# XPS Study of Polyimide Film by $Ar^+$ Ion Implantation

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**Abstract − The fluence of $Ar^+$ ion irradiation on the surface modification of polyimide film was investigated. This paper presents the relation between the changes in the chemical structure, as measure by using x-ray photoelectron spectroscopy (XPS) of the polyimide film before and after ion implantation. The results show that the content of carbon in the surface layer increased after ion irradiation, while the ratios of oxygen decreased after irradiation, especially in the case of polyimide film treated at ion fluence.**

**Key words : Surface modification, Ion implantation, Polyimide, XPS**

## INTRODUCTION

Polyimide (PI) film is used in many technological applications, especially in advanced microelectronics, aerospace and printed circuit industries, due to their excellent thermal stability, mechanical and dielectric properties. Several applications of the PI film can be further extended by modifying the physical and the chemical properties of the PI. The recent demand for electronic circuits within the area of optical science, where the direct metallization without any adhesive between the metal and polymer is required, and the resulting improvement of the adhesion between the metal and polymer, has become an important issue. However, for polymer materials such as PI film, surface modification of PI film is difficult (Eskildsen and Sorensen 1985; Xu *et al.* 1991; Qureshi *et al.* 2007).

Ion implantation provides a unique way to modify the mechanical, the optical and the electrical properties of the PI film by depositing the energy of ions in the material on an atomic scale (Venkatesan *et al.* 1987). Implantation of ions into polymers generally leads to radiation damage, which in many case, modifies the properties of the surface and the bulk of the material. These modifications result from changes in the chemical structure caused in their turn by changes in the chemical bonding when the incident ions are broken by the polymer chains, cut covalent bond, promote crosslinking and liberate certain volatile species. The nature of these changes depends on the properties of the PI, such as the composition and molecular weight, on the mass and energy of the incident ions and on the irradiation condition (Wang *et al.* 2002; Lee *et al.* 2005).

In this study, we used a high current ion source for ion beam application. Then we studied a detailed characterization of the surface chemical states and morphology of the PI film surface modified by ion implantation. The surface modification, chemical bonding states of the PI film surface implanted by $Ar^+$ ions are investigated by x-ray photoelectron spectroscopy (XPS).

## MATERIALS AND METHODS

The commercial PI film used in this study was purchased from the Du Pont Chemical Co. as Kapton HN type and 75 μm in thickness. The surface of the PI film was washed

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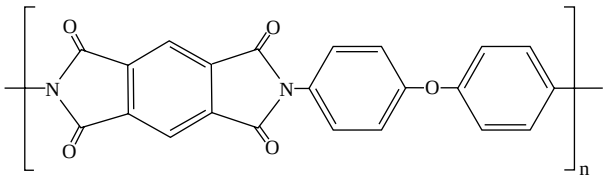

**Fig. 1.** Chemical structure of the polymeric repeat unit of PI film.

with acetone in an ultrasonic for 20 min and then dried at 60°C in vacuum oven. A chemical structure of the PI film is shown in Fig. 1 (Ziegler *et al*. 1985).

The PI films were then cut into suitable pieces for easier processing. The implantation was carried out with $Ar^+$ ions at the energy of 100 keV with fluence from $1 \times 10^{15}$ to $1 \times 10^{17}$ ions $cm^{-2}$ at room temperature. The pressure in the implanter target chamber was $10^{-5}$ torr, and the ion beam current density was lower than 1 μA $cm^{-2}$ to prevent the increase of the specimen temperature. The linear energy transfers during the implantation process were calculated by using the stopping and range of ions in matter (SRIM) simulation program with an ion dose implantation parameter on the PI material. The chemical state environment of the ion implanted polymer surface was investigated using XPS (Multi-Lab 2000, Thermo electron corporation, England) employing Mg-Kα radiation. The applied power was 14.5 keV and 20 mA and the base pressure of the analysis chamber was less than $10^{-9}$ torr.

## RESULTS AND DISCUSSION

The energy lost by the ion per unit path length, $dE/dR$, is related to the nuclear stopping power, $S_n(E)$, by the relation $dE/dR = NS_n(E)$, where $N$ is the atomic density of the target. The energy spectra were transformed into the depth profiles using the stopping powers calculated with the simulation from the SRIM code. The SRIM code was used for the calculation of the ion projected ranges and stopping powers. Depth profile of $Ar^+$ atoms, atomic displacement and energy transfer by electron excitation, were calculated average value at 128 nm (Hnatowicz *et al.* 2001; Kaneko *et al.* 2004).

