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Vasile, M. J., & Bachman, B. (1989). Aluminum Deposition on Polyimides: The Effect of in situ Ion Bombardment. *Journal of Vacuum Science & Technology A, 7*(5), pp. 2992-2997. Wiley.
The definitive version is available at https://doi.org/10.1116/1.576305

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Aluminum deposition on polyimides: The effect of *in situ* ion bombardment

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(Received 31 October 1988; accepted 8 April 1989)

The chemistry of the Al polyimide interface is examined by x-ray photoelectron spectroscopy sputter profiling. Al deposited on polyimide films without an *in situ* Ar backsputter shows a clearly defined 50-Å Al_2O_3 layer just prior to the polyimide. This layer is identified by the O/Al atom ratio at 1.5, and the binding energy of the Al $2p$ transition. There is a clear separation of the Al/Al_2O_3/polyimide layers in the sputter profiles. Deposition of Al on polyimide surfaces after Argon backsputtering produces a diffuse Al/polyimide interface with no Al_2O_3 present. There is evidence in the Al $2p$ spectra for Al–C or Al–O–C type bonds, while the C $1s$ spectrum clearly has a metal carbide component. Increased adhesion of Al to polyimide surfaces with Ar backsputtering may be due to the differences in chemistry observed in these two instances.

I. INTRODUCTION

The bonding of thin metal films (such as Al) to polyimides is an area of considerable importance and interest in microelectronic processing.[1–3] The adhesion of metal to the polyimide is critical, as well as the diffusion or lack of diffusion of the metal into the polyimide at elevated temperatures. The bonding of metals at polymer surfaces is a subject that has received considerable attention in recent years,[4] particularly metal–polyimide bonding as studied by electron emission spectroscopy. The general picture for the interaction of metals such as Cr, Ti, and Al is reasonably well established by surface experiments in UHV.[5–18] The metal–carbonyl interaction takes place at coverages less than one monolayer, while at uniform coverages of one monolayer or larger, there is an interaction with the carbonyl groups and with the arene carbons through the π-bonded electrons. Similar results have been found in a high-resolution electron energy-loss spectra (HREELS) study of the Al/polyimide interface in ultrahigh (UHV).[19]

The surface experiments in UHV present us with conclusions about bonds which are formed under very carefully controlled conditions, with almost no possible effect of residual gases. These are not the vacuum conditions that prevail when sputter-depositing Al onto polyimide in microelectronic fabrication, and the picture of chemical bonding derived from the UHV experiments may not be applicable. Experience has shown that improved adhesion of Al to polyimides results if the polyimide surface is sputtered with argon prior to Al deposition. We are left with the question of what the chemical nature of the Al/polyimide interface is when Al is deposited under these conditions. Does the argon sputtering change the polyimide surface so that no carbonyl functions are left? If so, the improved adhesion must result from stronger chemical bonding between Al atoms and constituents of the polyimide, or from a surface area increase due to roughening. Do the residual gases have any effect? Is the argon sputtering in the Al deposition chamber sufficient to just remove adsorbed residual gases without significant damage to the polyimide, so that the Al–carbonyl bonding observed in UHV experiments is preserved?

The purpose of this study is to answer some of the above questions about the nature of the interface between Al and polyimide films when the Al is deposited under process conditions, rather than UHV conditions. The interface between thin (100-Å) Al films on polyimide surfaces was studied by sputter profiling with x-ray photoelectron spectroscopy (XPS). Previous studies have shown the effect of ion bombardment on polyimides,[20,21] so we must recognize that there are limits on the chemical bonding information that we may get from this study: The sputter profiling will undoubtedly alter the polyimide composition at the Al/polyimide interface, and it may also "reduce" any oxides of Al (in the same way that $TiO_2 \xrightarrow{Ar^+} TiO$). Despite these detrimental factors, we attempted the measurements since there was a high probability that major differences in the chemistry of the interfaces would be observed, and allow for reasonable inferences about the bonding between the Al and the functional groups on the polyimide.

II. EXPERIMENTAL PROCEDURES

Solutions of biphenyl tetracarboxylic dianhydride and phenylene diamine (BPDA-PDA) polyamic acid in N-methylpyrrollidone were obtained from Hitachi chemical company. The polyamic acid solutions were spin coated at 2000 rpm for 60 s onto 100-mm diameter (100) Si wafers. These spinning conditions give films of $\sim 5\ \mu m$ in thickness when cured. The coated wafers were heated to 100 °C in air for 15 min, and then cured in a continuous nitrogen flow tube furnace at the following temperature/time intervals: 100 °C, 15 min; 150 °C, 60 min; 200 °C, 30 min, 250 °C, 30 min; and 400 °C, 60 min.

