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Ion bombardment of polyimide films

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Surface modification techniques such as wet chemical etching, oxidizing flames, and plasma treatments (inert ion sputtering and reactive ion etching) have been used to change the surface chemistry of polymers and improve adhesion. With an increase in the use of polyimides for microelectronic applications, the technique of ion sputtering to enhance polymer-to-metal adhesion is receiving increased attention. For this study, the argon-ion bombardment surfaces of pyromellitic dianhydride and oxydianiline (PMDA-ODA) and biphenyl tetracarboxylic dianhydride and phenylene diamine (BPDA-PDA) polyimide films were characterized with x-ray photoelectron spectroscopy (XPS) as a function of ion dose. Graphite and high-density polyethylene were also examined by XPS for comparison of C 1s peak width and binding-energy assignments. Results indicate that at low ion doses the surface of the polyimide does not change chemically, although adsorbed species are eliminated. At higher doses the chemical composition is altered and is dramatically reflected in the C 1s spectra where graphiticlike structures become evident and the prominent carbonyl peak is reduced significantly. Both polyimides demonstrate similar chemical changes after heavy ion bombardment. Atomic composition of PMDA-ODA and BPDA-PDA polymers are almost identical after heavy ion bombardment.

I. INTRODUCTION

With an increase in the use of polymers as dielectrics in multilevel very large scale integrated (VLSI) structures, understanding the basis of adhesion of the deposited metal layer to the underlying polymer film is becoming a matter of practical importance. Recent studies employing electron spectroscopies, such as x-ray photoelectron (XPS), ultraviolet photoelectron (UPS), and high-resolution electron energy loss (HREELS) have been applied to polyimide-metal layers for the purpose of characterizing their surfaces and interfaces.¹⁻⁴ Surface modification techniques such as wet chemical etching, oxidizing flames, and plasma treatments (inert ion sputtering or ion bombardment and reactive ion etching) have been used to change the surface chemistry of polymers and improve adhesion.⁵⁻¹¹ However, the mechanism responsible for the increased adhesion after ion bombardment of polyimide films is not well established.

Possible explanations for the enhanced adhesion include the following: the formation of a crosslinked or graphitic layer that may improve the mechanical strength of the surface, the increased amount of surface area that accompanies a transformation from a smooth to a rough topology, the removal of adsorbed species or contaminants which could eliminate a poor bonding layer, or the formation of chemical species that increase the surface free energy such as in carbon-metal bonding. Nuzzo and co-workers¹² have shown that ion bombardment of polyimide surfaces selectively reduces the carbonyl moiety, which cannot be restored by subsequent exposure to oxygen. In this case, the surface should contain little carbonyl functionality and presumably, no large concentrations of free radical sites. These findings suggest that increased polyimide-metal adhesion is due to increased surface area, rather than increased metal carbide bond formation. In addition, they suggest that a crosslinked surface exists after ion bombardment.

Backsputtering under typical process conditions involves the use of a 100-W discharge with a self-bias of ~ 700 V and an argon pressure of 3 mTorr for a duration of 2 min but the current density is generally unknown. It is possible that argon-ion bombardment under these conditions is sufficient to clear the surface of adsorbed water and other residual gases, but does not completely remove the imide carbonyl functional groups that are necessary for the initial stages of polyimide-metal bonding. In other words, the mechanism of increase adhesion with sputtering may also be a function of the ion energy, and the total ion dose.

In this study, the surfaces of polyimide films that had been bombarded with argon ions under controlled conditions were characterized by XPS as a function of ion dose. Ultra-high purity graphite and high-density polyethylene were also examined for comparison of C 1s peak width and binding-energy assignments.

II. EXPERIMENTAL PROCEDURE

Polyimide films were formed by spin coating polyamic acid solutions at 2000 rpm for 60 s onto 100-mm-diam (100) Si wafers. Prior to spin coating, the wafers were prebaked at 120 °C for 60 min and then cleaned in an oxygen plasma. Polyimides derived from pyromellitic dianhydride and oxydianiline (PMDA-ODA) and biphenyl tetracarboxylic dianhydride and phenylene diamine (BPDA-PDA) were used for this study. Hitachi Chemical Company supplied the polyamic acid solutions in *N*-methylpyrrolidone. Figure 1 shows the chemical reaction between a diamine and dianhydride that forms a polyamic acid which, on subsequent thermal treatment, cures to a polyimide film. Both PMDA-ODA and BPDA-PDA films were heated in a nitrogen environment according to the following procedure: 100 °C for 15 min, 150 °C for 60 min, 200 °C for 30 min, 250 °C for 30 min, and 400 °C for 60 min. Film thicknesses of ~ 5 μ m were

