Modification of Polyimide Coatings by High Energy Ion Bombardment

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Synopsis

Exposure of 25-μm films of polyimide and polyamideimide to high doses ($> 10^{15}$/cm^2) of energetic ions (energy $\geq$ 100 keV) resulted in physical and chemical modification of the film surface. Cross-section microscopy revealed damaged layers extending beyond the projected ion range; conductivity in this damaged layer was found to be as high as $10^3 \Omega^{-1}$ cm^{-1}. Surface conductivity was found to be a function of ion energy and dose, with an exponential energy dependence from 200 to 900 keV. The temperature dependence and thermal stability of the surface conductivity were determined.

INTRODUCTION

When energetic ion beams impinge on organic materials, such as synthetic polymers, several types of physical and chemical effects result: sputtering, implantation, formation of free radicals and ionic species, and chemical reorganization. The effect of low to moderate ion doses on the physical properties of plastics has been the subject of much study[1]; this work has focused in two areas: evaluation of materials for use in the nuclear power industry and the crosslinking of thermoplastic polymers by ion irradiation. Recently, it has been demonstrated that high doses (10^{14}–10^{17}/cm^2) of high energy ions can lead to useful changes in polymer properties.[2] Implantation of reactive ion species,[3] such as Br$^+$, has been found to increase the conductivity of semiconducting polyacetylenes, possibly via a doping mechanism. It has also been shown that polymers with resistivities in the range of 10^{-1}–$10^{-3} \Omega$ cm can be prepared by ion bombardment of highly insulating materials. Many details of the interaction of high energy ions with thin films of polymers or of organic aromatic anhydrides have been determined by Venkatesan and co-workers at Bell Labs.[4-6] The rise in conductivity upon ion bombardment of these materials has been attributed to damage of the organic film with subsequent formation of graphitelike structures. Bartko et al.[7] investigated the irradiation of poly(phenylene sulfide) with 323 keV Li, 5.6 MeV F, and 50 MeV I. They concluded that the conductivity change was primarily a function of the electronic energy deposition rate: ions with high energy deposition rates cause greater conductivity increases than lower energy ions.

We were interested in determining the feasibility of ion implantation as a means of preparing conductive surfaces on polymeric coatings. In the studies described above,[4-6] the organic film thickness was comparable to the projected ion range and the ion damage extended through the thickness of the film. The changes in the structure and conductivity of thick (25 μm) coatings of polyimide (PI) and of polyamideimide (PAI) upon bombardment by high doses of energetic ions are described in this paper. PI and PAI were chosen for study for two reasons: These polymers are thermally stable and would be expected to withstand the heating caused by ion bombardment of thermally and electrically insulating films. PI and PAI are used widely in the electronics industry; a means of making conductive surfaces on such films would enable new device designs.

EXPERIMENTAL

Preparation of Test Specimens

Most of the test specimens were prepared by electrophoretic deposition[8] of Torlon polyamideimide (PAI) or of Pyre ML-5019 polyimide (PI) onto 25 mil thick H14 aluminum panels. A typical procedure was to dissolve 25 mL Pyre ML-5019 in 5 mL 1-methylimidazole and 125 mL DMSO. The solution was poured slowly into 500 mL acetone to form a stable emulsion. Polyimide was electrodeposited at 100 V for 2 min and the coatings cured at 150°C for 2 h, then at 250°C for 10 h. Film thickness was 25 μm.

Ion Bombardment

Samples were irradiated at several facilities. The nature of the samples, irradiation conditions and the location of the irradiation facility are given in Table I.

Conductivity Measurements

Samples were analyzed with a four-in-line probe as described by Smets.[9] Probes were constructed of tungsten wire cut to sharp points. Those samples which exhibited low resistance ($> 10^4 \Omega$ cm) on initial testing were examined with a 1 MΩ resistor in series which regulated current flow through the

TABLE I
Parameters for Ion Implantation Experiments

Polymer	Ion	Fluence (ions/cm^2)	Energy (MeV)	Beam current (nA/cm^2)	Irradiation facility
PI	Ar$^+$	1×10^{16}	2	100	Univ. Pittsburgh HEIBS Facility
PAI	Cu^{+4}	5×10^{14}	~ 3[a]	400	Univ. Rochester
PI	Br^{+5}	5×10^{14}	~ 3[a]	77	Univ. Rochester
PI	Ar$^+$	1.5×10^{17}	0.1	200,000	Westinghouse R & D
PI	Ar$^+$	1.7×10^{16}	0.2–0.9	—	Georgetown Univ.

