

# Degradation of Polyimide by Implantation with Ar<sup>+</sup> Ions

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**ABSTRACT:** Polyimide (PI) samples were irradiated with 200 keV Ar<sup>+</sup> ions to fluences from  $5 \times 10^{13}$ – $1 \times 10^{17}$  cm<sup>-2</sup> and the concentration depth profiles of implanted Ar atoms as well as of carbon and oxygen atoms of the polymer matrix were determined using the Rutherford backscattering technique. The surface polarity, sheet resistivity, and thermoelectric power of PI samples were also determined as a function of the ion fluence and temperature. As a result of the ion irradiation, the polyimide surface layer is depleted of oxygen and enriched by carbon. The sheet resistivity exhibits a minimum at the ion fluence of  $5 \times 10^{16}$  cm<sup>-2</sup> and the temperature dependence of the sheet resistivity indicates the semiconducting character of irradiated PI and the variable range hopping mechanism of charge transport. The thermoelectric power of the PI samples irradiated to high fluences is small, of the order of  $\mu\text{V/K}$ , and independent of temperature. This behavior is typical for metals. The simultaneous appearance of metal and semiconducting properties is probably due to the complex structure of the PI surface layer modified by the ion irradiation. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 723–728, 1997

## INTRODUCTION

Irradiation of polyimide (PI) with energetic heavy ions leads to dramatic changes of the chemical structure of the polymeric chain: Imide groups transform into amides ones,<sup>1</sup> aromatic rings are scissioned,<sup>2</sup> and oxygen,<sup>3</sup> CO, and other volatile degradation products<sup>1,2,4</sup> are liberated and eventually expelled from the irradiated material. The changes in relative concentrations of carbon and oxygen in PI irradiated with Ag<sup>+</sup> and W<sup>+</sup> ions were reported earlier.<sup>3</sup> The production of amorphous carbon in PI implanted to fluences above  $1$

$\times 10^{14}$  cm<sup>-2</sup> has been observed.<sup>2,3,6</sup> Dehydrogenation of the PI molecular chain, production of conjugated double bonds, and carbonization contribute to increased conductivity of ion-irradiated PI.<sup>2,7</sup> At higher ion fluences, the resulting resistivity and hardness may be affected by crosslinking between molecular chains.<sup>8</sup> It has been shown that significant changes of electrical resistivity, optical transparency,<sup>9</sup> and hardness and wear resistance<sup>6,10</sup> are observed if the concentration of implanted ions is above 1 wt %.<sup>11</sup>

In this study, the structural and chemical changes induced in PI by irradiation with 200 keV Ar<sup>+</sup> ions to different fluences were studied. The polarity of the irradiated PI was also determined. The measurements of the sheet resistivity and thermoelectric power in dependence on temperature were performed to obtain new data on electrical charge transport in modified PI.

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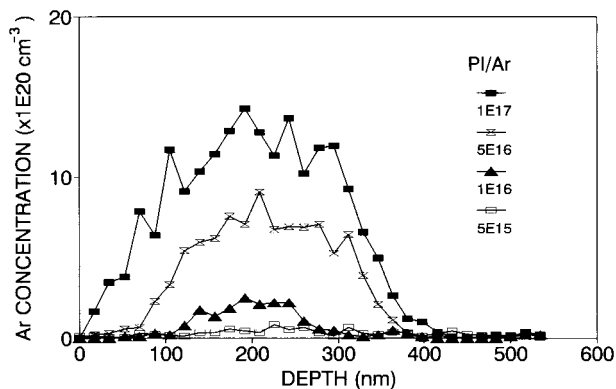
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**Figure 1** The concentration depth profiles of Ar atoms implanted into PI at 200 keV energy to different fluences. The profiles were obtained from RBS spectra.

