 30$  Å) of PAA deposited on Cr, (b) thin layer after  $\sim 400$  °C anneal, (c) thicker layer ( $\sim 80$  Å) of PAA deposited on Cr, (d) thicker layer after  $\sim 400$  °C anneal, (e) thick layer ( $\gg 80$  Å) of PAA deposited on Cr, and (f) thick layer after  $\sim 400$  °C anneal.

$400$  °C) produces dramatic effects. The C 1s spectrum (Figure 5b) shows a low binding energy feature at  $282.8$  eV, which indicates formation of carbide.<sup>3</sup> The O 1s spectrum (Figure 6b) consists almost solely of the low binding energy component, which can be assigned to chromium oxide. The N 1s spectrum (Figure 7b) now

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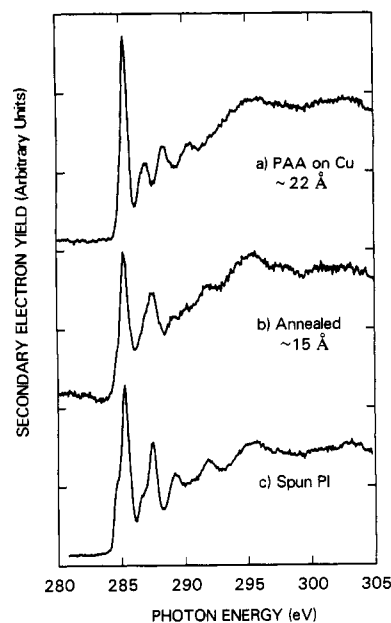
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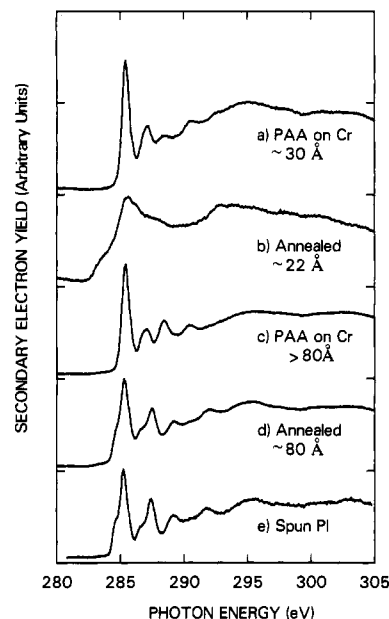
**Figure 7.** Sequence of N 1s core-level spectra for PAA deposited on Cr ( $h\nu = 460$  eV): (a) thin layer ( $\sim 30$  Å) of PAA deposited on Cr, (b) thin layer after  $\sim 400$  °C anneal, (c) thicker layer ( $\sim 80$  Å) of PAA deposited on Cr, (d) thicker layer after  $\sim 400$  °C anneal, (e) thick layer ( $\gg 80$  Å) of PAA deposited on Cr, and (f) thick layer after  $\sim 400$  °C anneal.

exhibits three features, with the main feature at 397.5 eV suggesting formation of nitride species and molecular fragmentation. Thicker deposits result in bulklike PAA films, with the underlying "reacted" features being attenuated. Upon annealing, the thick films undergo the condensation reaction to polyimide (Figures 5e,f, 6e,f, and 7e,f). Thus the growth of polyimide on Cr results in the formation of an interface chemically distinct from the rest of the polymer overlayer.