[a] 40 MeV Cu^{+4} and Br^{+5} beams were passed through 0.33 and 0.1 mil, respectively, Al films prior to impinging on the target.

circuit; otherwise, both the induced current and the voltage drop across the probe were measured at five applied voltages. Polyimide samples bombarded with 100 keV Ar^+ ions (fluence = $5 \times 10^{16}/cm^2$) were maintained at room temperature and at 90, 150, and 210°C (in circulating air ovens). Samples were periodically removed for conductivity measurements at room temperature. Conductivity measurements were also performed at elevated temperature by placing the sample mounted on the four point probe inside a circulating air oven.

Analysis of Implanted Polymer Surfaces

ESCA analyses of Ar^+-implanted PI (2 MeV, $1 \times 10^{16}/cm^2$) and of unimplanted PI were performed on a VG Scientific ESCALAB MKII. In addition to survey spectra covering binding energies (BE) from 0 to 1000 eV, expanded spectra were recorded from 275 to 300 eV (carbon, 1s), 390 to 415 eV (nitrogen 1s), and 522 to 547 eV (oxygen 1s). Cross-section views of the topography of the implanted regions were obtained by measuring the surface profile of implanted PI with a Sloan Dektak. In order to determine the depth of the implantation, sections of ion implanted PI supported on an aluminum substrate were processed through a typical metallography sequence. These specimens were clip mounted on edge and then encapsulated in a Hysol resin (12:1 resin:hardener ratio, by volume) in a 1.25 in. metallographic mold. Curing was done in a vacuum oven for 4 h at 50°C. Subsequent metallographic polishing began with wet grinding on 220-grit SiC paper and through various grades to finish with 1000-grit SiC. Final polishing was performed using 3-μm diamond spray, followed by 1 μm, both times using a microcloth polishing surface. Micrographs were obtained at magnifications up to 1000 $\times$ using a Leitz metallograph.

RESULTS AND DISCUSSION

Appearance of Ion Bombarded Films

Visual inspection of implanted PI or PAI revealed darkening of implanted regions; areas subjected to high ion fluences acquired a metallic reflectivity and were deep black in color. The modified regions were nonbrittle and could be flexed without obvious cracking. Similar high optical reflectivities have been reported[10] for Kapton films irradiated with 1 MeV N_2^+. Profile analysis showed the bombarded surfaces to be sunken below the unirradiated polymer surface. For example, a polyimide sample irradiated with 1×10^{16} Ar/cm^2 (2 MeV ions) showed a step of ~ 2 μm at the edge of the irradiated region. This step may have been formed by a combination of polymer densification, due to atomic displacement processes, and of surface sputtering during the implantation.

Optical micrographs of a cross section through a polyimide film implanted with 2 MeV Ar^+ ions at a fluence of 1×10^{16} Ar/cm^2 revealed two modified layers near the surface [Fig. 1(a)]. Each layer was approximately 7-μm thick. It is possible to predict two such layers from the theoretical damage distribution produced by implantation. A more highly damaged region should be produced near the end of the range (R_p) of the incident ions due to a large

(a)
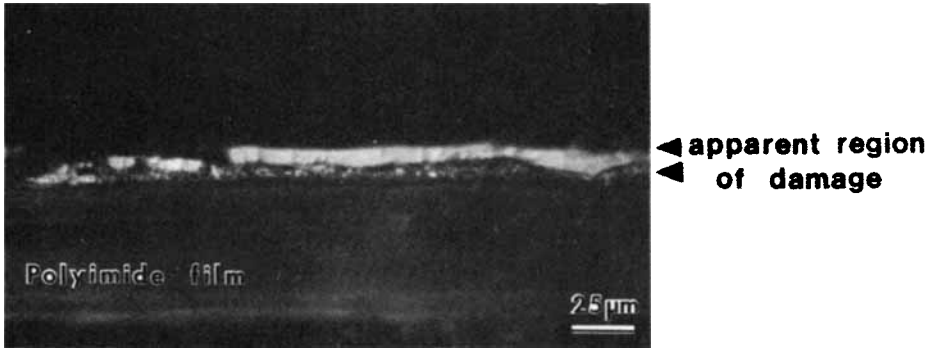
AI substrate

(b)