## EXPERIMENTAL

Foils, 50  $\mu\text{m}$  thick, of oriented polyimide Upilex (PI) with a density of  $\rho = 1.39 \text{ g cm}^{-3}$  produced by UBE Industries Ltd. were used in these experiments. The foils were implanted with 200 keV  $\text{Ar}^+$  ions to fluences from  $5 \times 10^{13}$ – $1 \times 10^{17} \text{ cm}^{-2}$ . The implantation was accomplished at room temperature with an ion current density of about  $0.1 \mu\text{A cm}^{-2}$ . The polar component of the free surface energy, characterizing the surface polarity, was determined by measuring the contact angle on the PI surface with a goniometer.<sup>12</sup> The sheet resistivity ( $R_s$ ) was measured by a two-point technique using a Keithley 487 device. The measurements were performed in laboratory atmosphere and at room temperature. The  $R_s$  vs. temperature dependence was measured on samples placed in  $\text{LN}_2$  cryostat evacuated to the pressure of about  $10^{-4}$  Pa. The samples were first cooled to  $\text{N}_2$  temperature and then slowly heated. The thermoelectric power (TEP) was determined in a temperature interval from 298 to 433 K using a direct method with a voltage supply and a Keithley 182 nanovoltmeter. The distance of Ag contacts was 1 mm, the temperature gradient was 5 K, and all measurements were accomplished at atmospheric pressure. The depth concentration profiles of the implanted Ar atoms and the atoms of the PI matrix were determined using the Rutherford backscattering method (RBS) with 1.3 MeV  $^4\text{He}$  ions ( $160^\circ$  laboratory scattering angle). The depth resolution at the sample surface was about 20 nm.

The samples were observed with a JOEL 6400 electron microscope. All doped specimens exhibited a perfectly smooth surface with irregularities not exceeding the SEM resolution of ca. 100 nm.

## RESULTS AND DISCUSSION

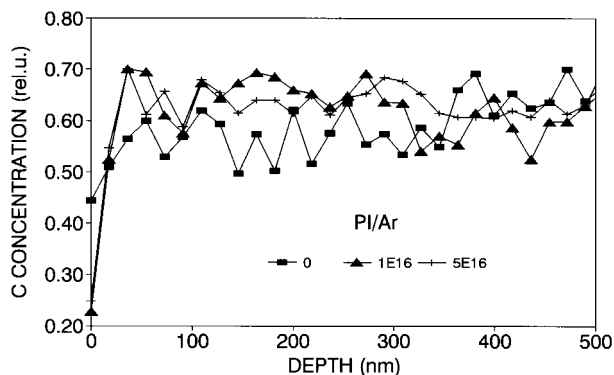
The depth distributions of selected elements in the PI surface layer modified by ion irradiation were determined using the RBS technique. The experimental depth profiles of implanted Ar atoms are shown in Figure 1 for different implanted fluences. The measured projected ranges  $R_p$  and range stragglings  $\Delta R_p$  are summarized in Table I together with theoretical values obtained using the TRIM 91 simulation code.<sup>13</sup> No significant dependence of the profile parameters on the ion fluence is observed within experimental uncertainties. The measured projected ranges are lower than those calculated by about 20% and the range stragglings exceed the theoretical value by about 45%. Similar discrepancies were reported earlier, e.g., in Refs. 10 and 14, and they are probably due to structural and compositional changes of the polymer during ion irradiation which are not taken into account in theoretical calculations. The RBS results show that an about 400 nm-thick surface layer of PI is modified by irradiation with 200 keV  $\text{Ar}^+$  ions.

The RBS method was used also for the determination of the depth profiles of carbon and oxygen atoms in the PI surface layer modified by ion irradiation. The observed changes of the carbon distribution are small and they lie mostly on or below present detection limits given by rather low measuring statistics. The most pronounced effect observed on the samples implanted to the fluences of  $1 \times 10^{16}$ – $5 \times 10^{16} \text{ cm}^{-2}$  is illustrated in Figure 2, where the carbon depth distributions from modified samples are compared with that from pristine PI. An increase of carbon concentration by about 20% is seen in a about 300 nm-thick surface layer.

**Table I** Projected Range  $R_p$  and Range Stragglings  $\Delta R_p$  of 200 keV  $\text{Ar}^+$  Ions in PI as Functions of the Ion Fluence