The backsputtering process and the Al deposition were performed in a Materials Research Corporation (MRC) C-to-C coater. Backsputtering was done with an argon discharge at 100 W at 3×10^{-3} Torr with a self-bias of -700 V for a duration of 2 min. The sputter deposition of the 100-Å Al films was also done in the MRC coater by magnetron sputtering. There was no exposure of backsputtered polyimide film to the atmosphere prior to Al deposition, and the base pressure of the MRC coater was $\sim 5 \times 10^{-6}$ Torr.

Sputter profiling was done in a Physical Electronics model

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5400 small-area XPS spectrometer under UHV conditions. A 6×6 mm area was rastered with a 3.75-keV Ar^+ beam from a differentially pumped ion gun. The ion current to the target was delivered under calibrated conditions and the removal rate was ~10 Å per sputter interval while in the Al film, and 4 Å per sputter interval at the Al/polyimide boundary. XPS spectra were obtained from a 1-mm diameter spot at the center of the rastered area. The photoelectrons were collected at an angle of 45°, with a 17.8-eV pass energy and a 0.1-eV step size. Mg K_α x rays (1253.6 eV) were used as the exciting radiation for these measurements. The binding energy scale is referenced to the Au $4f_{7/2}$ transition at 84.0 eV, which was verified several times during the course of these measurements. No provisions were made to correct for sample charging. Atomic compositions were computed from the peak areas and the elemental sensitivity factors in the Physical Electronics software.

III. RESULTS AND DISCUSSION

A. General

The results of this study are divided into two sections: those for the Al/polyimide boundaries which were produced by Al deposition on polyimide surfaces without an argon ion backsputter are shown in Figs. 1–3. The corresponding data for an Al film deposited on a polyimide surface after the *in situ* argon ion backsputter are shown in Figs. 4, 6, and 7. A comparison of the Al 2*p* spectra between the two interfaces is shown in Fig. 5.

B. Deposition without backsputtering

Aluminum deposition without prior, *in situ* sputtering results in a sharp metal–polyimide boundary. The metal-derived species at the boundary is Al_2O_3, which is clearly established by the XPS profile. The sputter profile is shown in Fig. 1 and includes the C 1*s* region and the Al 2*p* region for the first 100 Å: The C 1*s*, N 1*s*, O 1*s*, and Al 2*p* transitions were measured for the remainder of the profile.

The surface composition of the 100-Å Al film was principally Al_2O_3 contaminated by hydrocarbons. The signal for the Al 2*p* region at the surface is shown in Fig. 2(a), and shows a two-component fit to the experimental data which corresponds to Al metal (I) and Al_2O_3 (II). The peak position and full width at half-maximum (FWHM) for Al are 73.3 eV and 1.0 eV, respectively, while those of Al_2O_3 are 76.0 and 1.8 eV. The positions of the peaks are 0.2–0.3 eV higher on the binding energy (BE) scale than other reports,[22,23] but the ΔBE of the Al to Al_2O_3 (2.7 eV) is in excellent agreement with other observations.[22,24] Progressive sputtering showed the following results as indicated in Fig. 1: (i) The C 1*s* signal dropped into the noise level before 20 Å was removed and (ii) the amount of Al oxide decreased monotonically to a depth of ~80 Å, while the amount of Al° increased to a maximum at this depth. Figure 2(b) shows the curve-fitting components necessary for the Al 2*p* transition after sputtering to a depth of 40–45 Å. Component I, Al°, now appears at 72.9 eV with an FWHM of 1.0 eV, and