Fig. 1. Optical micrograph of Ar^+-implanted polyimide film. (A) The film was irradiated with 5×10^{16} Ar^+/cm^2 at 2 MeV; two damaged layers are apparent. (B) The dose was 5×10^{17} Ar^+/cm^2 at 100 keV; only one damaged layer, extending 1.5 μm into the surface is visible.

number of atomic displacements. The near surface region has less displacement damage but defects are created by electronic processes. The projected range of 2 MeV Ar^+ in polyimide (density = 1.4 g/cm^3) is 2 ± 0.35 μM. Between this zone, into which the ions transfer the bulk of their energy, and the surface is a region in which thermal and ionization processes are expected. Microscopic examination of a film implanted with 100 keV ions showed a modified layer extending ~ 1.5 μm below the surface [Fig. 1(b)]. In this instance, the presence of two distinct damaged layers was not observed. The expected implantation range at this energy is 0.14 ± 0.05 μm. At both ion energies, the damaged layer is deeper than the expected ion range. This variance can be attributed to a combination of thermal effects and secondary ion emission.[11] Both of these mechanisms are effective only at high ion fluxes and fluences. Implantation of poly(methyl methacrylate) with modest fluences of argon ions ($10^{11}-10^{13}/cm^2$) has been studied[12]; the thickness of damaged polymer was found to vary with the fluence, exceeding the calculated thickness by 50% at the higher fluence values. At the fluences of $10^{16}-10^{17}$ used in implanting the PI, it is not surprising that the damage zone extends even further beyond R_p. The ability of high ion fluxes to cause damage beyond the

TABLE II
Elemental Composition of the Near Surface:
ESCA Analysis of Ion Irradiated Polyimide

| | Composition | | |
	C	O	N
Expected	76	17	7
Unimplanted	82	13	5
Implanted	88	11	2

projected range of the ion is not limited to organic materials. For example, in HgCdTe (a "low use temperature" inorganic compound semiconductor) the damage zone exceeds R_p and is found to extend to a depth of 10 μm^{13}.

ESCA Analysis

The composition of both irradiated and unmodified polyimides was determined by ESCA analysis of a partly masked sample 1 month after implantation. Data were corrected for the varying sensitivities of C, O, and N to the ESCA experiment; the quantitative values may err by up to 10%. The data (listed in Table II) indicate a loss of most of the nitrogen and of a substantial quantity of oxygen as a result of irradiation. Comparison of the carbon 1s spectra (Fig. 2) shows a shift in the absorption region due to the absence of surface charging in the irradiated sample—an indication of surface conductiv-

A. Unimplanted

B. Implanted

300   275
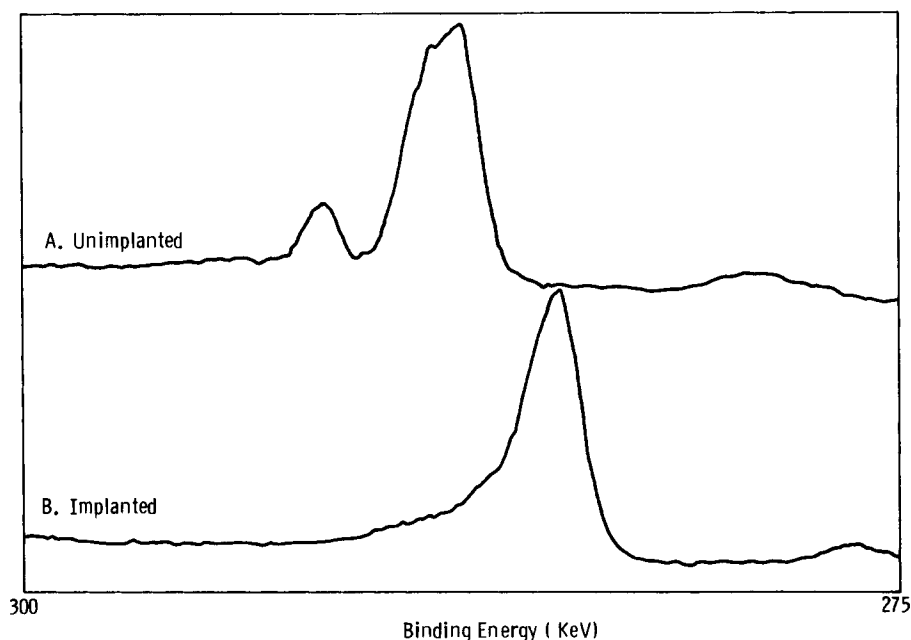Binding Energy (KeV)

