Ion Beam Ablation of Polytetrafluoroethylene

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ABSTRACT: Polytetrafluoroethylene (PTFE) was irradiated with 300 keV Ar^+ ions to the fluences of 1×10^{14} to 1×10^{16} cm^{-2}; the PTFE structural changes induced by the ion irradiation were studied by X-ray diffraction and UV–vis and IR spectroscopies. The electrical conductivity of the ion beam modified PTFE was also investigated using the standard technique, and the alterations of the surface polarity were determined by contact angle measurements. The ion irradiation leads to intensive PTFE ablation due to the breaking of the C—C bonds in the polymer molecular chains and due to the production and liberation of the molecular fragments C_xF_y. In contrast to other polymeric materials, the irradiated PTFE carbonizes to a lesser extent and the observed irradiation induced increase of the electrical conductivity is also not significant. Incoming ions cause a reduction of the crystalline phase content in the PTFE samples. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 1257–1261, 1998

INTRODUCTION

There has been much special interest devoted to the study of various modifications of fluorated polymers, such as polytetrafluoroethylene (PTFE); these can be used in different fields, such as medicine, microelectronics, and chemistry because of their chemical inertness, thermal and mechanical stability, nontoxicity, and special pyroelectric and piezoelectric properties.[1]

There are several techniques for the modification of PTFE surface properties. Changes in optical properties, an increase of the surface polarity,[2] and growth of hardness and strength[3,4] were reported for the ion irradiated PTFE. *In situ* mass spectrometric measurements accomplished on the PTFE irradiated with 200 keV Si^+ ions show emission of CF, CF_3, and traces of CF_2 degradation products in the first minute of the irradiation and monomers, dimers, and trimers during longer irradiation.[3,4] Laser irradiation leads to PTFE ablation that may be employed for the production of thin polymeric layers.[5,6] Laser ablation is accompanied with PTFE pyrolytic decomposition.[5] In the plasmatic plume created by the laser irradiation of PTFE, several ablation products were detected, such as CF_2, monomers, dimers, and trimers and compounds like CF, CF_3, C_2F_3, and C_2F_5. A similar composition of degradation products was also observed in pyrolytic decomposition of PTFE at 600°C.[6] Sputtering of PTFE in the temperature region from 400 to 600°C was studied by Nason et al.[7] to produce polymeric layers. Because the C—F bond is stronger than the C—C bond in PTFE, thermal decomposition is expected to result in preferential splitting of C—C bonds while the C—F bonds remain rather untouched.[8]

This work examines the compositional and structural changes in PTFE irradiated with Ar^+ ions to different ion fluences. Also studied are op-

tical and electrical properties of ion beam modified PTFE, together with changes in PTFE surface polarity. The goal of the work was to obtain more complete experimental data on the effects of irradiation with medium energy heavy ions on highly radiation sensitive PTFE.

EXPERIMENTAL

All the present experiments were performed on 25 μm thick PTFE foils (supplied by Goodfellow Corp.) with an average density of 2.2 g cm^{-3} and a melting temperature of 340°C.[9] The foils were irradiated at room temperature with 300 keV Ar$^+$ ions to the fluences of 1×10^{14} to 1×10^{16} cm^{-2}. The pressure in the implanter target chamber was 10^{-4} Pa, and the ion beam current density was 30–40 nA cm^{-2}.