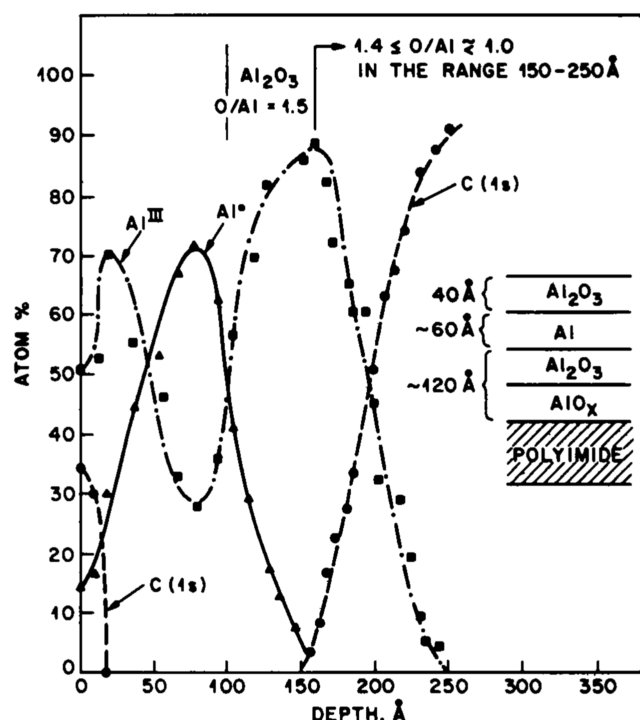

FIG. 1. The composition profile of the 100-Å Al/polyimide film in which Al was sputter deposited without prior *in situ* back sputtering of the polyimide.

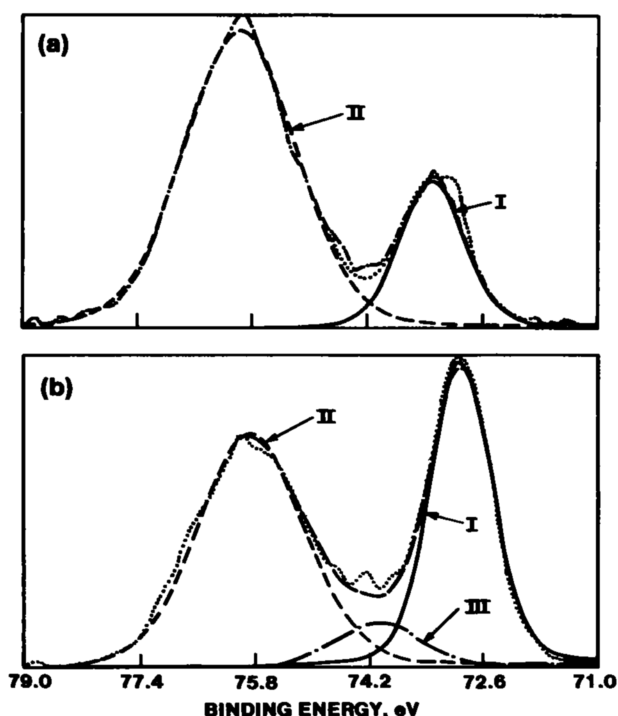

FIG. 2. The Al 2*p* experimental line shapes and the curve fits in terms of components corresponding to Al°(I) and Al_2O_3(II). (a) Signal at the surface of the film profile in Fig. 1. (b) Signal at a depth of 45 Å in the profile shown in Fig. 1. Component III and relevant parameters for components I and II are given in the text.

component II appears at 75.8 with an FWHM at 1.8 eV. We note a small additional component III which is necessary in Fig. 2(b) to achieve a reasonable fit to the data while preserving the peak splitting and parameters of components I and II.

Charging effects are responsible for the small offset in binding energy at the sample surface, however, after sputtering the sample the Al°(2*p*) transition appeared at 73.0 $\pm$ 0.1 eV, while the splitting between components I and II ranged between 2.7 and 3.0 eV. Component III is shifted ~1.2 to 1.4 eV above the binding energy of Al°, and we attribute this peak to a substoichiometric oxide of Al, which could be the result of ion bombardment. Flodström *et al.*,[22] and Eberhardt and Kunz[24] report a shoulder at 1.4 eV above the Al 2*p* transition for chemisorbed oxygen on Al.

Metallic aluminum decreases monotonically to zero between 80 and 150 Å, and the component assigned to Al_2O_3 increases to a maximum as shown in Fig. 1. The atomic ratios also show O/Al = 1.5 in this region, and furthermore there is no evidence of C 1*s* anywhere between depths of 40 and 150 Å. Thus, we may conclude that the Al which is deposited on BPDA-PDA polyimide without prior backsputtering contains a discrete Al_2O_3 layer adjacent to the polyimide boundary.