Fig. 2. ESCA analysis of polyimide films—carbon 1S spectra: (A) result from as-prepared film; (B) spectrum after irradiation of PI with 1×10^{16} Ar$^+$/cm^2 at 2 MeV. Note the loss of fine structure and shift to lower binding energy in the implanted film due to formation of a conductive layer.

ity. The change in the binding envelopes indicates a loss of carbon–oxygen and carbon–nitrogen double bonds and the formation of an array of carbon–carbon and carbon–heteroatom single bonds different from those in the unimplanted polymer. No evidence for Ar incorporation was found in this month-old sample; XES analysis of a sample 2 days after implantation revealed small amounts of Ar in the film. This indicates that the Ar, as expected, does not react into the polymer but diffuses out of the film over a period of several days to a few weeks. It should be noted that the ESCA data are representative only of the uppermost atomic layers in the films; for those samples in which two modified layers were observed, no chemical composition of the lower layer was determined.

Venkatesan et al.[14] studied the change in chemical composition of PMMA films irradiated with argon ions by monitoring the loss of volatile species, principally H_2 and CO_2. They concluded that evolution of volatile species enriches the remaining polymer in carbon atoms and that the emission of low molecular weight species produced by the ion beam was diffusion limited. In a separate study,[5] it was found that, following irradiation, oxygen was incorporated into the irradiated polymer, presumably by the reaction of ionic species with air and water in the atmosphere.

Conductivity at Ambient Temperature

The surface conductivity $\sigma(s)$ of the irradiated surface was calculated[9] from four-point probe current–voltage measurements and is given by

$$\sigma(s) = (\ln 2/\pi)(I/V) \tag{1}$$

where I/V is the sample conductance determined by least squares evaluation of measurements at five induced voltages. It is clear from the edge-on microscopy that the conducting region is of varying composition; it is likely that there is a distribution of conductivities as a function of depth in the bombarded region. Consequently, assignment of a bulk conductivity would involve large uncertainties. For the PI samples irradiated with $1 \times 10^{16} Ar^+$ at
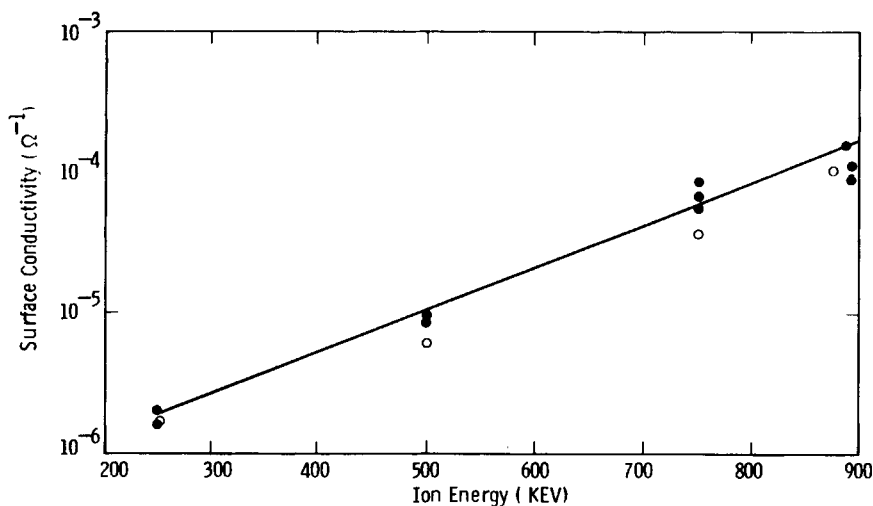

Fig. 3. Surface conductivity of polyimide films irradiated with Ar^+ ions over a range of ion energies at fluences of 1.7×10^{16} (●) and 2.1×10^{16} (○).