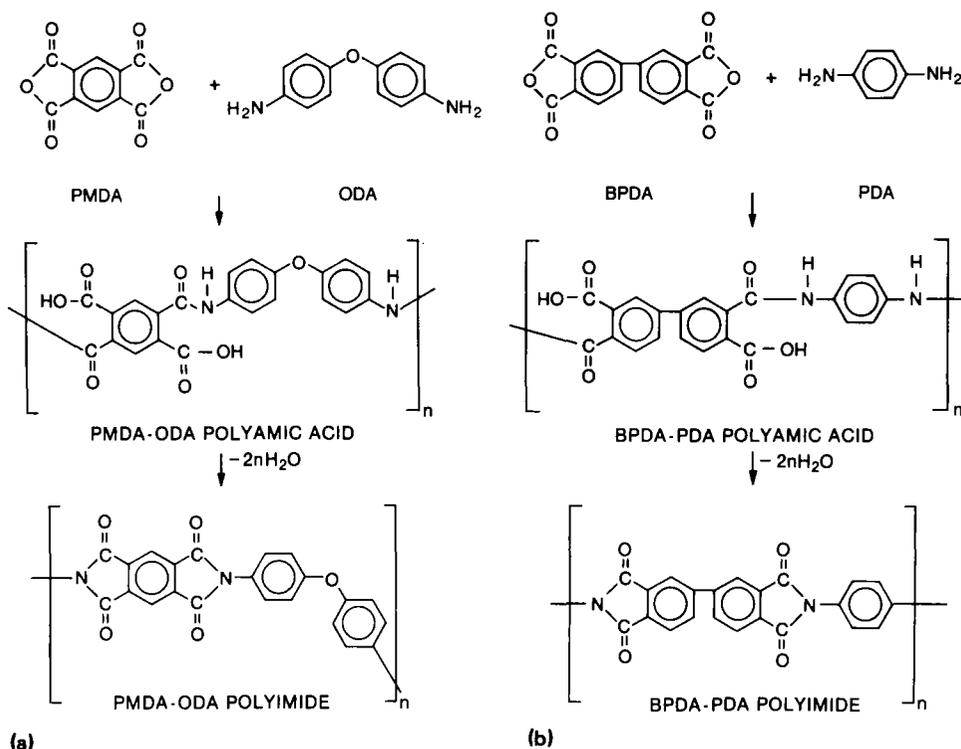


FIG. 1. Polyimide chemistry: A dianhydride reacts with a diamine to form a polyamic acid which, when thermally cured, undergoes cyclization and involves the elimination of water for (a) pyromellitic dianhydride and oxydianiline (PMDA-ODA) and (b) biphenyl tetracarboxylic dianhydride and phenylene diamine (BPDA-PDA).

measured using a stylus profilometer.

Cured polyimide films were characterized by angle resolved XPS under ultrahigh vacuum conditions. Spectra were obtained using a PHI Perkin-Elmer model 5400 small-area spectrometer system consisting of a hemispherical analyzer and a Mg K_{α} radiation source. The binding-energy scale is determined with the Au $4f_{7/2}$ transition at 84.0 eV, and spectra are measured using a constant 17.9-eV pass energy, with a resolution of 0.1 eV. Incident angles used for obtaining spectra were 20° , 45° , and 90° . No compensation is made for sample charging, since the entire surface is irradiated while the electron lens is set to accept photoelectrons from a nominal 1-mm-diam circular area. All samples were well outgassed before exposure to the x rays and the vacuum did not exceed 2×10^{-9} Torr while the spectra were being acquired. The x-ray source-to-sample distance is ~ 1 cm. Ion bombardment of the polyimide films was performed prior to acquiring XPS spectra in the same UHV chamber using bombardment energies of 1, 2, and 3.75 keV. Reference spectra for C 1s line shape were taken with ultrahigh purity spectrographic grade graphite and samples of high-density polyethylene.

Argon-ion bombardment was performed with a well-characterized, differentially pumped ion gun. The ion beam was focused to a point at the target plane using a true Faraday cup collector. Ion current was then calibrated for total ion current as a function of argon pressure (in the ion gun) at the bombardment energy desired (1, 2, and 3.75 keV). The ion beam raster size is calibrated using thin Cr films on glass substrates. A feedback control mechanism based on argon pressure yields a steady, reproducible, incident ion current so that the ion dose may be calculated independently of the secondary particle emission current of the target. Partial pressures of residual gases were measured with a quadru-

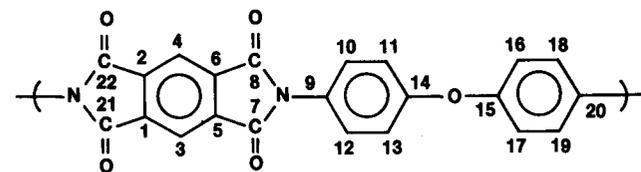
pole mass spectrometer during analysis and during ion bombardment of the samples.

III. RESULTS AND DISCUSSION

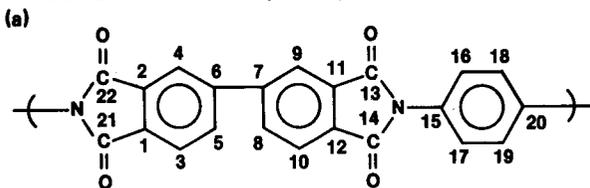
Polyimide C 1s XPS spectra are interpreted using assignments for the chemical shifts similar to those reported by Silverman and co-workers,¹³⁻¹⁵ which are based on their *ab initio* calculations of model compounds for PMDA-ODA polyimide. Our analyses follow their general method. However, we do not use their exact assignments for each of the C 1s components, but rather employ curve-fitting routines using two major peaks and one minor peak for the main PMDA-ODA C 1s transition. The assignments used for the C 1s components in this study for both the PMDA-ODA and BPDA-PDA repeat units are shown in Figs. 2(a) and 2(b). We are relying on curve fitting to provide some insight into the changes of our polyimide surface chemistry. To make this procedure realistic and relevant, the initial parameters for the components of the C 1s line were determined experimentally using ultrahigh purity graphite and high-density polyethylene. Samples of these two materials were also subjected to ion bombardment as described earlier. Previous work on polyethylene suggests that crosslinked structures can be formed with ion sputtering.¹⁶⁻¹⁸ It has been proposed that ion bombardment of polyethylene causes hydrogen abstraction at the surface, thus creating radical sites which inactivate and form crosslinks.¹⁶