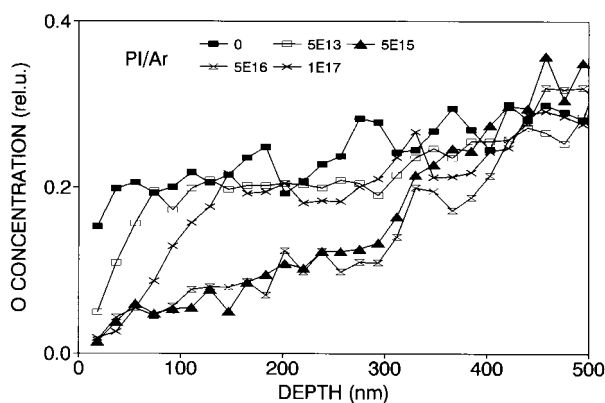
Ion Fluence ( $\text{cm}^{-2}$ )	$R_p$ (nm)	$\Delta R_p$ (nm)
$1 \times 10^{17}$	203 (4)	88 (8)
$5 \times 10^{16}$	219 (3)	74 (3)
$1 \times 10^{16}$	213 (14)	75 (18)
$5 \times 10^{15}$	270 (30)	130 (40)
TRIM code	263	55

The error convention  $\text{YYY}(\text{XX}) = \text{YYY} \pm \text{XX}$  is used and the quoted errors are 1 standard deviation. The measured values can be compared with theoretical estimates obtained using the TRIM simulation code for pristine PI.

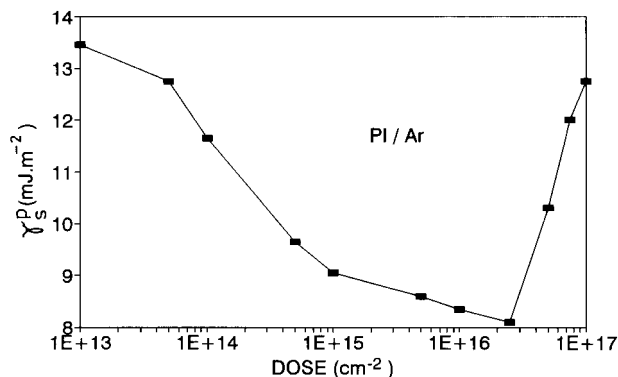


**Figure 2** The concentration depth profiles of carbon in the PI surface layer modified by the implantation with 200 keV Ar<sup>+</sup> ions to different fluences.

The depth profiles of oxygen in a 500 nm-thick surface layer, accessible in the present experimental setup, are shown in Figure 3. One can see a rather complex change of the oxygen depth distribution with increasing ion fluence. For pristine PI and PI implanted to the lowest fluence, a nearly homogeneous oxygen distribution is observed. The irradiation to higher fluences leads to oxygen depletion up to 25–50% of its initial concentration in the 350 nm-thick surface layer bombarded by Ar<sup>+</sup> ions. The degree of the oxygen depletion is a decreasing function of the depth in accordance with theoretical depth distribution of Ar<sup>+</sup> ion energy losses as determined with the TRIM 91 code. For the highest ion fluence of  $1 \times 10^{17} \text{ cm}^{-2}$ , an increase of the oxygen concentration compared to  $5 \times 10^{16} \text{ cm}^{-2}$  in a 100–300 nm-depth interval is observed, which indicates an incorporation of ambient oxygen in the final stages of the ion irradiation. This effect may be due to deep structural changes of the polymer, but its



**Figure 3** The same as in Figure 2 but for oxygen.

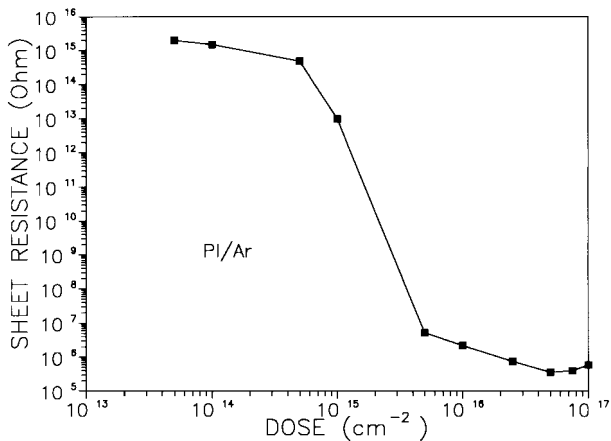


**Figure 4** The dependence of the polar component of the surface free energy  $\gamma_s^p$  on the ion fluence.

microscopic mechanism remains still unclear. The deoxygenation effect of the ion irradiation is known and it has been observed earlier, e.g., in Kapton irradiated with Ag<sup>+</sup> and W<sup>+</sup> ions<sup>2</sup> or in Upilex modified with N<sup>+</sup> ions.<sup>1</sup>