The thickness of the ablated PTFE surface layers was determined by optical microscopy with the typical uncertainty of about ±10%. X-ray diffraction (XRD) measurements were accomplished on a Philips diffractometer using CoK$_{\alpha 1,2}$ radiation; the X-ray spectra were registered in on-line mode with a velocity of $\frac{1}{2}$° min^{-1}. The sheet resistance (R_s) was measured by the two-point technique using a Keithley device. The R_s measurements were performed at room temperature and in a vacuum of 10^{-1} Pa. The contact angle characterizing the specimen surface polarity was measured in a water–polymer system on a reflexive goniometer.[10] The UV–vis spectra were measured by means of a standard UV–vis spectrometer (Perkin–Elmer) and IR spectra were measured using a FTIR spectrometer (Nicolet). For comparison, all measured spectra (i.e., X-ray, UV–vis, and IR) were recalculated to the original specimen thickness. The theoretical projected range of 300 keV Ar$^+$ ions in pristine PTFE calculated by TRIM (version 91) code[11] was $R_p = 325$ nm (range straggling $\Delta R_p = 74$ nm). The theoretical projected range gives an estimate of the thickness of the PTFE surface layer affected by the ion irradiation. However, straightforward comparison of this figure with experimental data is not possible in view of the specimen rapid ablation and strong compositional and structural changes during the ion irradiation. On the other hand, the above mentioned recalculation of the measured spectra to the original sample thickness was quite possible because the ion beam modified surface layer was about 2 orders of magnitude thinner than the
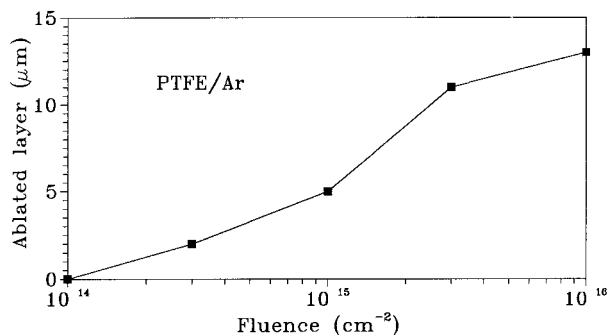
Figure 1 The thickness of ablated layers of PTFE as a function of the 300 keV Ar$^+$ ion fluence.

whole specimen. Differential IR spectra were obtained by subtracting the IR spectrum of pristine PTFE from that of the ion beam modified spectrum that was recalculated to the original sample thickness. The melting of the PTFE samples was examined by differential scanning calorimetry (DSC) with a DSC DuPont device and using a temperature rise velocity of 20 K min^{-1}. The DSC measurements showed that the present PTFE samples contained 58% crystalline phase and melted in an interval from 270 to 330°C.

RESULTS AND DISCUSSION

As mentioned earlier, the irradiation with ionizing radiation, laser light, or heating leads to rapid degradation of PTFE, liberation of volatile degradation products, and surface ablation. Here the ablation of the PTFE surface during irradiation with 300 keV Ar$^+$ ions was studied in dependence on the ion fluence. It can be seen from the results presented in Figure 1 that the irradiation at fluences above 1×10^{14} cm^{-2} results in considerable PTFE ablation. The thickness of the removed surface layer is an increasing, but obviously nonlinear function of the ion fluence. For the highest fluence of 1×10^{16} cm^{-2}, the thickness of the ablated layer is 13.1 μm (i.e., more than 50% of the original sample thickness). Measured changes of the sheet resistivity R_s and the contact angle (CA) dependent on the ion fluence applied are summarized in Table I. The present experimental arrangement allows us to measure sheet resistivities $< 1 \times 10^{16}$ Ω. One can see from Table I that R_s is a decreasing function of the ion fluence and that the fluence increase from 3×10^{14} to 1×10^{16} cm^{-2} leads to a conductivity increase by 1.5 orders of magnitude. PTFE is an unpolar polymer. As
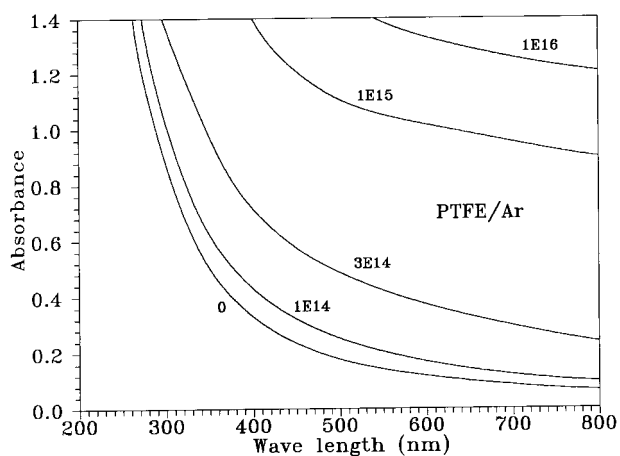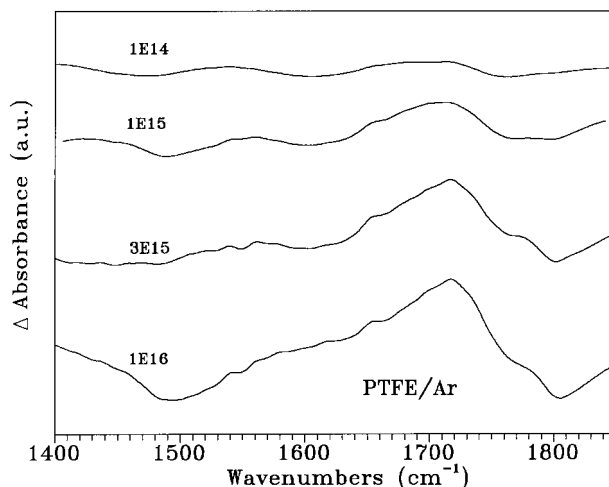
Table I   Dependence of Sheet Resistance and Contact Angle of PTFE on 300 keV Ar$^+$ Ion Fluence

