Appearance of Surface Wrinkles with Heat Treatment of Ion Implanted Polyimide Films

Yoshikazu TERANISHI, Eiichi YASUDA, Tomohiro KOBYASHI*, Masato KAKIHANA, Masahiro YOSHIMURA, Manabu FUKUSHIMA, Kazumasa NAKAMURA and Yasuhiro TANABE

Materials & Structure Laboratory, Tokyo Institute of Technology
*The Inst. of Phys. and Chem. Res. (RIKEN)

We investigated the morphological change of Kapton derived carbon films by introduction of Ar and N ion implantation. Ar or N ions were implanted into the Kapton type Polyimide films at an energy of 100 keV with fluences ranging from $1 \times 10^{12}$ to $1 \times 10^{17}$ ions/cm². Microstructural changes were examined by UV Raman spectroscopy (363.8 nm). Morphological changes on surfaces were observed with SEM and TEM. After heat-treatment at 1000°C for 30 min with a rate of 10°C/min, implanted surface with $1 \times 10^{16}$ ions/cm² fluences showed irregular wrinkle surfaces. Moreover, the wrinkle morphology remained and a new type of highly graphitized films with wrinkle surfaces was obtained after heat-treatment at 3000°C. No microstructural changes were observed as compared with non-implanted specimens by visible Raman spectroscopy (514.5 nm).

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1. Introduction

Ion implantation is frequently used for the modification of polymers. The implantation results in polymer degradation followed by carbon enrichment in modified surface layers. However, some papers described an increase in surface roughness of polymers after the implantation.1-4 On the other hand the ion implantation is little used for the modification of carbons. For analyzing the structure of organic matters it is difficult to use visible Raman spectroscopy (514.5 nm) because of the relatively weak Raman scattering and continuous background due to fluorescent emission. On the contrary ultraviolet (UV) Raman spectroscopy is effective to eliminate the fluorescence interference from the signal.5,6

In this paper we study the modification of carbons from ion-implanted polymers. Therefore we investigated suitable procedures to obtain carbons with different graphite surface by changing implantation fluences and heating rate in carbonization of Kapton films. Characterization of the carbonized and graphitized specimens was carried out using visible Raman spectroscopy with 514.5 nm Ar⁺ excitation in a laser beam.7-9

2. Experimental

Ar or N ions were implanted in the polyimide film (Kapton; Du Pont Electronics & Toray) with a thickness of 25 μm at an energy of 100 keV with fluences ranging from $1 \times 10^{12}$ to $1 \times 10^{17}$ ions/cm² at room temperature. The projected thicknesses for Ar, or N ions were calculated with the TRIM code.10 The structures of the implanted specimens were characterized using UV Raman Spectroscopy. The spectra were taken at room temperature using a Triple Raman spectrometer (T64000, Atago-Joban Yvon) with a CW (continuous-wave) ultraviolet argon-ion laser (363.8 nm) for the investigation of organic films.5,6 The laser power was maintained at 20 mW and integrated times were 30 s. The specimens were carbonized (heat-treated) at 1000°C for 30 min in Ar flow with heating rate of 10°C/min and 0.25°C/min. Some specimens were further heat-treated at a temperature of 3000°C for 30 min in flowing Ar atmosphere. After heat treatment at 1000 and 3000

°C, the structures of the specimens were characterized using visible Raman Spectroscopy. Visible Raman spectra were taken at room temperature using a triple Raman spectrometer (T64000, Atago-Joban Yvon) with 514.5 nm Ar⁺ excitation in a laser beam. The surfaces of the specimens were observed by scanning electron microscopy (SEM, S-4500 Hitachi Electronics). The specimens of the cross-section were analyzed by SEM and transmission electron microscopy (TEM Hitachi Electrons). The TEM observations were performed at 300 keV and cross-sectional specimens thinned for 100 nm thick by Focused Ion Beam (FIB, FB2000A Hitachi Electronics).

3. Results and discussion

Figure 1 shows the changes in UV Raman spectra for the specimens implanted with various fluences of Ar-ions. The Raman spectrum for the pristine film was composed of two peaks around 1590 and 1360 cm⁻¹. The former peak corresponds to $E_{2g}$ mode of the structure of graphite, and the latter to a breathing mode of $A_{1g}$. After ion-implantation, the both peaks decreased at the fluences above $1 \times 10^{15}$ ion/cm². It was found that the implanted surfaces of the specimens were

![Fig. 1. Raman spectra on the Kapton films Ar⁺-implanted at various fluences.](Image)
changed into an amorphous structure by the implantation. These results suggest that the pristine polymer structure was destroyed by the implantation.