TABLE III
Experimental Parameters and Results Ion Irradiation of Polyimide Coatings

Experiment	Ion	Fluence (ions/cm^2)	Energy (MeV)	Surface conductivity (Ω^{-1})
I	Ar$^+$	1×10^{16}	2	$\sim 10^{-3}$
II	Cu^{+4}	5×10^{14}	3	4.4×10^{-5}
III	Br^{+5}	5×10^{14}	3	2.3×10^{-4}
VI	Ar$^+$	5×10^{16}	0.1	3.7×10^{-7}
VII	Ar$^+$	1×10^{17}	0.1	2.0×10^{-7}
		2×10^{17}		1.7×10^{-6}
		5×10^{17}		5.2×10^{-3}

2 MeV, or 5×10^{17} Ar$^+$ at 100 keV, the average bulk conductivity is approximately 10^3 Ω^{-1} cm^{-1}. This is an increase of some 17 orders of magnitude above the conductivity of native polyimide.

As shown in Figure 3, the surface conductivity was found to vary exponentially with the ion beam energy over energies ranging from 200 to 900 keV. Least squares analysis of the data show the surface conductivity to be given by

$$\sigma(s) = 3.13 \times 10^{-7} \times e^{(0.00687 \times E)} \qquad (2)$$

where the ion energy E is expressed in keV and the surface conductivity is in units of Ω^{-1}. Studies at high ion energies show the conductivity to be a function of the energy deposition rate rather than the beam energy.[7] At the low energies used in this study, the energy deposition rate is proportionate to the energy, hence the apparent dependence of $\sigma(s)$ on E. While the data displayed in Figure 3 show no difference in the conductivities obtained with fluences of 1.7 and 2.1×10^{16}, the data in Table III show an increase in the conductivity is achieved with higher fluences. The change in conductivity of ion beam irradiated polymers is likely to depend on the ion flux and the sample temperature as well as the fluence and energy. The data in Figure 3 show that, within the precision of the measurement, the change in conductivity is reproducible.

Thermal Cycling and Elevated Temperature Studies

Polyimide samples implanted with 100 keV argon ions at a fluence of 5×10^{16}/cm^2 were exposed to elevated temperatures for 6 weeks, following which their conductivity was determined at room temperature. A sample maintained at 90°C retained some 80% of its original conductivity while a sample at 150°C exhibited only 60% of its original conductivity. The conductivity of a sample heated at 210°C could not be determined since the voltage and the current in the probe circuit were both below the detection limits of the apparatus. No change was found in the conductivity of a sample left at room temperature.