Implanted Fluence (cm^{-2})	Sheet Resistance (Ω)	Contact Angle (°)
0	$>1 \times 10^{16}$	110.0
1×10^{14}	$>1 \times 10^{16}$	106.5
3×10^{14}	7.6×10^{15}	104.0
1×10^{15}	5.5×10^{15}	100.5
3×10^{15}	2.3×10^{15}	98.0
1×10^{16}	1.6×10^{14}	93.0

can be seen from Table I, for pristine PTFE and water a rather high contact angle was measured. With increasing fluence of Ar$^+$ ions, the CA declines significantly so that the ion irradiation increases PTFE surface polarity.

The elevated electrical conductivity of the ion beam modified nonaromatic polymers is often explained as a result of excessive conjugated double bonds created on polymeric chains.[12] Their concentration and length may be estimated from UV–vis spectra.[13] The above mentioned increase of the PTFE surface polarity may be caused, besides other factors, by incorporation of oxygen from the implanter residual atmosphere and the creation of oxidized structures in the radiation damaged surface layer. The presence and the concentration of oxidized structures can be determined by means of IR spectroscopy.[14]

Typical UV–vis spectra of the PTFE samples irradiated to different ion fluences are shown in Figure 2. From the measured dependence of the

Figure 3   Differential IR spectra ($1400–1850$ cm^{-1}) from the PTFE samples irradiated by 300 keV Ar$^+$ ions to various fluences.

UV–vis spectra it is seen that the length and the concentration of the conjugated double bonds both increase with increasing ion fluence.[13] The conjugation length also affects the color of the modified PTFE. The PTFE samples irradiated to the fluences above 1×10^{14} cm^{-2} exhibit brown color that darkened with increasing ion fluence. A similar qualitative conclusion for PTFE was obtained.[4] Darkening of other polymers due to ion irradiation is explained by gradual carbonization[15] and eventually by graphitization (e.g., in polyimide[16]).

Typical differential IR spectra are shown in Figures 3 and 4. The $1400–1850$ cm^{-1} region depicted in Figure 3 is characteristic for production of C=C ($1400–1500$ cm^{-1}), C=CF$_2$ ($1500–1700$

Figure 2   UV–vis spectra from the PTFE samples irradiated by 300 keV Ar$^+$ ions to various fluences.
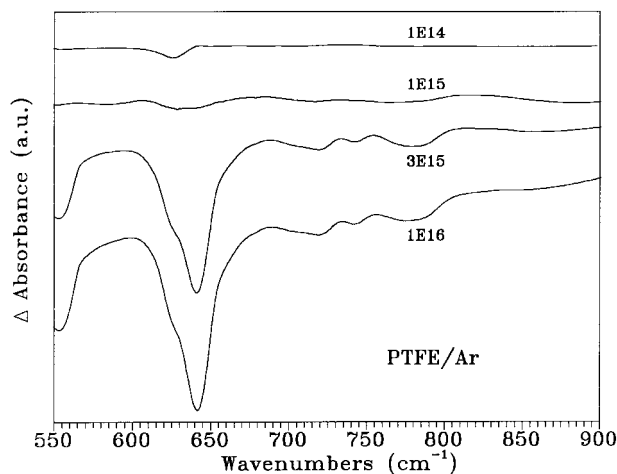
Figure 4   The same spectra as in Figure 3 but for the $550–900$ cm^{-1} region.