Figure 2 shows SEM micrographs of non-ion implanted face (left) and Ar-ions implanted face (right). Ar-ions were implanted at an energy of 100 keV at a fluence of $1 \times 10^{16}$ ions/cm$^2$ at a room temperature. From these observations the implanted surface is little different from no implanted one except for the occurrence of some cracks.

3.2 Heat-treatment at 1000°C

Figure 3 shows SEM images of implanted surface of the films after heat-treatment at 1000°C for 30 min with a heating rate of 10°C/min. Oriented wrinkles were observed on the ion implanted surfaces as shown in Fig. 3(a). Figure 3(b) shows an image at the center of the specimen. Entangled wrinkles were observed at the center. The wrinkles at the center indicated random orientation, being different from the wrinkles at the periphery of the implanted area. No clear differences in visible Raman spectroscopy were observed between implanted area and non-implanted ones. On the contrary, the ion-implanted surface was flat by slow heating rate, i.e., 0.25°C/min. The visible Raman spectroscopy (514.5 nm) did not show any difference between the two heating rates. These results suggest that the surface morphology could be modified by adjusting heating.

Figures 4(a)–(c) shows cross-sectional SEM images of Kapton films after heat-treatment at 1000°C for 30 min with a rate of 10°C/min. The surface of no-implanted specimens was flat after heat-treatment at 1000°C as shown in Figure 4(a). On the contrary many small hills were observed on surface of the implanted specimens at a fluence of $1 \times 10^{15}$ ions/cm$^2$ as shown in Fig. 4(b). Figure 4(c) shows the image of ion implanted films with $1 \times 10^{16}$ ions/cm$^2$. Entangled wrinkles are present on the ion-implanted surface.

Figure 5 shows cross-sectional TEM image of the implanted Kapton films. From the TEM observation, the surface region at about 100 nm was different from the interior. The thickness of ion-implanted layer was estimated to be about 100 nm using the calculated one. The thickness of the different region in Fig. 5 was in good agreement with the TEM observation. However, the height of wrinkles was much larger than the thickness of the ion-implanted region. Structural change of 100 nm by ion implantation provides morphological modification in the range of 1 μm. After heat-treatment at 3000°C, the wrinkles still remained on the graphitized specimens. Visible Raman spectroscopy with 514.5 nm revealed that the wrinkle surfaces were well graphitized.

Figure 6 is a linear shrinkage of the Ar$^+$-implanted and the pristine specimens during heat treatment with two different heating rates. At 10°C/min, the ion-implanted specimens were less shrunk over heat treatment up to 1000°C than no-ion implanted specimen. On the contrary, the shrinkage of ion-implanted specimens at 0.25°C/min up to 1000°C was higher than that of no-ion implanted specimen. This difference indicated that the higher heating rate is an important factor for appearance of the wrinkle morphology.

4. Conclusion

The effect of ion-implantation was investigated in the viewpoint of structural and morphological changes. The structure of polyimide film was destroyed by Ar or N ion implantation over $1 \times 10^{15}$ ions/cm$^2$. wrinkled morphology appeared on the implanted film after heat treatment at 1000°C with the heating rate of 10°C/min. No wrinkled morphology appears with the heating rate of 0.25°C/min. The thickness of the microstructure change of the wrinkled surface well agreed with the thick-
Fig. 4. Cross-sectional SEM images of Kapton film after heat-treatment at 1000°C with different fluences.
(a) Non-implanted Kapton films.
(b) Ar⁺-implanted Kapton films at a fluence of $1 \times 10^{14}$ ion/cm².
(c) Ar⁺-implanted Kapton films at a fluence of $1 \times 10^{16}$ ion/cm².

ness of ion-implanted layer calculated by TRIM code. The wrinkled morphology was maintained after heat treatment at 3000°C. These results indicated that a new type of highly graphitized films with wrinkle surfaces could be produced.

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Fig. 5. Cross-sectional TEM image of implanted Kapton film at a fluence of $1 \times 10^{16}$ ion/cm² after heat-treatment at 1000°C for 30 min with a heating rate of 10°C/min.

Fig. 6. Shrinkage as a function of heat treatment for the non ion implanted and Ar⁺-implanted Kapton films at a heating rate of 0.25 and 10°C/min.

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