A. Graphite

The spectrum of high-purity (polycrystalline) graphite, Fig. 3(a), shows the main C 1s transition at 284.8 eV with a curve fit component of 1.0 eV full width at half-maximum (FWHM). The inelastic losses on the high-binding-energy



COMPONENT I	(11,13,16,17)
COMPONENT II	(1,2,3,4,5,6,8,10,12,18,19,20)
COMPONENT III	(14,15)
COMPONENT IV	(7,8,21,22)
COMPONENT V	(π - π^*)



COMPONENT I	(3,4,5,6,7,8,9,10,16,17,18,19)
COMPONENT II	(1,2,11,12,15,20)
COMPONENT III	(13,14,21,22)
COMPONENT IV	(π - π^*)

(a)

FIG. 2. Carbon 1s components of polyimide repeat units: (a) repeat unit of the PMDA-ODA polymer, numbered according to the scheme used by Silverman *et al.* (Ref. 13) and (b) repeat unit of BPDA-PDA polymer with arene carbon atoms numbered for identity within the text.

side which cause the asymmetry in the graphite C 1s line shape are approximated by two additional components listed in Table I. The C 1s line shape showing the P 1 inelastic losses prior to background subtraction are shown in the inset

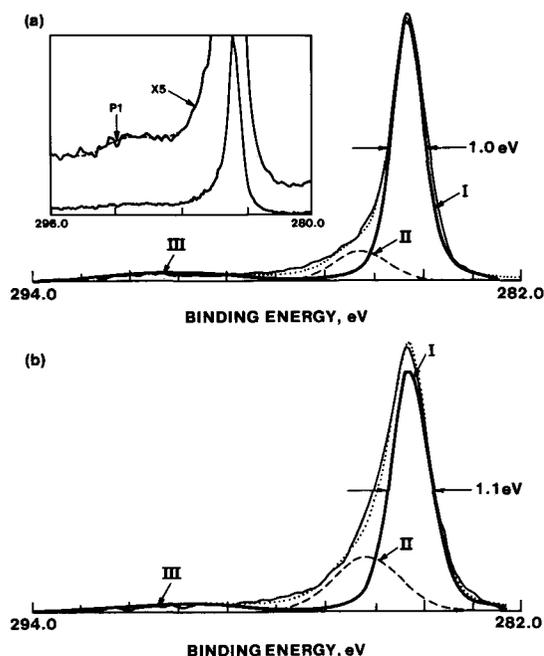


FIG. 3. Spectrographic grade graphite: (a) XPS spectra (45° exit angle) of a 12-eV window of the C 1s peak in high-purity (spectrographic grade) graphite prior to ion bombardment. The inset show a 16-eV window of the same peak with a $\times 5$ vertical sensitive trace which delineates the P1 transition. (b) The C 1s spectra of graphite after 8×10^{15} ions/cm 2 at 3.75 keV. The parameters for components I, II, and III of the data reconstructions of (a) and (b) are given in Table I.

TABLE I. C 1s components for the curve fit to the experimental line shape of graphite and high-density polyethylene.

	Component	BE	FWHM	% area	
Graphite:	No ion	I	284.8	1.0	75
	bombardment	II	286.0	1.6	15
		III	290.5	4.0	10
After 8×10^{15} ions/cm 2 at 3.75 keV		I	284.7	1.1	66
		II	285.8	1.9	27
		III	290.1	4.0	8
Polyethylene:	No ion	I	286.9	1.3	100
	bombardment				
After 8×10^{15} ions/cm 2 at 3.75 keV		I	284.8	1.5	62
		II	285.6	1.4	38

of Fig. 3(a) at five times the vertical sensitivity.¹⁹ The results for graphite are in excellent agreement with previous measurements,¹⁹⁻²¹ and provide a lower limit of 1.0 eV for the FWHM of unsputtered carbon. Figure 3(b) shows the C 1s transition fit with components after the graphite was Ar ion bombarded at 3.75 keV with a dose of 8×10^{15} ions/cm 2 (1×1 cm rastered area). The net effect is to broaden the main peak, curve I, to 1.1 eV FWHM, and to increase the asymmetry (as seen by a larger component of curve II which is necessary to fit the experimental line shape). The C 1s line shape in graphite remains unchanged from that shown in Fig. 3(b) after doses up to 2×10^{16} ions/cm 2 .

B. Polyethylene

The C 1s spectra for high-density polyethylene obtained prior to sputter and after two doses of 3.75-keV argon ions are shown in Fig. 4. The non-ion-bombarded curve shown in Fig. 4(a), can be fit with a single, symmetric Gauss-Lorentzian peak of 1.3 eV FWHM. Two peaks shown as components I and II in Fig. 4(b) are the minimum necessary to fit the data after 8×10^{15} ions/cm 2 . These components have half-widths of 1.5 and 1.4 eV, respectively, which is not an unreasonable amount of broadening in view of the graphite results.