NEXAFS spectra of the carbon K-edge complement the C 1s XPS spectra by showing interfacial effects on the  $\pi^*$  and  $\sigma^*$  molecular orbitals of PAA. NEXAFS is used to probe the low-lying unoccupied excited electronic states by using tunable synchrotron radiation to excite core level  $\rightarrow$  excited-state transitions and to measure the yield of secondary electrons upon deexcitation. An explanation of the interpretation of NEXAFS spectra of organic compounds can be found in ref 14. A sequence of carbon K-edge NEXAFS spectra for deposited and annealed thin PAA on Cu is shown in Figure 8. The carbon NEXAFS spectrum of PAA can be assigned as follows: The first peak, at  $\sim 285$  eV, is typically the resonance energy for  $1s$  to  $1\pi^*$  transitions of arene ring carbon electrons.<sup>15</sup> The peak at  $\sim 287$  eV is probably from the ODA ring  $1\pi^*$  orbital resonance<sup>16</sup> and from the C  $1s \rightarrow \pi^*$  transition of the amide carbonyl group. The peak at 288 eV indicates carboxylic acid carbonyl  $\pi^*$  resonances, as reported by Outka et al.<sup>17</sup> Figure 8b shows the NEXAFS spectrum for the annealed film. It is essentially identical with that for a cured spun polyimide film (Figure 8c). Assignments



**Figure 8.** Carbon K-edge NEXAFS spectra of (a) thin ( $\sim 22$  Å) PAA on Cu, (b) annealed thin layer, and (c) solution-spun and cured polyimide (PI) for purposes of comparison (from ref 16).



**Figure 9.** Carbon K-edge NEXAFS spectra of (a) thin ( $\sim 30$  Å) PAA on Cr, (b) annealed thin layer, (c) thick ( $\gg 80$  Å) PAA on Cr, (d) annealed thick layer, and (e) solution-spun and cured polyimide (PI) for purposes of comparison (from ref 16).

for the  $\pi^*$  resonances in the polyimide spectra are taken from ref 16. The lower energy shoulder on the 285-eV peak is contributed by the PMDA ring resonance. The 285 eV resonance is assigned to the ODA ring carbon atoms not bonded to oxygen or nitrogen. The lower energy shoulder at  $\sim 287$  eV arises from the C  $1s \rightarrow \pi^*$  transition for the ODA carbon atoms bonded to oxygen and nitrogen. The peak at 287.5 eV is assigned to the carbonyl carbon  $\pi^*$  resonance.

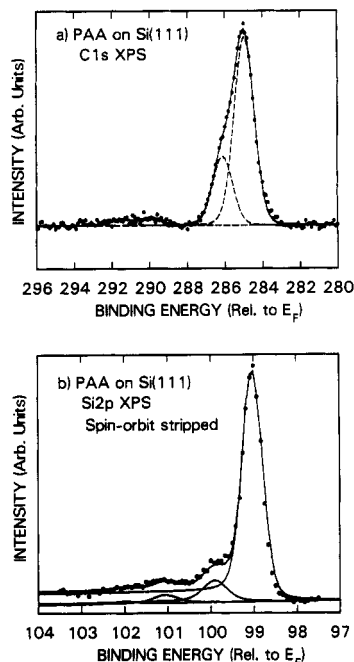
Figure 9a shows the NEXAFS spectrum for a thin film of PAA on Cr. The carbonyl  $\pi^*$  peak is quite diminished in comparison to that in Figure 9c (thick PAA on Cr). When the specimen is annealed, the spectrum (Figure 9b) becomes broad with loss of all sharp  $\pi^*$  features. This indicates a large amount of molecular dissociation. The shoulder at low energy may be due to chromium carbide.

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**Figure 10.** (a) C 1s and (b) Si 2p after deposition of 4 Å of PAA on Si (the Si 2p<sub>1/2</sub> spin-orbit component has been subtracted for clarity).

**Table I.** Energy (electronvolts) and Intensity Relative to Elemental Si 2p<sub>3/2</sub>

	Si				
	+0	+1	+2	+3	+4
energy	0.00	0.9	2.0	3.0	
intensity	1.00	0.12	0.05	0.02	0.00

Figure 9d shows that the spectrum for an annealed thick film is virtually identical with that for a cured spun polyimide (Figure 9e).