Surface properties of the modified polymers, which may be of practical importance (e.g., for biopolymers<sup>15</sup>), are determined mainly by the concentration of oxidized structures at the polymer surface. Most of the oxygen-containing structures, including the imide group —CO—N—CO— of PI, are polar and their presence may be determined by measuring of polar component of the surface energy  $\gamma_s^p$  with a goniometer.<sup>11</sup> The measured dependence of  $\gamma_s^p$  on the ion fluence is shown in Figure 4. Up to a fluence of  $2.5 \times 10^{16} \text{ cm}^{-2}$ , the surface polarity decreases, but for higher fluences, a rapid polarity increase is observed. This finding correlates well with the above discussed RBS results (see also Fig. 3). Irradiation to lower ion fluences leads mainly to degradation of polar groups and deoxygenation of the PI molecular chains. For ion fluences above  $5 \times 10^{16} \text{ cm}^{-2}$ , the strongly modified PI surface is oxidized again and the surface polarity increases.

It was reported earlier that the ion irradiation of different polymers results in a significant decrease of their sheet resistivity  $R_s$ . Such results have been obtained, e.g., for polystyrene,<sup>15</sup> polyethylene, polypropylene and polyimide,<sup>16</sup> and poly(ethylene terephthalate).<sup>17</sup> The dependence of the PI sheet resistance on the Ar<sup>+</sup> ion fluence is shown in Figure 5. The sheet resistance is a decreasing function of the ion fluence. A very slow change of  $R_s$  observed for fluence below  $5 \times 10^{14} \text{ cm}^{-2}$  is followed by a rapid  $R_s$  decrease by 8 orders of magnitude in the fluence interval from  $5 \times 10^{14}$



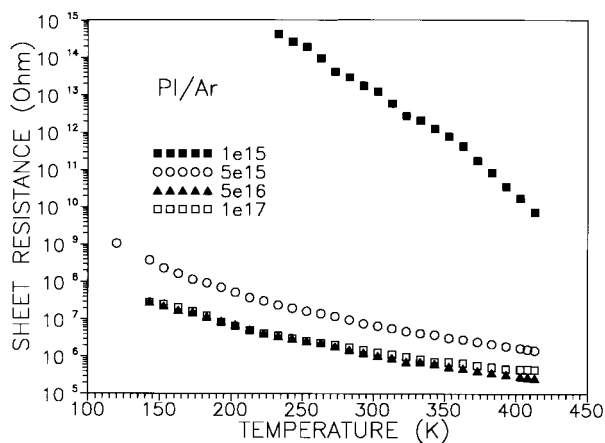
**Figure 5** The dependence of the sheet resistivity  $R_s$  on the ion fluence measured at room temperature.

to  $5 \times 10^{15} \text{ cm}^{-2}$ . For still higher fluences, a much slower  $R_s$  decrease, by 1 order of magnitude, is observed followed by a minor  $R_s$  increase for highest fluences. In the present case, a saturation of  $R_s$  takes place already at a fluence of  $5 \times 10^{15} \text{ cm}^{-2}$ , which is 10 times lower than the saturation threshold reported by Iwaki et al.<sup>3</sup> for PI irradiated with  $\text{Ag}^+$  and  $\text{W}^+$  ions. The absolute value of  $R_s$  observed in Ref. 3 is by 3–4 orders of magnitude lower than the present one. The differences are obviously due to the different mass and ionization ability of ions used in Ref. 3 and in the present study.