The assignment of the curve-fitting components in Fig. 4(b) as a single new bonding component in polyethylene is a point of interest, since there is no heteroatom introduced into the polymer surface to cause the chemical shift. The curve-fitting procedure was initiated using five components, each having a half-width of 1.0 eV, with the result that two of the components dominated the fit, and a third component had an unrealistically small half-width. Thus, the envelope of the C 1s peak in Fig. 4(b) may be due to a variety of bonds which are differentiated from normal sp^3 carbon-carbon bonds in polyethylene by structural changes due to the ion bombardment. We may, however, represent this multiplicity of bonding by two or possibly three peaks with realistic half-widths as shown in Fig. 4(b).

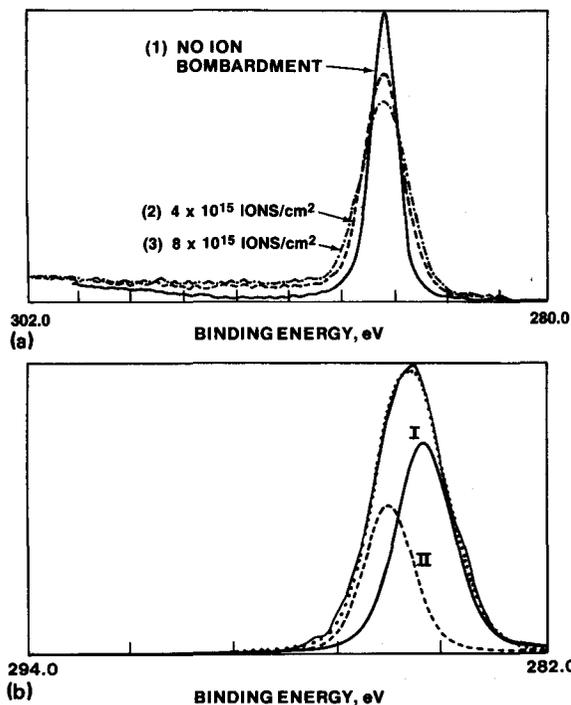


FIG. 4. High-density polyethylene: (a) XPS spectra (45° exit angle) of a 20-eV window of the C 1s transition in high-density polyethylene, with no ion bombardment, and after 3.75-keV ion bombardment doses of 4×10^{15} and 8×10^{15} ions/cm 2 . (b) Components of the curve fit for the C 1s in Fig. 3(a) after 8×10^{15} ions/cm 2 . The parameters for components I and II are given in Table I.

Figures 4(a) and 4(b) illustrate that the effect of ion bombardment can be represented by at least one principal new C 1s transition. The data for Fig. 4 are summarized in Table I. The asymmetry toward the high binding energy shown in Fig. 4(a) suggests that the surface of the polyethylene is becoming graphitic under ion bombardment. Continued bombardment of the polyethylene to a dose of 2×10^{16} ions/cm 2 at 3.75 keV produces no further broadening of the main peak, but a distinct component similar to the P1 transition in graphite is observed.

C. PMDA-ODA polyimide

Figure 5(a) shows the XPS C 1s line shape of PMDA-ODA prior to ion bombardment. This line shape is essentially the same at an exit angle of 20° or 90° , indicating the surface and bulk compositions are similar, and hence little contribution from adsorbed species in UHV. There are five components used in the curve-fitting routine over an interval of 12 eV. The initial components were determined from a consideration of the chemical shifts resulting from the calculations of Silverman and co-workers.¹³ These authors calculated the binding-energy shifts for each of the 22 atoms in the PMDA-ODA monomer unit, and then grouped them into three components for a reconstruction of the experimental data.

The grouping of the individual, calculated core levels into major C 1s components by Silverman *et al.* is not explicitly discussed in their paper. Therefore, we make our own judg-

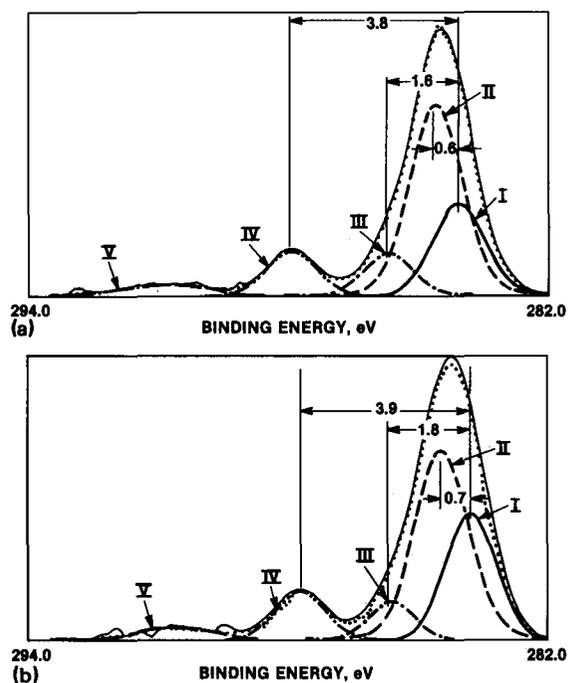


FIG. 5. PMDA-ODA polyimide: (a) The reconstruction of the experimental C 1s XPS 45° line shape in PMDA-ODA, with no ion bombardment. (b) The reconstruction of the C 1s line shape in PMDA-ODA after 7×10^{14} ions/cm 2 at 1 keV. The curve-fitting results for (a) and (b) are given in Table II.