cm^{-1}), and C=O (1720 cm^{-1}).[18] Despite the apparent interferences, it may be concluded that the ion irradiation leads to the production of the C=O group. There concentration is an increasing function of the ion influence. Production of other oxidized structures is also possible. The IR spectrum region of 550–900 cm^{-1} characteristic for the CF$_2$ group (645 cm^{-1}) and for the C—C bond (705–805 cm^{-1}) is shown in Figure 4.[19] The irradiation to fluences above 3×10^{15} cm^{-2} results in a significant decrease of the CF$_2$ group and C—C bond concentrations. Therefore, it may be concluded that the ion irradiation to high fluences leads to C—C bond splitting and, at the same time, to liberation of CF$_2$ groups that, together with other degradation products containing C and F, were detected earlier during the PTFE irradiation.[3,4] The outgassing at higher ion fluences is naturally connected with intensive ablation and structural changes of PTFE (Fig. 4).

The main difference between PTFE and other common polymeric materials when subjected to ionizing radiation is the high radiation sensitivity and extremely high ablation yield. The difference can be explained by the different mechanisms of degradation product creation and their different structures. The irradiation of PTFE preferentially breaks weaker C—C bonds (290 kJ/mol) while much stronger C—F bonds (480 kJ/mol) (see Doležel[8]) remain untouched. As a result, gaseous degradation products of the C$_x$F$_y$ type are produced that contain C atoms. According to previous study,[4] practically no molecular fluorine is observed among PTFE degradation products. In contrast, the main gaseous degradation product in other polymers (such as polyethylene, polypropylene, etc.) is molecular hydrogen accompanied with only minute amounts of other carbonaceous fragments. The liberation and escape of such degradation products preferentially leads to the polymer carbonization and production of rather rigid structures preventing ablation. Generally, the polymer irradiation to higher fluences results in deep structural changes and in an increase of available free volume, which may facilitate subsequent penetration of various agents from the ambient medium.[17] For the ion fluences above 1×10^{14} cm^{-2}, the structure and composition of the degraded material are very similar for a wide class of polymers and they have little in common with the polymer original constitution.[15]

PTFE is a crystalline polymer. In this study, the crystallinity of pristine PTFE and PTFE irradiated to different fluences was examined by XRD.
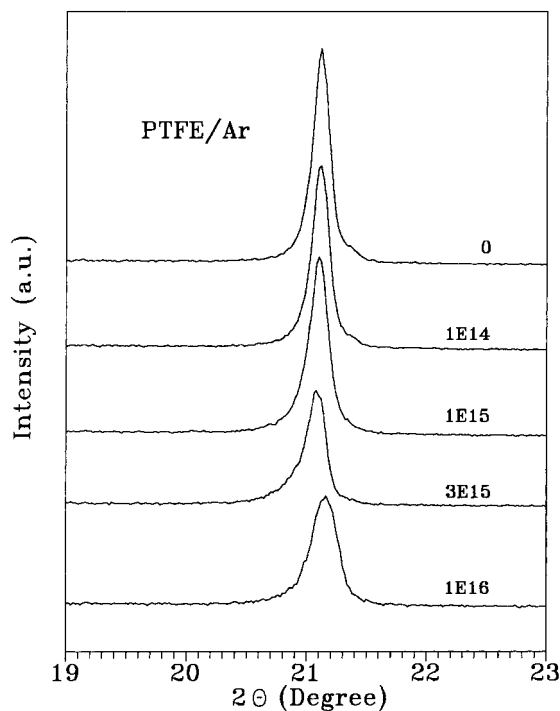
Figure 5 XRD pattern measured on the PTFE after irradiation with 300 keV Ar$^+$ ions to various fluences.

