Carbon Structure in Polyimide Membrane Formed by Ion Irradiation

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1. Introduction

The choice of electrode material for electronic devices is one of the important factors affecting both performance and cost of the materials [1-3]. The materials with high electrical conductivity, such as carbon nanotubes, carbon nanofibers, carbon rods, and graphite powder, are required for ideal performance of electrodes. However, the cost of these materials is not so cheap, and their formability for electronic devices is also not so good.

Polyacrylonitrile (PAN) fibers were carbonized at high temperature with high yield commercially; however its carbon fiber mat had limited electrical conductivity and poor mechanical strength. Recently, high-temperature-resistance organic polymers as polyimide have been successfully converted into carbon fibers with high carbonization yields [4]. The carbonized material showed an increase in electrical conductivity to 2.5 S/cm. In addition, the material is required to have good mechanical strength.

Ion irradiation is a well-established technique for the post-processing of materials [5]. The properties of materials modified using the ion irradiation or implantation have strongly depend on the irradiation parameters, such as ions species, energy, and ion fluences. Recently, we reported that an asymmetric polyimide membrane with an ultrathin and defect-free carbonized skin layer prepared by the modification of the skin surface using ion-beam irradiation had a high gas permeability and selectivity [6-8]. As mentioned above, it is well known that ion-beam irradiation can directly modify the surface of a membrane and that the polymer surface irradiated under high ion

fluence is carbonized [9]. The asymmetric membrane with the carbonized skin layer was characterized by its toughness and good mechanical properties, and we demonstrated that the ultrathin and defect-free carbonized skin layer was able to realize both a high gas permeability and selectivity.

In this paper, we describe the carbon structure of the polyimide membranes prepared by the ion-beam irradiation. In addition, we investigate the structure in other aromatic polymers by the irradiation. The objective of our study is to elucidate the mechanism of carbon formation induced in the polymer membrane by the ion irradiation. In this preliminary study, He⁺ as small molecular weight were irradiated for the membranes at 50 keV from 1×10^{14} to 3×10^{15} ions/cm², and Kr⁺ as large molecular weight was irradiated for the membranes at 150 keV from 1×10^{14} to 1×10^{16} ions/cm².

2. Experimental Section

2.1. Materials

2,2'-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) was purchased from the Central Glass Co., (Saitama, Japan) and purified by sublimation prior to use. The diamine monomer was 2,2'-bis(4-aminophenyl)hexafluoropropane (6FAP), which was purchased from the Central Glass Co., (Saitama, Japan) and recrystallized twice in ethanol prior to use.

The polyimide, 6FDA-6FAP, was synthesized by chemical imidization of the poly(amic acid) precursors as reported in the literature [10-13]. The structures of 6FDA-6FAP are shown in Fig. 1. The synthesized

6FDA-6FAP had an Mw of 4.8×10^5 with a polydispersity index of 1.7. The membranes were prepared by the solvent cast method.

Fig. 1. Chemical structure of 6FDA-6FAP polyimide.

2.2. Ion-beam Irradiation for Membranes

Ion-beam irradiation is a physico-chemical surface-modification process resulting from the impingement of a high-energy ion beam (Riken ion implanter, Riken, Saitama, Japan). The ion depth through the top skin layer was regulated by changing the ion specie and its energy. In this study, ion irradiation was performed on polyimide membranes and He^+ was used. Ion irradiation was carried out on a $2 \times 2 \text{ cm}^2$ surface area at an energy of 50 or 150 keV with a fluence ranging from 1×10^{14} to 1×10^{16} ions/ cm^2 .

2.3. Characterization of Membranes

The surface change in the polyimide membranes before and after ion irradiation was measured by laser Raman spectroscopy (LabRam, Jobin Yvon, Tokyo, Japan). A square Ge crystal in an ATP objective was used, and sixty-four scans of 2 cm^{-1} resolution were averaged to achieve a sufficient signal-to-noise ratio. The Raman spectra were observed using an He-Ne laser of 632.817 nm.

3. Results and Discussion

3.1. He^+ -irradiated Membranes

Irradiating ions penetrating into a polymer membrane lose energy by several interactions between the ions and the polymer. The energy loss mechanism is considered to be an electronic energy loss, which involves the process of electronic excitation and ionization of the atoms in the polymers, as the exchanges of electrons between incident ions and the atoms in the polymer, and to be an nuclear energy loss, which involves atomic collisions between the incident ions and the atoms in the polymer. The depth profiles of the energy loss for He^+ irradiation at 50 keV in the 6FDA-6FAP membrane were estimated using a well-established Monte Carlo simulation method (TRIM code). As is apparent from the He^+ depth in Fig. 2, the relative contribution of the electronic energy loss becomes greater for a thinner surface of the membrane and that of the nuclear energy loss becomes greater for a thicker layer, and He^+ in the

6FDA-6FAP membrane irradiated at 50 keV completely loses the electronic and nuclear energies at a 837 nm depth.