ment. Carbon 1s assignments for the PMDA-ODA repeat unit are shown in Fig. 2(a). We assume that the ether (C14 and C15) and carbonyl (C7, C8, C21, and C22) carbons form distinct groups shifted from component I by ~ 1.9 eV and 4 eV, respectively, and are shown as components III and IV in Fig. 5(a). After designating the $\pi-\pi^*$ transition as component V, we then have to consider how to assign initial intensities to the two components, I and II, of the main C 1s transition. Silverman *et al.* show that these two components may be made up of 16 individual carbon atoms with shifts ranging from 0.13 to 1.4 eV. We assume C20 is shifted by ~ 1.3 eV, since it is bonded to nitrogen in the repeat polymer similar to C9. The shifted component II will be made up from 12 atoms designated C1-C6, C9, C10, C12, C18, C19, and C20. C18 and C19 are assigned to the shifted component II since their electronic environment in the polymer is the same as that of C10 and C12. The unshifted component is then comprised of four atoms: C11, C13, C16, C17. In other words, for purposes of curve fitting, carbon atoms with calculated core level shifts less than 0.3 eV are grouped into component I, while those with calculated core level shifts of $0.46 \leq \delta \leq 1.44$ eV are grouped into component II.

The actual fit to the experimental data is reasonable, as shown in Fig. 5(a). The adjustments to intensities and half-widths of the components necessary to fit the data are rather small: The initial population and Δ BE assumed for the components of the C 1s line shape were I, 18%, no shift; II, 55%, 0.7 eV; III, 9%, 1.8 eV, and IV, 18%, 3.9 eV. The curve fit for PMDA-ODA which was not ion bombarded (Table II) is I, 25%; II, 52%, 0.5 eV; III, 11%, 1.6 eV; IV, 12%, 3.8 eV.

TABLE II. C 1s components for the curve fit to the experimental line shape of PMDA-ODA, as a function of ion bombardment.

Ion dose ^a	Angle	% component area (Δ BE)			
		I	II(Δ BE)	II(Δ BE)	IV(Δ BE)
None	45°	25	52,(0.5)	11,(1.6)	12,(3.8)
(a)	45°	29	50,(0.7)	8,(2.0)	13,(3.8)
(b)	45°	54	28,(0.9)	10,(2.1)	8,(3.6)
(c)	45°	59	28,(1.0)	10,(2.7)	3,(4.5)
(d)	90°	61	25,(0.9)	8,(2.4)	5,(4.4)
(d)	20°	67	21,(1.1)	8,(2.6)	4,(4.6)
Initial components					
None	...	18	55 (0.7)	9 (1.8)	18 (3.9)
FWHM of components I-III range from					
None		1.2-1.3 eV			
(a)		1.1-1.4 eV			
(b)		1.1-1.4 eV			
(c)		1.5-1.6 eV			

^a Ion dose: (a) 7×10^{14} ions/cm², 1 keV; (b) 1.6×10^{15} ions/cm², 2 keV; (c) 2.5×10^{15} ions/cm², 2 keV; and (d) 1.7×10^{15} ions/cm², 3.75 keV.

These results suggest that one or two of the carbon atoms in the polymer repeat unit assigned to component II might be better assigned to component I. We note that the half-widths of the peaks in the curve fit for Fig. 5(a) range only from 1.2 to 1.3 eV, and the BE shifts for III and IV are the current ones for ether and carbonyl groups. There is less carbonyl on the surface than expected (11% observed, 18% expected) on the basis of the perfect repeat unit, as Silverman *et al.*¹³ also observed. The atomic composition of the unspattered PMDA-ODA given in Table III also shows significantly less oxygen than expected (13% observed, 17% expected) which corroborates the C 1s components.

Components I-IV are as reasonable a representation of the C 1s bonding in PMDA-ODA as we can achieve. The final parameters of each of the components is realistic in terms of half-widths and intensities. We believe the results are consistent with the *ab initio* calculations of Silverman *et*

TABLE III. Atomic composition of PMDA-ODA as a function of ion bombardment.

Ion dose ^a	Atomic compositions			Photoelectron angle
	% C	% N	% O	
None	82	5	13	45°
(a)	82	5	13	45°
(b)	89	5	6	45°
(c)	92	5	4	45°
(d)	93	5	2	90°
(d)	94	4	2	20°
Ideal repeat unit	76	7	17	...
Loss of carbonyl oxygens only	88	8	4	...

^a Ion dose: (a) 7×10^{14} ions/cm², 1 keV; (b) 1.6×10^{15} ions/cm², 2 keV; (c) 2.5×10^{15} ions/cm², 2 keV; and (d) 1.7×10^{15} ions/cm², 3.75 keV.

al.,¹³ differing only by considering the ether carbons as a separate component, and a regrouping of the constituents of the two main components of the C 1s transition. We add here that alternative starting assignments, e.g., inverted intensities of components I and II, did not yield satisfactory fits to the data. Numerous combinations of starting assignments were explored, and none were found that could fit the data as well as that shown in Fig. 5(a), with realistic component parameters.