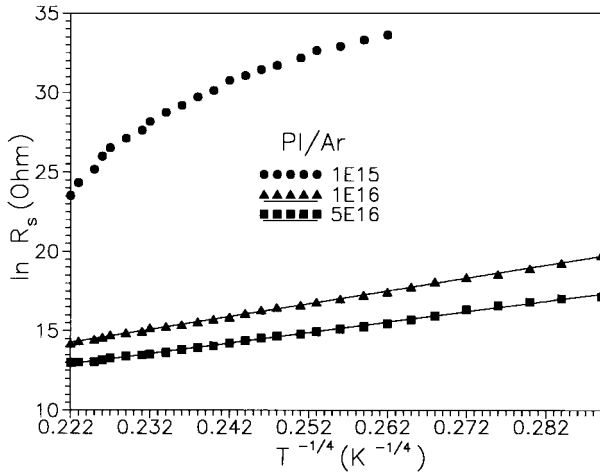
The enhanced conductivity of the polymers modified by ion irradiation is due to the presence of conjugated double bonds as well as of carbon clusters.<sup>7</sup> It was observed<sup>3</sup> that the irradiation with  $\text{Ag}^+$  ions leads to a higher degree of carbonization than does the irradiation with heavier  $\text{W}^+$  ions, but the electrical conductivity of the modified PI is higher in the latter case. The irradiation with 200 keV  $\text{Ar}^+$  ions does not produce significant carbonization of PI (as shown in Fig. 2) and the observed decrease of  $R_s$  may partly be due to the creation of conjugated double bonds by the destruction of the benzene rings.<sup>18</sup> The data of Ref. 3 together with the present results show that the irradiation with heavier ions generally leads to a larger decrease of the resulting sheet resistivity of the modified PI. The role of the carbon clusters was recently studied on polymer + carbon black mixtures<sup>19</sup> with various carbon black concentrations. It was found that the effect of the ion irradiation on the sheet conductivity of the mixture depends strongly on the carbon black concentration. For concentrations below the percola-

tion threshold, the ion irradiation leads to a conductivity increase, while for concentrations above the percolation threshold, the effect is opposite. This observation shows that the ion irradiation degrades the conductive system of carbon clusters initially present in the mixture. The small increase of  $R_s$  observed for the fluences above  $5 \times 10^{16} \text{ cm}^{-2}$  (see Fig. 5) may be caused by the same effect and/or by the additional oxidation of the PI surface layer which may also deteriorate the conductive structures created in initial stages of the ion irradiation.

The temperature dependence of the sheet resistivity measured on PI modified by ion irradiation is shown in Figure 6. Only selected specimens characteristic for different regions of  $R_s$  vs. fluence dependence were examined (in Fig. 5). In the present experimental arrangement, the temperature dependence could be measured only using the samples with  $R_s \leq 1 \times 10^{15} \Omega$ . For all samples, the sheet resistance is a decreasing function of the temperature; this behavior is typical for semiconductors. It is also seen from Figure 5 that the activation energy needed for elevation of electrons into the conductive band decreases with increasing ion fluence. This fact indicates a thermal mechanism of the excitation of charge carriers in the present case. In the polymer + carbon black mixtures studied<sup>19</sup> as a model of carbonized polymer, the sheet resistivity after the ion irradiation remains constant or slowly increases with increasing temperature, i.e., the system exhibits metal-like conductivity. The semiconducting character of irradiated PI as observed in the present experiment indicates that the conductivity has to be contributed to not only by carbon clusters but



**Figure 6** Temperature dependence of the sheet resistivity  $R_s$  for PI irradiated to different ion fluences.



**Figure 7** Temperature dependence of the sheet resistivity  $R_s$  for PI irradiated to different ion fluences.

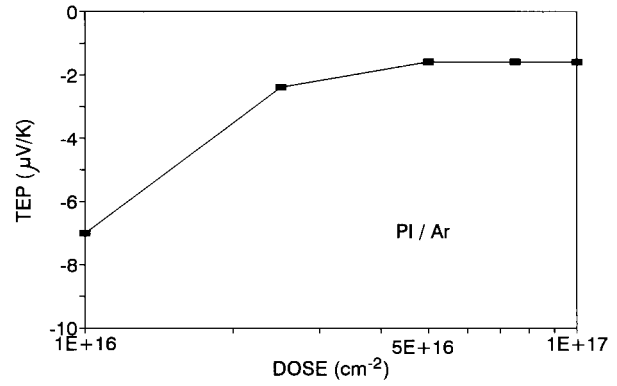
also by another conducting structures, e.g., by conjugated double bonds.<sup>7</sup>