The transition into the polyimide starts at a depth of ~150 Å. In this region, the Al 2*p* signal is essentially a symmetric single peak of FWHM $\simeq$ 1.8 to 2.0 eV, and the measured O/Al ratio decreases from 1.5 at a depth of 150 Å, to 1.0 at a depth of 230 Å. The position of the Al 2*p* transition also remains strongly shifted, i.e., closer to 76 than 74.5 eV after accounting for charging shifts. Thus, we have an Al/polyimide boundary in which the Al chemistry is predominantly that of the oxide.

The C 1*s* spectra observed in the transition region between the Al_2O_3 and the polyimide ($150 \leqslant d \leqslant 230$ Å) are shown in Fig. 3. Figure 3(a) shows the experimentally measured C 1*s* line shape at a depth of ~185 Å where the Al accounts for ~60% of the material present as Al oxides, and the O/Al ratio is 1:1. The line shape and its characteristic components are only qualitatively similar to what is observed when BPDA-PDA is sputtered with sufficient ion dose and energy to transform the top 15 Å, as shown in the companion study[20] of the ion bombardment of polyimides. Figure 3(b) shows the C 1*s* transition and its components at a depth of ~210 Å, where the Al composition has dropped to ~30%, and the O/Al ratio is still 1:1. Table I contains a summary of the composition and binding energy shifts for the curve fits shown in Fig. 3, as well as data from the ion bombardment of BPDA-PDA from the companion study.[20] We can see that the curve fit components of the main peak (i.e., components I and II) in either Figs. 3(a) or 3(b) match the nonsputtered BPDA-PDA better than they match the ion-bombarded sample. This suggests that the aromatic ring structure of the BPDA-PDA polyimide has not been altered by the depth profiling through the interface in the way that it is by simply ion bombarding BPDA-PDA *in vacuo*, as done in Ref. 20.

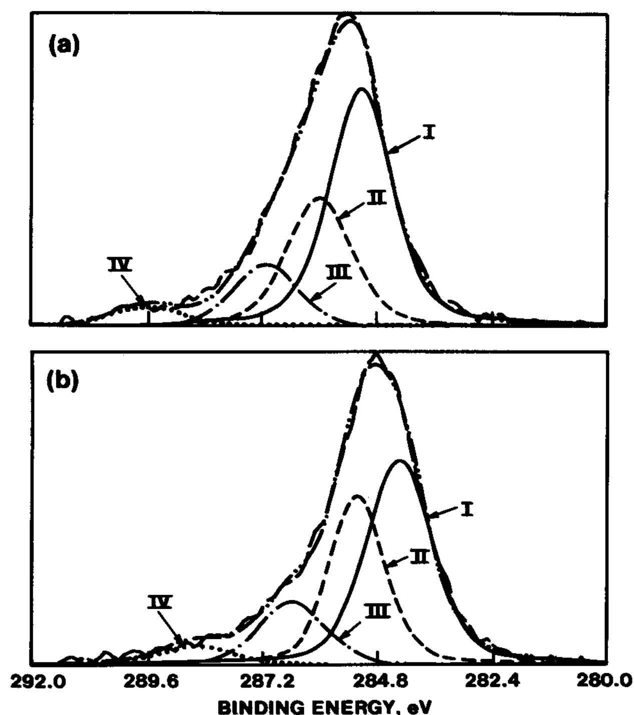

FIG. 3. C 1*s* line shapes for the profile given in Fig. 1, (a) at depth 185 Å and (b) at depth 210 Å. The data relevant to components in the curve fits are given in Table I.

TABLE I. Curve fit components for the C 1*s* peak in BPDA-PDA as shown in Fig. 3.

	Component			
	I	II	III	IV
	% Area[a]	% Area (ΔBE)[b]	% Area (ΔBE)	% Area (ΔBE)
Figure 3(a)	53	28 (0.9)	14 (2.0)	5 (4.4)
Figure 3(b)	47	33 (0.8)	14 (2.2)	5 (4.2)
BPDA-PDA, 3.75-keV Ar^+ Ion bombardment	73	22 (1.2)	···	5 (3.5)
No Ar^+ ion bombardment	51	34 (0.7)	···	15 (3.6)

[a] % Area is the percent of the total area under the C 1*s* envelope for each component.
[b] ΔBE is the shift in eV from the main C 1*s* component (component I).