The effect of ion bombardment on the PMDA-ODA C 1s line shape is shown by using curve fits of the components to the experimental data in Figs. 5(b), 6, and 7. The corresponding alteration in the stoichiometry of the polymer surface is summarized in Table III. Figure 5(b) shows that exposure to 7×10^{14} ions/cm² at 1 keV has virtually no effect on the C 1s line shape or the stoichiometry of the surface. An additional dose (line b in Tables II and III), of 9×10^{14} ions/cm² at 2 keV, results in significant alterations in the surface chemistry as shown in Fig. 6(a) and Tables II and III. The carbonyl oxygens show a decrease (component IV) while it appears that the ether link and the nitrogen content remain virtually unaffected. The shift in relative intensities of components I and II is also expected with a loss of the carbonyl oxygens. Finally, an additional dose (line c in Tables II and III) of 9×10^{14} ions/cm² at 2 keV reduces the carbonyl intensity to only 3% of the total carbon 1s signal, while the

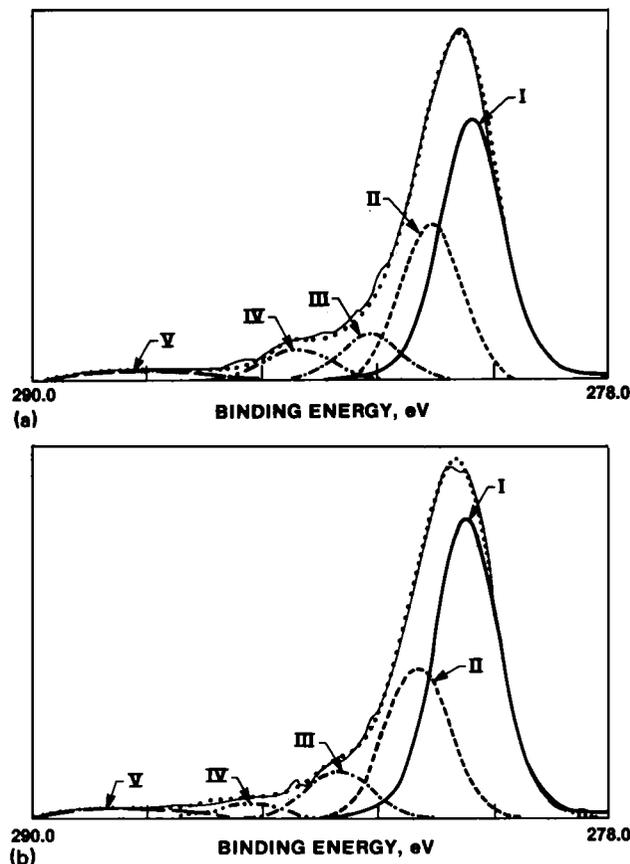


FIG. 6. PMDA-ODA polyimide: (a) Reconstruction of the experimental C 1s 45° line shape in PMDA-ODA after 1.6×10^{15} ions/cm² at 2 keV. (b) Reconstruction of the experimental C 1s 45° line shape in PMDA-ODA after 2.5×10^{15} ions/cm² at 2 keV. Data for the curve-fitting results are given in Table II.

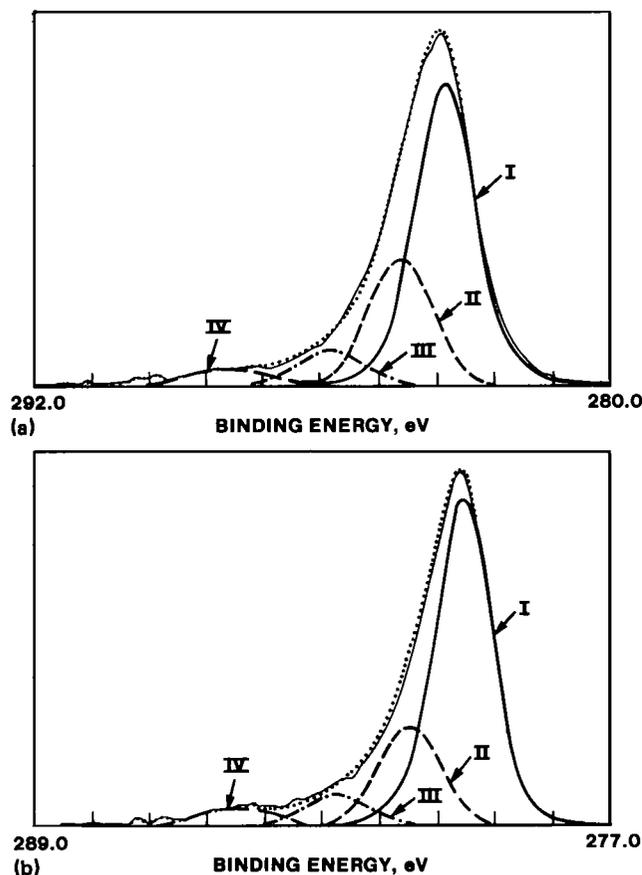


FIG. 7. Reconstruction of the experimental C 1s line shape in PMDA-ODA after 1.7×10^{15} ions/cm² at 3.75 keV: (a) spectra taken at an exit angle of 90° and (b) spectra taken at an exit angle of 20°. Data for the components are given in Table II.

ether component is still relatively strong. The overall surface stoichiometry (Table III) at this total dose of 2.5×10^{15} ions/cm² is also consistent with a loss of the carbonyl oxygen and preservation of the ether and nitrogen links in the polymer backbone.