From the results shown in Figure 5, it may be concluded that the XRD peak related to the crystalline phase portion diminishes with increasing ion fluence and that for the highest applied fluence the peak maximum is shifted significantly to a higher angle. It is therefore evident that the ion irradiation leads to a melting of the crystalline phase and to a rearrangement of PTFE macromolecular chains. The shift of the XRD peak maximum to higher angles indicates the changes of the internal structure of the crystalline regions. Because the PTFE surface layer modified by the ion irradiation is very thin in comparison with the specimen full thickness, the observed changes in the XRD spectra are suspected to be partly due to the changes of the crystalline phase of the specimen bulk during the ion irradiation. The physical reason for this phenomenon is not yet understood. Beam heating effects should be ruled out because the deposited power is very low due to the low ion beam current density (30 nA cm^{-2}) during irradiation. Investigations with different ion implantation parameters are expected to elucidate the phenomenon.

CONCLUSION

The present results can be summarized as follows:

- the irradiation with 300 keV Ar$^+$ ions to flu-

ences above 1×10^{14} cm^{-2} leads to rapid ablation of the PTFE surface;

- ion irradiation results in a significant increase in the PTFE specimen electrical conductivity, which is due mainly to creation of conjugated double bonds;
- ion irradiation increases PTFE surface polarity, the effect being probably due to oxygen incorporation and creation of oxidized structures;
- the PTFE ion irradiation leads preferentially to the splitting of weaker C—C bonds and to the liberation of degradation products of the type C_xF_y;
- the PTFE carbonization yield is much lower than in other common polymers; and
- the ion irradiation leads to the melting of the crystalline phase of PTFE.

REFERENCES

1. L. Torrisi and R. Percola, *Nucl. Instrum. Methods,* **B117,** 387 (1996).
2. V. Švorčík, V. Rybka, I. Miček, and V. Hnatowicz, *Eur. Polym. J.,* **30,** 1411 (1995).
3. E. H. Lee, M. B. Lewis, P. J. Blau, and L. K. Mausur, *J. Mater. Res.,* **6,** 610 (1991).
4. M. B. Lewis and E. H. Lee, *Nucl. Instrum. Methods,* **61,** 457 (1991).
5. G. B. Blanchet and S. I. Shah, *Appl. Phys. Lett.,* **62,** 1026 (1993).
6. G. B. Blanchet, C. R. Fincher, Jr., and K. H. Gauduer, *Science,* **262,** 719 (1993).
7. T. C. Nason, J. A. Moore, and T. M. Lu, *Appl. Phys. Lett.,* **60,** 1866 (1992).
8. B. Doležel, *Die Beständigkeit von Kunststoffen und Gummi,* Hauser, München, 1978.
9. W. Jiang, M. G. Norton, L. Tsung, and J. T. Dickinson, *J. Mater. Res.,* **10,** 1038 (1995).
10. V. Švorčík, V. Rybka, K. Volka, and V. Hnatowicz, *Jpn. J. Appl. Phys.,* **B31,** 287 (1992).
11. J. F. Ziegler, J. P. Biersack, and U. Littmark, *The Stopping and Ranges of Ions in Solids,* Pergamon, New York, 1985.
12. V. Švorčík, V. Rybka, V. Hnatowicz, and L. Bačáková, *J. Mater. Chem.,* **5,** 27 (1995).
13. B. Ranby and J. F. Rabek, *Photodegradation, Photooxidation and Photostabilization of Polymers,* Wiley, London, 1975.
14. L. Bačáková, V. Švorčík, V. Rybka, and V. Hnatowicz, *Biomaterials,* **17,** 1121 (1996).
15. L. Calcagno, G. Compagnini, and G. Foti, *Nucl. Instrum. Methods,* **B65,** 413 (1992).
16. V. Švorčík, E. Arenholz, V. Rybka, and V. Hnatowicz, *Nucl. Instrum. Methods,* **B122,** 663 (1997).
17. V. Švorčík, V. Rybka, O. Jankovskij, and V. Hnatowicz, *J. Appl. Polym. Sci.,* **61,** 1097 (1996).
18. S. Kawanishi, Y. Shimizu, S. Sugimoto, and N. Suzuki, *Polymer,* **32,** 979 (1991).
19. S. Sacher, A. Dominque, and J. B. Lhotest, *Appl. Surface Sci.,* **84,** 227 (1995).