The large fraction of the total C 1*s* signal which appears as component III at 2-eV BE shift suggests that the original carbonyl function on the polymer has been converted to another type of carbon link at the polyimide/Al boundary. A 2-eV binding energy shift is in the right range for an ether link, or it may also be due to an Al-O-C interface bond[9] and we note that ether links are not present[20] in BPDA-PDA. Ion bombardment of this polymer results mainly in a loss of the carbonyl groups, without the creation of an easily detected ether component, as shown in Table I. It is therefore likely that the component at $\Delta BE = 2$ eV at the AlO_x/polyimide interface is a result of Al-O-C bonding (or from ether links created from that bond during the depth profiling). We also stress the observation that the C 1*s* signal is asymmetric only on the high binding energy side, with no apparent metal–carbon bonds, which would produce an asymmetric peak shape toward binding energies < 285 eV.

We do not wish to place too much emphasis on the results of the C 1*s* data reconstruction shown in Fig. 3, except to say that what we infer from the peak positions and intensities is plausible. It is difficult to conclude anything unequivocal when one considers that the ion bombardment necessary for the depth profile can alter the bonding at the interface. We do, however, conclude that the thin (50-Å) Al_2O_3 layer at the boundary of the polyimide is beyond doubt. In general, considering the depth resolution of the sputtering procedure and the escape depth of the photoelectrons, the data of Fig. 1 also suggest that the Al_2O_3/polyimide boundary is sharp and continuous. We must really be concerned with differences between the spectra observed at the AlO_x/polyimide interface for those films which were deposited without and with *in situ* backsputtering.

C. Deposition with backsputtering

The XPS sputter profiles for the Al/polyimide deposition which has been backsputtered prior to Al deposition are shown in Fig. 4. The only similarities to the data in Fig. 1 are the presence of Al_2O_3 on the surface, and the maximum in the Al° signal at 70–80 Å depth. Every other feature of the depth profile and the chemistry at the Al/polyimide interface is different. There is no abrupt boundary between either Al or its oxide and the polyimide. No discreet and well-defined Al_2O_3 layer exists below the outermost surface, and the Al that is detected is either Al° or a species that is shifted only 1.4 eV above the Al 2*p*. The Al–polyimide transition extends over a total depth of ~300 Å, which is only 50 Å deeper than the transition observed for the unsputtered sample. It is tempting to attribute the profile observed in Fig. 4 to a roughening of the surface. If this is the case, the dimensions of the microstructure created by the backsputtering must be small enough to be planarized by the 100-Å Al deposition, since the sample surface was a mirror.

The differences in the Al oxidation state at the Al–polyimide transition for the backsputtered sample (Fig. 4) and the unsputtered sample (Fig. 1) are emphasized by Fig. 5. Figure 5(a) shows superpositions of the Al 2*p* transition taken from depths of 90 to 150 Å for the backsputtered sample

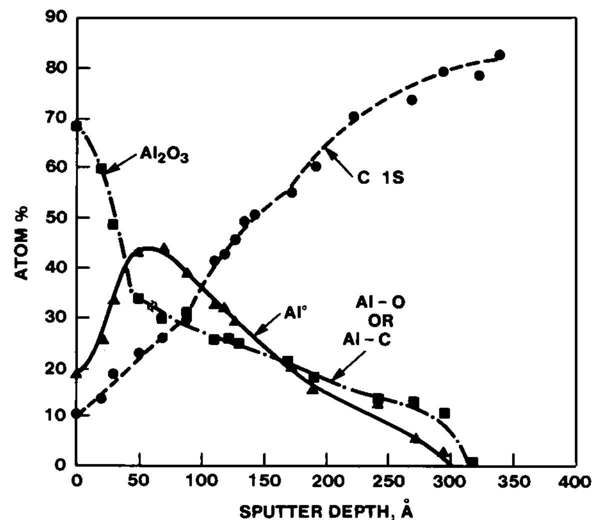

FIG. 4. The composition profile of the 100-Å Al/polyimide film in which the polyimide has been backsputtered by an argon discharge at a self-bias of 700 eV.

using the depth profile of Fig. 4. It is clear there is no major component of Al_2O_3, but as the midpoint in the gradual transition from Al to polyimide is reached, the shoulder at ΔBE 1.4 eV becomes pronounced. By contrast, Fig. 5(b) shows the same depth range for the Al 2*p* signal in the unsputtered sample. It is clear from Fig. 5(b) that as the sharp AlO_x/polyimide boundary is approached, the dominant species is Al_2O_3.