The variation of the conductivity at temperature as a function of time was studied at 124, 167, and 190°C (Fig. 4). At 124°C, no significant variation of the conductivity was seen over 26 h. At 167°C the conductivity was found to increase at first, then fall off slightly, while, at 190°C, data taken between 42 and 97 h show the conductivity to fall off toward a constant value. At both
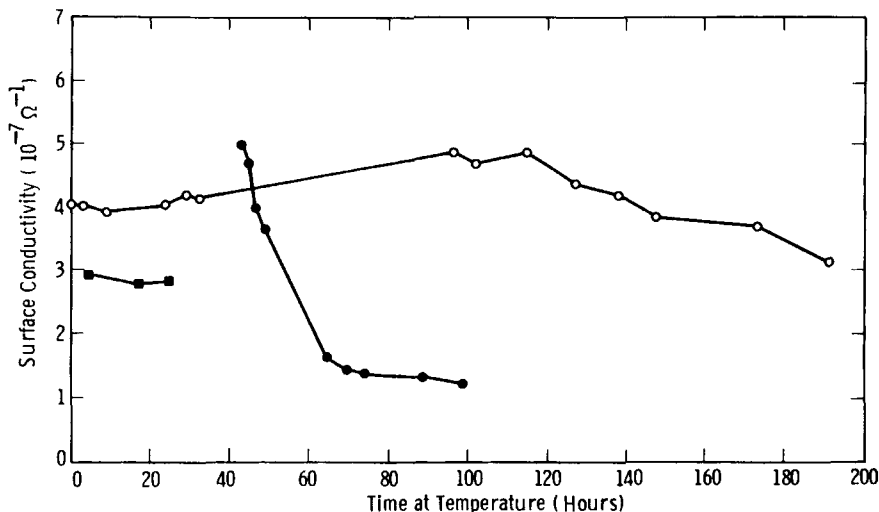
Fig. 4. *In situ* measurement of surface conductivity of ion implanted polyimide at 124 (■), 167 (○), and 190°C (●). Polyimide had been implanted with 100 keV Ar$^+$ ions at a fluence of $5 \times 10^{16}/cm^2$.

167 and 190°C, compensating decreases in both the measured voltage and the measured current were observed during the course of the experiments. In fact, these experiments were terminated because current–voltage signals fell below the detection limits of the equipment. This phenomenon may signal increased resistance at the electrode–polymer contact due to surface oxidation of the polymer.

The temperature dependence of the conductivity over the range 295 to 398 K is shown in Figure 5. Forrest et al.[15] proposed a model for the conductivity in implanted materials based on charge hopping between highly conductive islands in an insulating matrix. This model requires an exponential $T^{-1/2}$ dependence for the conductivity; data over the temperature range 50–360 K were found to support this hypothesis. The data presented in Figure 5 show an exponential $T^{-1/2}$ dependence at temperatures up to 383 K; at higher temperatures the conductivity was found to have a stronger dependence on temperature.
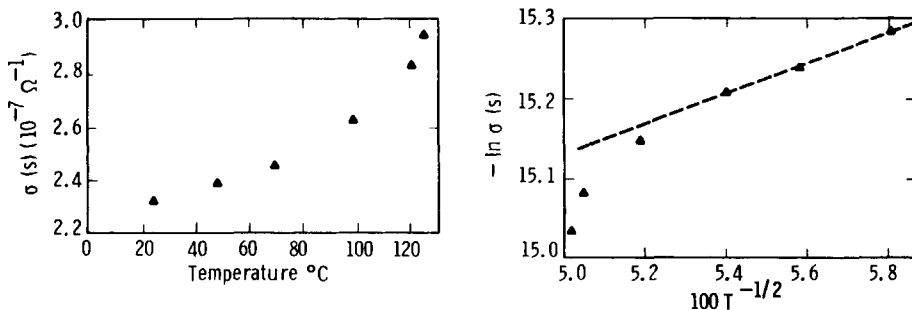

Fig. 5. Surface conductivity [σ(S)] vs. temperature for polyimide irradiated with 100 keV Ar$^+$ at a fluence of $5 \times 10^{16}/cm^2$. Logarithmic dependence of σ(S) on $T^{-0.5}$ is shown at $T < 100°C$.

CONCLUSIONS

Implantation of thick films of polyimide and polyamideimide results in modifications of the surface similar to the changes found in thin polymer films. In the case of the thick films, the damage layer extends only partially through the film, but is several times thicker than the projected ion range. The surface conductivity obtained by ion implantation varies with both the dose and the energy; conductive surfaces are most rapidly attained by implantation with keV ions, since the higher beam currents obtainable at such energies permit high fluences to be reached quite rapidly. The surface conductivity was stable at room temperature but decayed with time at elevated temperatures: after 6 weeks at 150°C a sample lost 40% of its initial surface conductivity. Polymers rendered conductive by ion implantation have much greater thermal and oxidative stability than most conducting polymers; nevertheless, the eventual decay of the conductivity at elevated temperatures and the thinness of the conductive layer may limit the industrial application of such materials.

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