The ion bombardment shown in Figs. 5 and 6 was performed sequentially on the same sample. A separate sample was mounted and exposed to a single dose of 1.7×10^{15} ions/cm² at 3.75 keV (line d in Tables II and III). The angle resolved spectra obtained at 20° and 90° are shown in Fig. 7. In this experiment, the nitrogen link remains, although the spectra show it to be a multiplet. Considerable molecular rearrangement of the polymer surface has occurred with this dose, and the spectral invariance with angle suggests that the damage is deeper than the escape depth of the photoelectrons, i.e., ~ 15 Å. Somewhat more damage has been done to the polymer by the single 3.75-keV ion dose than by the sequential 2-keV ion doses. Note that component V (the π - π^* transition) is not necessary to achieve a curve fit, indicating breakup of the aromatic rings.

The representation of the components III and IV as ether and carbonyl links after an ion dose 1.6×10^{15} or 2.5×10^{15} ions/cm² is questionable. While there is clearly some oxygen remaining in the polymer, the amount is too small to account for the total intensities of components III and IV. The N 1s

signal simply broadens with ion doses larger than 7×10^{14} ions/cm², indicating a multiplicity in C-N bonding, but no significant loss of nitrogen. The O 1s signal shows the concomitant loss of signal indicated by the change in stoichiometry (Table III) and the loss of the carbonyl component in the C 1s spectrum. The small oxygen signal remaining after ion doses of 1.6 and 2.5×10^{15} ions/cm² at 2 keV is too broad to assign as carbonyl or ether, but it is clearly detectable as O 1s. Some of the intensity under the C 1s envelope in this region may be due to a graphitization of the surface, as suggested by Nuzzo,¹² or to C-N or C-O bonds which are geometrically strained.

D. BPDA-PDA polyimide

The repeat unit of BPDA-PDA is shown in Fig. 2(b), and it is clearly a different structure from PMDA-ODA in terms of the electronic environment of the aromatic carbons. We have no calculated core level shifts to begin our curve fitting, but we can adopt some of the procedures used for the PMDA-ODA fit as a guide for initial assignments. Referring to Fig. 2(b), we note that in the repeat unit there are four carbonyl carbon atoms, two carbon atoms bonded directly to nitrogen, and no ether links. There is no ambiguity in assigning these atoms, along with the aromatic carbons, to a three-peak reconstruction as shown in Fig. 8(a). Carbon

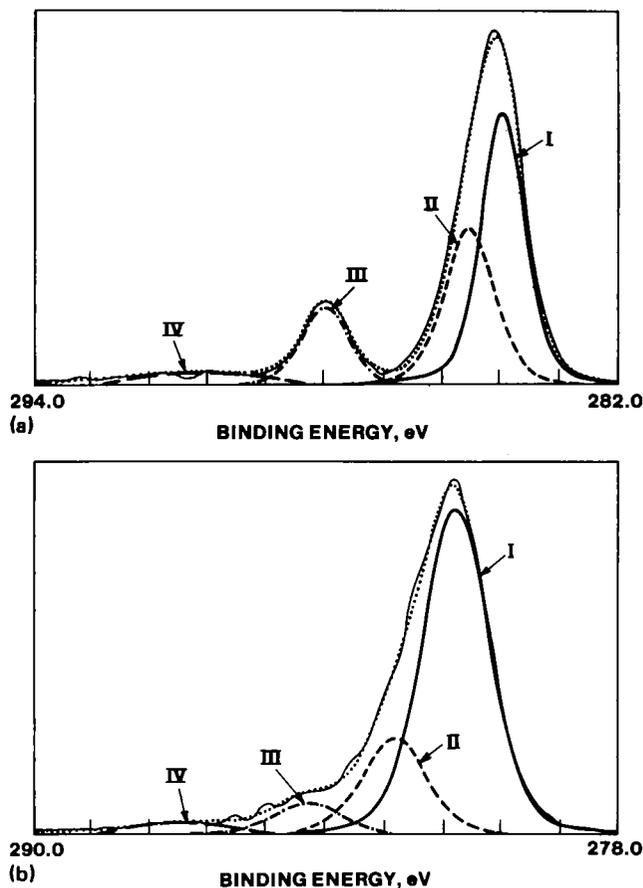


FIG. 8. BPDA-PDA polyimide: (a) The experimental C 1s XPS (45°) line shape for the polymer BPDA-PDA with no ion bombardment. (b) The same spectral region after 2.5×10^{15} ions/cm² at 2 keV. The curve-fitting data for BPDA-PDA polymers as a function of ion dose are given in Table IV.

atoms C1, C2, C11, and C12 are assigned to the shifted component II, which has a ~ 0.7 -eV shift from component I, the main C 1s transition. Carbon atoms C5–C8 and C16–C19 are considered as comprising component I, leaving the assignment of carbon atoms C3, C4, C10, and C12 in doubt. Assuming these atoms are not sufficiently shifted to be included in component II, we start with an assignment of I = 55%, II = 27%, and III = 18%. The curve fit in Fig. 8(a), shows an excellent fit to the data with component I at 51%, component II at 34%, and component III at 15% of the total C 1s intensity. Again, we do not include component IV, the peak area for the π - π^* transition. The reconstruction of the experimental data could not be improved with other starting assignments for components I and II. Additionally, no difference was observed if we start with components I and II in an approximate 1:1 intensity ratio.