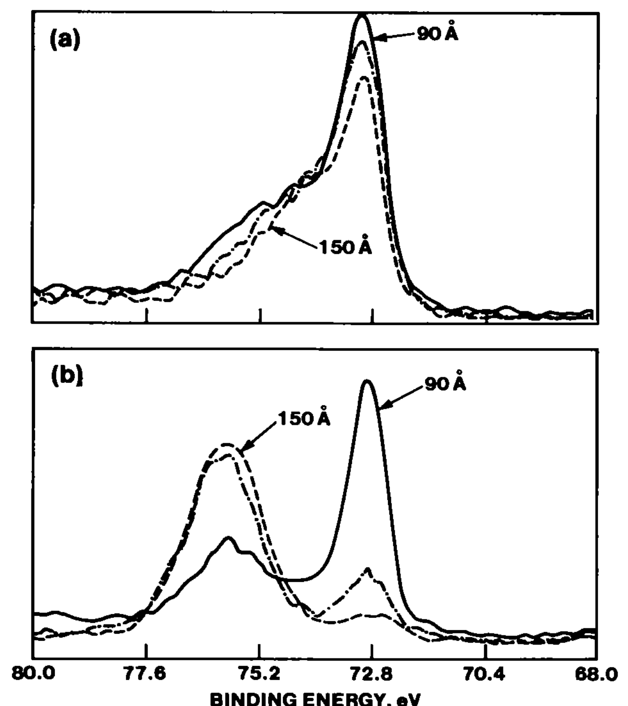

FIG. 5. A comparison of the oxidation state of Al at comparable depths for the profiles in Figs. 1 and 4. (a) The Al 2*p* transition between 90 and 150 Å, corresponding to depths shown in Fig. 4. (b) The Al 2*p* transition between 90 and 150 Å corresponding to depths shown in Fig. 1. Note the emergence of the Al_2O_3 as the depth increases.

The differences in the Al chemistry are significant. Figure 6 shows the reconstruction of the Al $2p$ experimental data for the backsputtered sample at depths of 130 Å (a), and 225 Å (b), where the total Al signal accounts for ~55% and ~25% of the composition as shown in Fig. 4. These data emphasize that at no point in the transition to polyimide do we encounter Al_2O_3, but rather the unusual species (possibly characterized as a suboxide of Al) which causes a $2p$ core level binding energy shift of 1.2 to 1.4 eV. Cross-checking the possibility of Al suboxides with the overall composition shows that the oxygen concentration is in the range of 5 to 8 at. % which is not significantly different from the low-dose ion bombarded polyimides.[20] If the oxygen were entirely accounted for by an Al–oxygen species, the stoichiometry suggest Al_3O to Al_2O between depths of 175 to 275 Å.

There is a good possibility that some of the peak shifted to 1.2 to 1.4 eV shown in Fig. 6 is due to Al–carbon bonding. The C 1s signal also indicates that such is the case, as shown in Fig. 7. Figure 7 shows the reconstruction of the C 1s peak acquired at depths of 145 Å, Fig. 7(a), and 225 Å, Fig. 7(b). Each of the components I, II, and III have peak areas and binding energy shifts almost equal to those found for the C 1s reconstruction of unsputtered BPDA-PDA.[20] The major difference occurs in the additional component A, which is shifted 1.2 eV lower in binding energy from the main C 1s peak, i.e., component I. The presence of this peak strongly suggests carbide-like bonding, as observed in some of the UHV experiments at high Ti,[5,6] and Cr[7] metal overlayer coverages on polyimides and polyimide model compounds.[9]