Fig. 2 which illustrated XPS survey graphs of the PI film, shows distinct carbon and oxygen peaks at around 277.1 and 543.1 eV, respectively. The atomic ratio and binding energy (BE) of each element on the surface of untreated PI

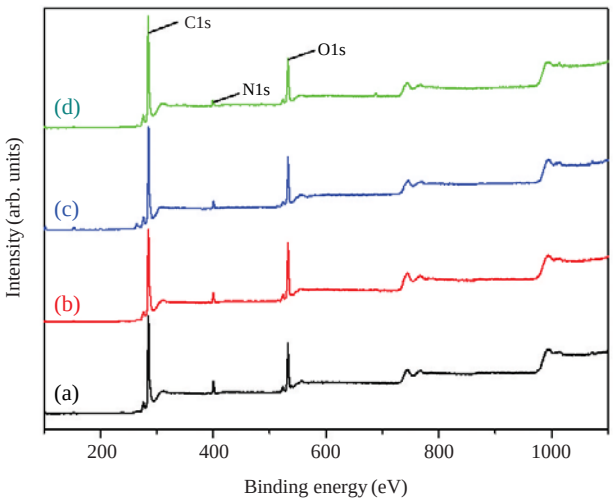


**Fig. 2.** XPS survey spectra of C1s, N1s and O1s from PI film with different $Ar^+$ ion treatments; (a) untreated, (b) $1 \times 10^{15}$, (c) $1 \times 10^{16}$ and (d) $1 \times 10^{17}$ ions $cm^{-2}$.

**Table 1.** The surface composition (in at. %) of the untreated and implanted PI film samples

| Samples | Ion fluences (ions $cm^{-2}$) | Elemental ratio (at. %) | | | [O]/[C] ratio | [N]/[C] ratio |
|---|---|---|---|---|---|---|
| | | C1s | N1s | O1s | | |
| Untreated | | 75.49 | 6.75 | 17.77 | 0.23 | 0.09 |
| | $1 \times 10^{15}$ | 78.43 | 3.78 | 17.79 | 0.22 | 0.05 |
| $Ar^+$ ions | $1 \times 10^{16}$ | 83.58 | 2.58 | 13.84 | 0.16 | 0.03 |
| | $1 \times 10^{17}$ | 87.41 | 1.97 | 12.59 | 0.14 | 0.02 |

film was listed in Table 1. The BE of all peaks were corrected to compare with graphite C1s peak at 285.0 eV. The component C1s peak increased from its original value of 75.49 to 87.41% after $Ar^+$ ion beam irradiation. However, in order to investigate the changes of surface properties of the PI film as nitrogen and oxygen condition, such as the component N1s and O1s peak decreased from its original value of 6.75 and 1.97% to 17.77 and 12.59%, respectively, after $Ar^+$ ion irradiation. Likewise, the [O]/[C] and [N]/[C] atomic ratio on the particle surface decreased from 0.23 to 0.14% and from 0.09 to 0.02% for the PI film, respectively, in Table 1. These results assume that the presence of the O1s group, C=O and C-O-C species, on the plasma treated PI surface is attributable to the carbonization of the active species on the PI surface induced by the $Ar^+$ plasma treatment (Zktessabi and Hakamata 2000; Wang *et al.* 2002; ThermoFisher Scientific).

XPS survey spectra of the C1s group expand to the respective wide scan and C1s region of XPS spectra of the