The results of ion bombarding BPDA–PDA are summarized in Table IV, which gives both the C 1s components for data reconstruction, and the stoichiometry of the polymer surface. Components of the C 1s at dose c, 2.5×10^{15} ions/cm², are shown in Fig. 8(b). We note similarities of the C 1s components of the BPDA–PDA and PMDA–ODA data as a function of ion dose: (i) the peak broadening of the main arene C 1s requires that the ΔBE of component II increases from ~ 0.7 to 1.2 eV; (ii) the initial ion dose of 7×10^{14} ions/cm² at 1 keV has little effect on the surface composition; (iii) the carbonyl function is lost with increasing ion dose/energy, while the nitrogen remains within the polymer framework; (iv) a fraction of component II decreases relative to I. Finally, a dose of $\sim 1.7 \times 10^{15}$ ions/cm² at 3.75 keV is sufficient to eliminate virtually all of the oxygen, to a depth of ~ 15 Å.

Comparing the atomic composition or the curve fit components I, II, and III for PMDA–ODA and BPDA–PDA at

ion bombardment doses c or d (1.6×10^{15} and 2.5×10^{15} ions/cm², respectively) indicates that the surface of the two polymers are essentially the same. Minor differences in the peak area and position of components III and IV for PMDA–ODA versus those of peak III for BPDA–PDA may be due to retention of more oxygen by PMDA–ODA. However, these apparent differences are within the precision of the atomic composition measurements, and are certainly within the boundary of uniqueness for the curve-fitting procedures. We may in fact superimpose the C 1s line shapes from PMDA–ODA and BPDA–PDA at dose d, as shown in Fig. 9, for the 90° data.

IV. CONCLUSIONS

These data show that the surfaces of two distinctly different polyimides, PMDA–ODA and BPDA–PDA, are reduced to nearly identical structures by an argon-ion bombardment of sufficient dose and energy. The carbonyl functions of both polymers are diminished, and the initial chemically shifted arene component (II) in the main C 1s transition decreases in intensity with increasing ion dose. The decrease in intensity accompanies the loss of the carbonyl oxygen, which is consistent with the analysis of Silverman and co-workers. The XPS data also show that carbon bonding changes with increased ion doses or ion energies. At high doses, the data suggest that the surface is more similar to graphite than to the ion bombarded surface of polyethylene, which becomes crosslinked.

One monolayer equivalent doses of low kinetic energy ions (e.g., 7×10^{14} ions/cm² at 1 keV) have a negligible effect on either polymer within the limits that we can detect with XPS under UHV conditions ($\sim 1\%$ of a monolayer). These data have implications for the adhesion of polyimide to metals: a small, low-energy ion dose will do little to remove carbonyl groups, and also do negligible damage to the aromatic structure. Hence, bonding dependent on formation of metal–oxygen–carbon links at the carbonyl sites will not

TABLE IV. Curve fit components for BPDA–PDA and atomic compositions as a function of ion bombardment.

% component area (ΔBE)				
Ion dose ^a	I	II	III	Angle
None	51	34(0.7)	15(3.7)	45°
(a)	62	22(0.8)	16(3.5)	45°
(b)	67	23(1.1)	10(3.0)	45°
(c)	71	22(1.2)	7(3.0)	45°
(d)	73	22(1.2)	5(3.5)	90°
(d)	72	22(1.2)	6(3.1)	20°
Ion dose ^a	% C	% N	% O	Angle
None	77	7	15	45°
(a)	79	8	13	45°
(b)	85	7	8	45°
(c)	89	7	4	45°
(d)	94	5	1	90°
(d)	93	6	1	20°
Ideal unit	79	7	14	
Loss of carbonyl oxygen	92	8	...	

^a Ion dose: (a) 7×10^{14} ions/cm², 1 keV; (b) 1.6×10^{15} ions/cm², 2 keV; (c) 2.5×10^{15} ions/cm², 2 keV; and (d) 1.7×10^{15} ions/cm², 3.75 keV.

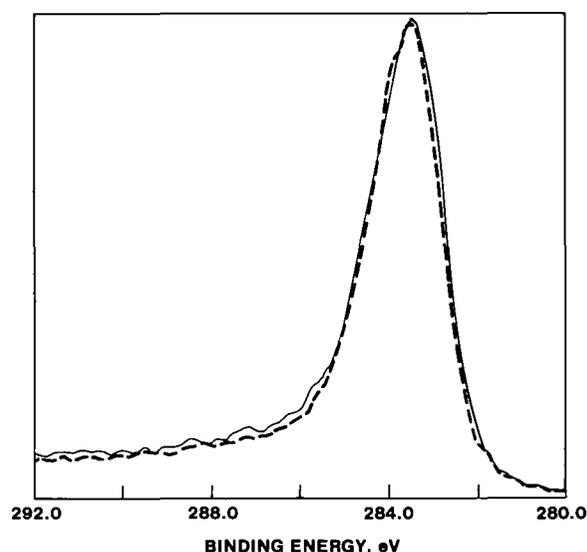


FIG. 9. Superposition of the 90° C 1s XPS spectra of PMDA–ODA and BPDA–PDA after 1.7×10^{15} ions/cm² bombardment at 3.75 keV.

be disrupted. A light ion dose followed by *in situ* metal deposition may therefore be expected to improve bonding when depositing metal in a non-UHV environment, since adsorbed gases will be removed and the carbonyl function will be preserved. An ion dose heavy enough to eliminate the carbonyl oxygen (e.g., 1.7×10^{15} ions/cm² at 3.75 keV) may do little to promote metal adhesion, except through the surface roughening that increases the interfacial contact area and/or through the formation of graphite structures that may increase the mechanical strength of the surface.

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