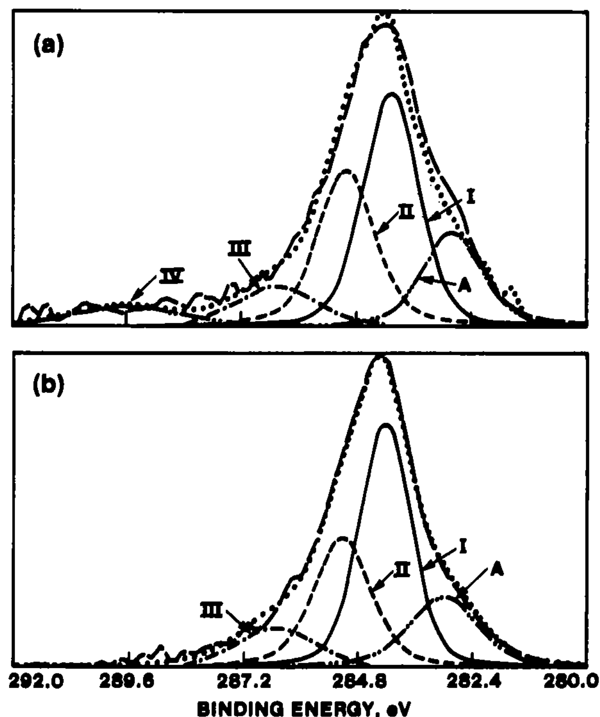

FIG. 7. The reconstruction of the C 1s line shape for the backsputtered sample at depths of (a) 145 Å, and (b) 225 Å. The additional component indicated as A is due to Al–C bonding of a carbide nature.

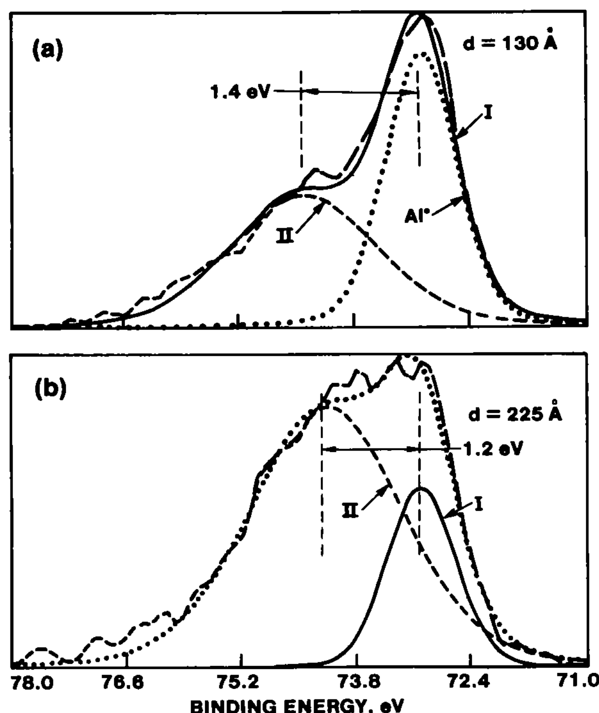

FIG. 6. The oxidation state of Al at the transition between Al and polyimide corresponding to the backsputtered profile (Fig. 4). (a) Curve fit to the experimental data at a depth of 130 Å, (b) Curve fit to the experimental data at a depth of 225 Å.

We have a preponderance of Al bonded as Al–O–C or as Al–C at the diffuse boundary between Al and the polyimide in cases where the polyimide surface has been backsputtered prior to Al deposition. In addition, there is also good evidence for Al–C bonding directly, in the C 1s spectrum. Bartha *et al.*,[9] have attributed the 1.5 eV increased binding energy peak in the Al $2p$ transition to the formation of an Al–O–C complex through the carbonyl function in the polyimide. They also show evidence for an Al–C bond at Al coverages of 10 monolayers and above, and furthermore they suggest that Al intermixes via chemical reaction with polyimide surfaces at elevated deposition temperatures (300 °C). Much of what Bartha *et al.*, observe and conclude is consistent with the findings of this study for the Al deposition on backsputtered polyimide, even though the deposition substrate temperature was lower in this study. Pireaux *et al.*, also observe the interaction[19] of Al to be with the carbonyl functional group of the polyimide by HREELS, for low Al coverage. At higher coverage, these authors observe $-CH_x$ aliphatic groups, and –OH groups, which indicates scission of the polymer repeat unit.

IV. CONCLUSION

In situ sputtering of polyimide surfaces with low energy, low-dose ion bombardment result in an Al–polyimide interface which can be interpreted in terms of bonding through both Al–O–C bonds and Al–C bonds. The interface is not sharp and suggests a gradual, uniform mixing of Al with polyimide over a depth of ~250 Å. If the polyimide surface is not backsputtered prior to Al deposition, then the Al

which initially deposits must getter residual gases and react with adsorbed water and oxygen to produce a thin layer of Al_2O_3. The Al bonding in the resultant Al_2O_3 is fully satisfied, leaving no valence electrons for sharing with available sites on the polyimide. The result is a loss of adhesion, since fewer strong chemical bonds from the Al to the polyimide are formed. The bonding differences and the interfacial chemistry is clearly different between the two preparations, in spite of the fact that the profiles were obtained by argon ion bombardment at 3.75 keV.

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