Several models of charge transport in modified polymers have been suggested based on variable range hopping (VRH) or tunneling concepts with solitons or polarons as mediators<sup>20,21</sup> The validity of a particular model can be judged from the temperature dependence of the resistivity.<sup>20</sup> The temperature dependence of the sheet resistivity  $R_s$  for PI irradiated with Ar<sup>+</sup> ions is shown in Figure 7 in  $\ln R_s$  vs.  $T^{-1/4}$  form. For the samples irradiated to fluences above  $1 \times 10^{16} \text{ cm}^{-2}$ , the  $\ln R_s$  vs.  $T^{-1/4}$  dependence is linear in the whole temperature region from 140 to 415 K. It may be concluded that, at least for higher ion fluences, the temperature dependence of the sheet resistivity follows the theoretical dependence

$$R_s(T) \approx \exp[(T_0/T)^{1/4}] \quad (1)$$

typical for VRH mechanism of charge transport suggested by Mott.<sup>22</sup>

Another quantity which may characterize the mechanism of charge transport is thermoelectric power (TEP).<sup>20</sup> The dependence of the TEP on the ion fluence is shown in Figure 8. In the present experimental setup, the TEP could be measured only on the samples with  $R_s \leq 2 \times 10 \ \Omega$ , i.e., the PI samples implanted to the fluences above  $1 \times 10^{16} \text{ cm}^{-2}$ . The measured  $|\text{TEP}|$  is a decreasing function of the ion fluence. Similarly to results from a previous study,<sup>23</sup> the TEP values are low on the samples implanted to higher fluences. The temperature dependence of TEP is illustrated in Figure 9 on the PI samples irradiated to the flu-

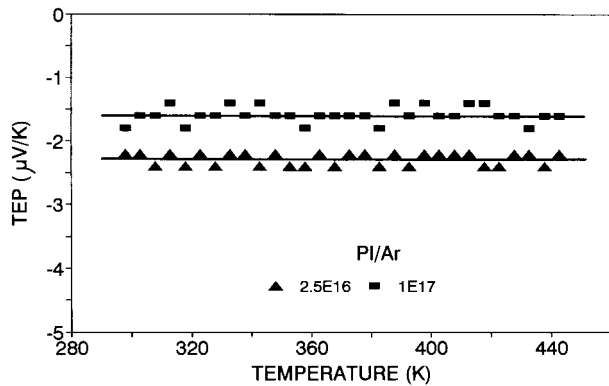


**Figure 8** The dependence of thermoelectric power TEP on the ion fluence measured at room temperature.

ences of  $2.5 \times 10^{16}$  and  $1 \times 10^{17} \text{ cm}^{-2}$ . In the temperature interval from 300 to 450 K, the TEP is negative and it does not depend on the temperature. Negative and constant TEP is typical for strongly damaged polymers and for metals.<sup>24–26</sup> The charge transport proceeds mostly via a VRH mechanism. A similar conclusion has been made by Isotalo and Stubb<sup>27</sup> for polythiophene irradiated with F<sup>+</sup> ions to the fluence of  $2 \times 10^{17} \text{ cm}^{-2}$ . The results are not so surprising in the view of complexity of the structures created on the PI surface by the ion irradiation.

## CONCLUSION

The properties of PI irradiated with 200 keV Ar<sup>+</sup> ions to different fluences were studied using various techniques. Ion irradiation leads to degradation of PI surface layer about 400 nm thick. Low carbonization, around the present sensitivity level, is observed on the PI surface regardless of



**Figure 9** Temperature dependence of TEP for PI irradiated to different ion fluences.

the ion fluence applied. The oxygen, on the other side, is liberated and expelled by the ion impact and strong deoxygenation is observed for higher ion fluences. The sheet resistivity  $R_s$  of the ion beam-modified PI is a decreasing function of the ion fluence. An abrupt decrease of  $R_s$  by 8 orders of magnitude is observed in the fluence interval  $5 \times 10^{15}$ – $5 \times 10^{16}$  cm<sup>-2</sup>. A minor  $R_s$  increase observed above the ion fluence of  $5 \times 10^{16}$  cm<sup>-2</sup> is probably due to additional oxidation of irradiated PI and to deterioration of initially produced conductive structures based on carbon clusters. The temperature dependence of  $R_s$  in irradiated PI is typical for semiconductors and the charge transport proceeds via a variable range hopping mechanism. The measured thermoelectric power is negative and independent of temperature, i.e., it has properties typical for metals. This complex behavior is due to the extremely complicated and fluence-dependent structure of the PI surface layer modified by ion irradiation.

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