Finally we present the results for the initial interface formation on a Si (111) 7 × 7 surface. Similar to the PAA/Cr case, the C 1s spectrum (Figure 10a) is essentially devoid of the carbonyl feature characteristic of bulk PAA. The O 1s and N 1s spectra also do not indicate the presence of PAA at the interface. The most interesting observation in the PAA/Si system is in the silicon core-level spectrum. In most previous studies and in the Cu and Cr work reported here, it has been difficult to observe dramatic changes in the substrate core levels. These levels are usually broad and the observed chemical shifts are small. However, the Si 2p spectrum (Figure 10b) displays very interesting and complex behavior. The initial interaction produces three new oxidation states: in decreasing intensity, +1, +2, and +3.<sup>18</sup> Table I summarizes the energies and intensities of these features. The +1 state is the largest. This is may be the interaction that results

(18) For a review of core-level XPS of Si interfaces, see: Himpsel, F. J.; Meyerson, B. S.; McFeely, F. R.; Morar, J. F.; Taleb-Ibrahimi, A.; Yarmoff, J. A. *Proceedings of the Enrico Fermi School on Photoemission and Absorption Spectroscopy of Solids and Interfaces with Synchrotron Radiation*, Varenna, North Holland, 1988, in press.

in the loss of carbonyl signal in the C 1s and O 1s spectra. However, there is significant Si +2 (and some +3), which may indicate that some part of the PAA interacts through two Si bonds and disrupts Si-Si bonding.

## Discussion

There are a number of conclusions that can be drawn readily from this work. The initial interaction is room-temperature chemisorption, which involves reduction of the PMDA part of PAA via one or more of the carbonyl groups. This is manifested by the reduction of the carbonyl signature in both the C 1s and O 1s spectra. In the weakly reactive system (Cu), incomplete imidization at the interface is observed upon curing. We suggest this is due to carboxylate formation at the interface. A carboxylate complex is the initial reaction product in a reaction that results in eventual cuprous oxide precipitation when solution-spun PAA films on Cu are cured.<sup>7</sup>

There are a number of striking similarities between the case of the interface of PAA on Cr surfaces investigated here and the Cr on polyimide surface studies of ref 5, both for the initial room-temperature interaction and for the subsequent enhancement upon annealing. Core-level and NEXAFS spectra for the initial PAA/Cr interface are similar to those for small (submonolayer) amounts of Cr on polyimide. Likewise, when annealed, thin PAA on Cr produces spectra very similar to those for thicker Cr deposits on polyimide. In highly reactive systems (Cr) we eventually see formation of carbide, nitride, and oxide species, which implies molecular fragmentation. Further deposition of PAA over this "reacted" interfacial layer and subsequent annealing result in formation of good polyimide film. An important extension of this work will be to investigate the interface formation starting with an oxidized Cr surface, as would be the case in real processing.

The results for PAA on Si show the complexity that can be found in polymer/metal interfaces. Three chemical states of Si are induced by interaction with PAA. There are a number of possible explanations. There may be more than one geometric adsorption site, the interaction may involve more than one reactive functional group on PAA, there may be a stepwise interaction pathway, and there could be more than one bonding configuration. These results suggest that further work on the Si system, particularly annealing experiments, would be very interesting.

Finally, the relevance of this work to adhesion is clear. Comparison of adhesion of Cu and Cr to polyimide has shown greater strength of Cr over Cu, as well as the greater adhesion of interfaces of polyimide polymerized onto Cu and Cr, than of Cu or Cr evaporated onto polyimide.<sup>12,13</sup> On the basis of our results, we also predict that the polyimide/Si interface is strong.

**Acknowledgment.** Research was carried out in part at the National Synchrotron Light Source, Brookhaven National Laboratory, which is funded by the U.S. Department of Energy, Division of Materials Science and Division of Chemical Sciences. Numerous discussions with Drs. Joachim G. Clabes and Martin J. Goldberg have been stimulating during the course of this work.