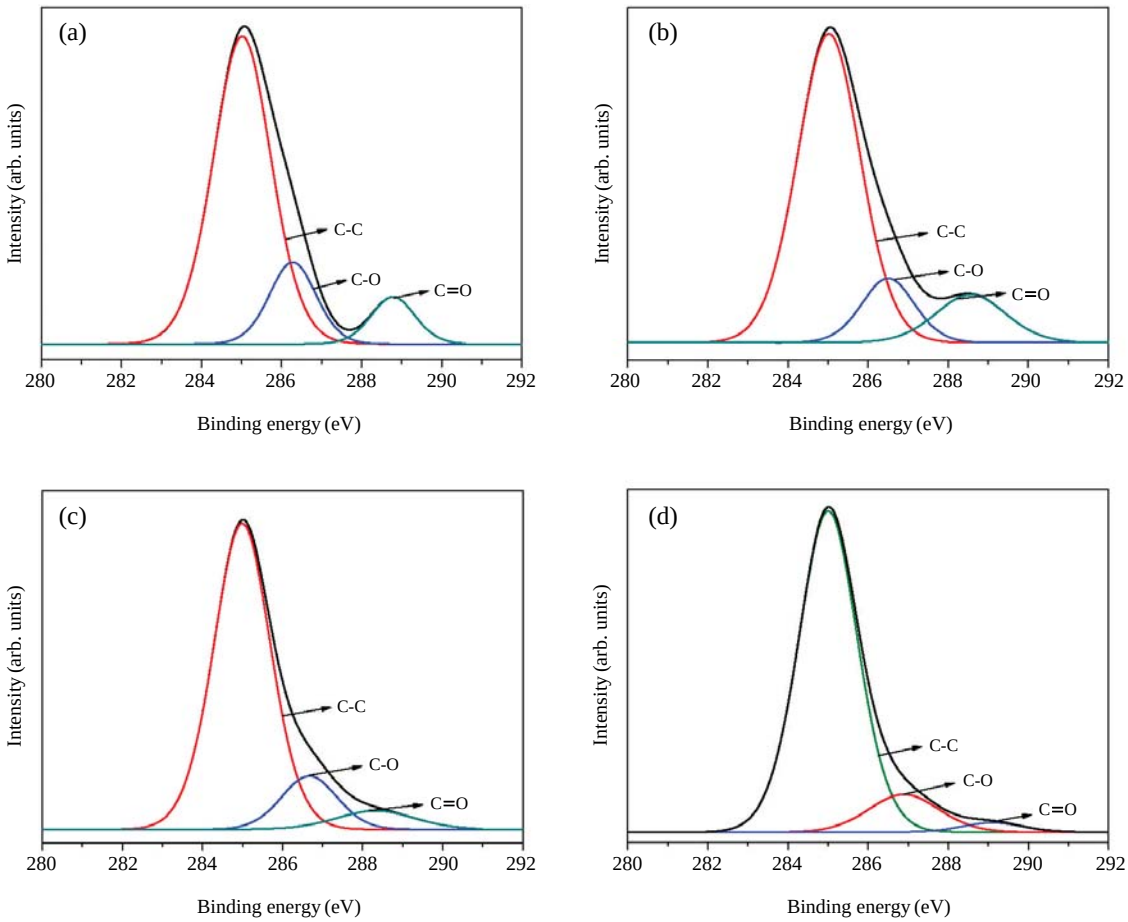


**Fig. 3.** XPS spectra of C1s from PI film with different $Ar^+$ ion treatments; (a) untreated, (b) $1 \times 10^{15}$, (c) $1 \times 10^{16}$ and (d) $1 \times 10^{17}$ ions $cm^{-2}$.

**Table 2.** The component ratios of PI film surface of untreated and ion implantation under various conditions

| Samples | Ion fluence (ions $cm^{-2}$) | Component ratio (at. %) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Carbon | | | Nitrogen | Oxygen | |
| | | C-C | C-O | C=O | Original N | C=O | C-O-C |
| Untreated | | 67.0 | 20.8 | 12.2 | 100 | 78.9 | 21.1 |
| $Ar^+$ ions | $1 \times 10^{15}$ | 72.0 | 17.2 | 10.8 | 100 | 80.9 | 19.1 |
| | $1 \times 10^{16}$ | 79.8 | 15.1 | 5.1 | 100 | 83.3 | 16.7 |
| | $1 \times 10^{17}$ | 87.0 | 10.2 | 2.8 | 100 | 85.6 | 14.4 |

untreated PI film surface (Fig. 3a), the $1 \times 10^{15}$ (Fig. 3b), $1 \times 10^{16}$ (Fig. 3c) and $1 \times 10^{17}$ ions $cm^{-2}$ $Ar^+$ plasma treated PI film (Fig. 3d), after air exposure. Fig. 3 shows core level C1s spectra of untreated and $Ar^+$ ion implanted with different ion fluence. The C1s peaks were obtained in the range of BE from 277.1 and 295.3 eV. The C1s region spectra of untreated PI film can be curve fitted with three peak components, having BE at 284.6 eV for the C-C species, at 286.4 eV for the C-O species and at 288.8 eV for the C=O species in Fig. 3. The relative ratios of C-C, C-O and C=O bond were 67.0, 20.8 and 12.2%, respectively, after ion irradiation, while they were 87.0, 10.2 and 2.8%, respectively, before ion implantation in Fig. 3 and Table 2. Surface modification of the PI film by $Ar^+$ plasma treatment, followed by air exposure, result in the signification chain breaking in the C-O and the C=O groups induced by ion beam is indicated by the decrease in the intensity of both the C-O peak and C=O peak. However, the intensity of the C-C peak is