Fig. 2. TRIM simulation of He^+ ion at 50 keV. (■) : electronic energy loss, (□) : nuclear energy loss.

Fig. 3 shows the Raman spectra of the 6FDA-6FAP membranes irradiated by a 50 keV He^+ . The ion fluences were 1×10^{15} and 1×10^{14} ions/ cm^2 . The peaks at 1240, 1380, 1620, and 1780 cm^{-1} correspond to C-F₃, C-N, and C=C in the aromatic ring, and C=O, respectively. After the irradiation of a 50 keV He^+ , these peaks on the polyimide surface did not change and depend on the ion fluences.

Fig. 3. Raman spectra of He^+ -irradiated 6FDA-6FAP at 50 keV. (a) 6FDA-6FAP, (b) 1×10^{14} ions/ cm^2 , (c) 1×10^{15} ions/ cm^2 .

On the other hand, Raman spectra of the polysulfone (PSF) membranes irradiated by a 50 keV He^+ significantly changed, as shown in Fig. 4. The peak corresponding to C-O-C at 1140 cm^{-1} decreased with ion fluence and the H^+ -irradiated PSF membrane at 3×10^{15} (ions/ cm^2) showed a broad peak at around 1550 cm^{-1} . The peak at 1550 cm^{-1} correspond to amorphous carbon (AC) [14,15], indicating that PSF forms the disordered carbon structure.

Fig. 4. Raman spectra of He^+ -irradiated polysulfone at 50 keV. (a) PSF, (b) 1×10^{14} ions/ cm^2 , (c) 1×10^{15} ions/ cm^2 , (d) 3×10^{15} ions/ cm^2 .

3.2. Kr^+ -irradiated Membranes

Fig. 5 shows the depth profiles of the energy loss for Kr^+ irradiation at 150 keV in the 6FDA-6FAP membrane estimated using a well-established Monte Carlo simulation method. Kr^+ in the 6FDA-6FAP membrane irradiated at 50 keV completely losses the electronic and nuclear energies at a 232 nm depth. Fig. 6 shows the Raman spectra of the 6FDA-6FAP membranes irradiated by a 150 keV Kr^+ from 1×10^{14} and 1×10^{16} ions/ cm^2 . After the irradiation of a 150 keV Kr^+ at a fluence of 1×10^{15} ions/ cm^2 , the peaks on the polyimide surface disappeared. However, two broad peaks on the polyimide surface irradiated at the fluence appeared at around 1360 and 1580 cm^{-1} . These peaks correspond, respectively, to the well-known D and G broad bands of disordered graphitic materials, indicating that the surface on the membrane changed to a carbon-enriched material.

Fig. 5. TRIM simulation of Kr^+ ion at 150 keV. (■) : electronic energy loss, (□) : nuclear energy loss.

Fig. 6. Raman spectra of Kr^+ -irradiated 6FDA-6FAP at 150 keV. (a) 6FDA-6FAP, (b) 1×10^{14} ions/ cm^2 , (c) 1×10^{15} ions/ cm^2 , (d) 1×10^{16} ions/ cm^2 .

Fig. 7 shows the Raman spectra of the PSF membranes irradiated by a 150 keV Kr^+ from 1×10^{14} and 1×10^{16} ions/ cm^2 . After the irradiation of a 150 keV Kr^+ at 1×10^{16} ions/ cm^2 , the peaks on the PSF surface disappeared and new two broad peaks on the surface appeared. These peaks correspond, respectively, to the D and AC broad bands of disordered graphitic materials, indicating that there were significant different in carbon structure between 6FDA-6FAP and PSF membranes.

Fig. 7. Raman spectra of Kr^+ -irradiated polysulfone at 150 keV. (a) PSF, (b) 1×10^{14} ions/ cm^2 , (c) 1×10^{15} ions/ cm^2 , (d) 1×10^{16} ions/ cm^2 .

Conclusions

The above studies have led to some interesting conclusions for carbon structure in the polyimide membrane induced by ion irradiation. It was found that the irradiated polyimide structure selectively changed to graphite-rich material. On the other hand, the irradiated polysulfone structure preferentially changed to amorphous carbon-rich material.

It is desirable to prepare carbon fiber with high carbonization yields. The polyimide prepared by ion-beam irradiation showed interesting carbon structure, and we consider that the carbonized polyimide would be one of the important materials for realizing high electronic device performances.

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