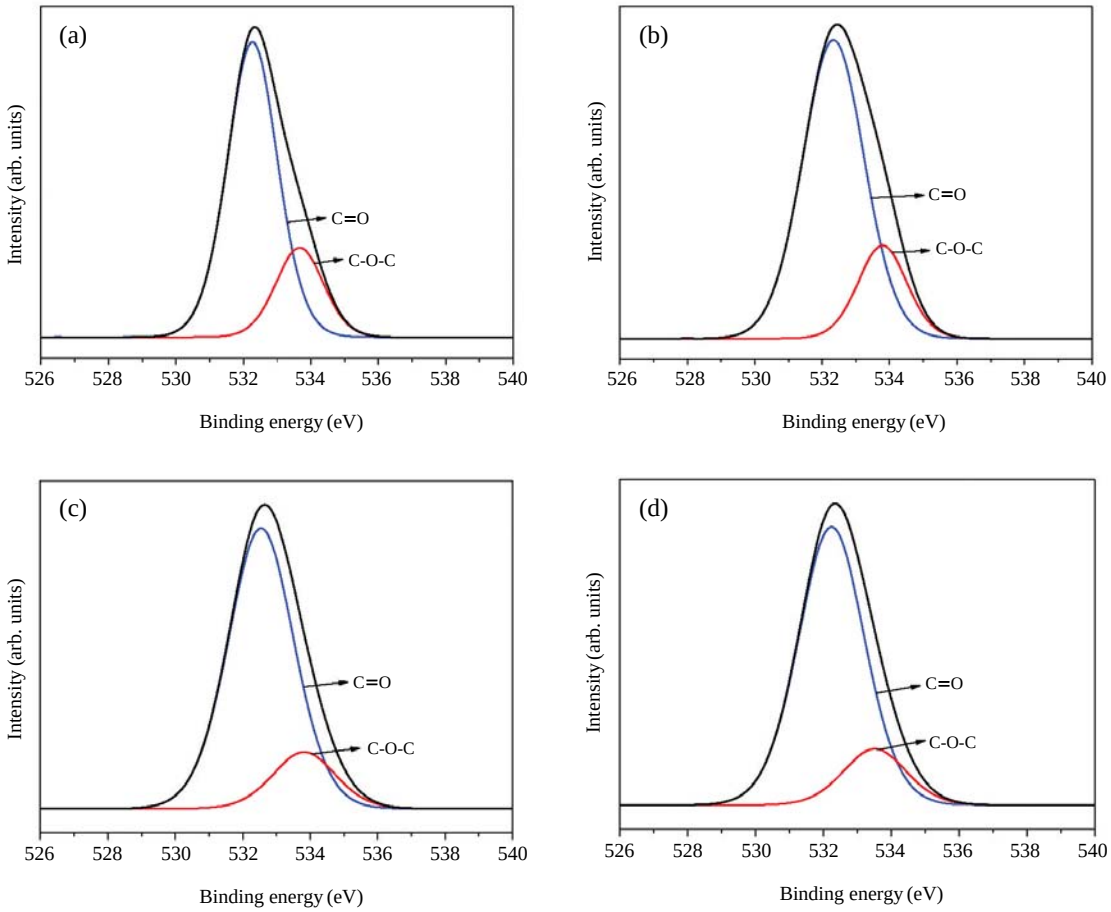


**Fig. 4.** XPS spectra of O1s from PI film with different $Ar^+$ ion treatments; (a) untreated, (b) $1 \times 10^{15}$, (c) $1 \times 10^{16}$ and (d) $1 \times 10^{17}$ ions $cm^{-2}$.

found to increase, which may suggest that a crosslinking and carbonization between carbon chains happens under ion irradiation in Table 2.

Likewise, XPS spectra of the O1s peak expend to component peak at 531.8 eV for the C=O species and at 533.1 eV for the C-O-C species. Chemical structure in surface modification of the PI film, the increase in the ratio of C=O bond was observed in the O1s components. It is apparent from O1s peak that C=O bond became larger and C-O-C bond became relatively smaller after irradiation by $Ar^+$ ions. The relative ratios of C=O and C-O-C bond were 85.6 and 14.4%, respectively, after irradiation, while they were 78.9 and 21.1% before irradiation in Fig. 4 and Table 2 (Zktessabi and Hakamata, 2000; Wang *et al.* 2002; ThermoFisher Scientific).

Like the preceding, the decrease in the oxygen concentration on the PI surface with the ion implantation is consistent with the face that the higher ion fluence will lead to the formation of more active species on the PI surface. This result is also in agreement with those commonly observed for other polymer surfaces after $Ar^+$ plasma treatment. It could be ascribed to the fact that, as the increase of ion fluence, the C-O and C=O bond in the surface of implanted PI is formed through the reaction between the radicals formed on the implanted surface and the carbonization on the irradiated surface mainly occurs.

## CONCLUSION

In this study, ion implantation induced changes in the surface properties of PI film. The PI surface before and after ion implantation was investigated by using XPS analysis. The oxygen and nitrogen atoms were removed (such as the [O]/[C] and [N]/[C] atomic ratio decreased from 0.23 to 0.14% and from 0.09 to 0.02%, respectively) and the re-

lative ratio carbon increased. This could be due to the carbonization of the PI surface. Also the higher the ion fluence, the more intense the carbonization occurred (C1s peak increased from its original value of 75.49 to 87.41% after $Ar^+$ ion implantation).

## ACKNOWLEDGMENT

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