

Inner Surface Modification of a Polymer Bottle by Plasma-Based Ion Implantation

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In order to improve the gas barrier characteristics of PET (polyethylene terephthalate) we have carried out two experiments; a preliminary experiment using film samples and an applied experiment to modifying inner surfaces of bottles. The measurements of film samples by both ATR (Attenuated Total Reflection) FT-IR and Laser Raman spectroscopy show that most PET molecules in the near surface volume are destroyed and modified into DLC (Diamond Like Carbon) by ion implantation. Gas permeability of the sample is also measured. For applying PBII (Plasma-Based Ion Implantation) to bottles we develop a new technique to implant ions onto the inner surfaces while plasma is generated inside the bottle. An electrode that is supplied with positive high-voltage pulses differently from negative ones as in the preliminary experiment is inserted into the bottle. The inner surface of the PET bottle is investigated by both ATR FT-IR and Laser Raman spectroscopy, too.

1. INTRODUCTION

PET is widely used as beverage containers and food or medicine packages due to the easy handling as well as the low cost. It is also suitable for recycling. However, the barrier characteristics against a certain kind of gases such as CO₂ and O₂ are not so good that the long-period maintenance of quality is hard for some beverages, beers, wines and medicines. The use of other polymer, PEN (Poly ethylene naphthalate) is effective to some extent for resolving the gas barrier problem [1]. But, the cost is higher and the material is not suitable for recycling. Recently, a European company developed a new technique that deposits thin DLC on the inner surface of a PET bottle in order to enhance the gas barrier characteristics [2]. It has shown that thin-DLC deposit of 0.02 to 0.04 micron enhances the barrier characteristics more than ten times as large as the uncoated PET. However, as far as they use coating technique, there remains a peeling problem of the deposit [3]. Then, we have proposed to use surface modification by ion implantation in order to simultaneously resolve the both problems, the low gas barrier and the DLC-deposit peeling. We have previously reported the experimental results of modifying PET film surface by PBII (plasma based ion implantation) [4]. In the experiment the PET film was put in plasma on a metallic holder that was supplied with negative high voltage pulses. Ion implanted PET film was investigated by both ATR (Attenuated Total Reflection) FT-IR and Laser Raman spectroscopy. It has been shown that most PET molecules in the near surface volume are destroyed and modified into DLC by 10 keV N₂⁺ ion implantation with dose of 10¹⁶ cm⁻².

In this paper we develop a new PBII technique to

implant ions into the inner surface of a PET bottle instead of PET-film surface while plasma is generated inside the bottle.

2. PRELIMINARY EXPERIMENT FOR MODIFYING PET FILM SURFACE INTO DLC

2.1 Experimental setup

Ion implantation into PET film is carried out with the experimental equipment as shown in Fig.1. Nitrogen plasma is generated at a pressure of around 10⁻² Pa by off-resonant microwave discharge in magnetic field [5]. Plasma density of 10¹⁰ to 10¹¹ cm⁻³ is obtained with microwave power of 50 to 200 W. Usually, microwave nitrogen plasma generated at this condition consists of roughly equal amounts of N⁺ and N₂⁺ ions [6]. The ratio of atomic ion N⁺ increases with higher microwave power and/or at lower pressure.

Sometimes, ion implantation into insulator has a problem due to ion-charge accumulation on the surface.

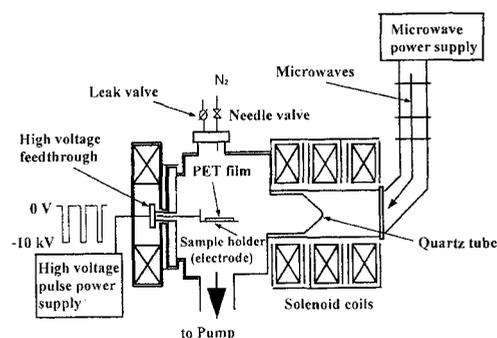
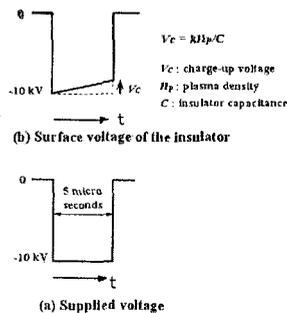
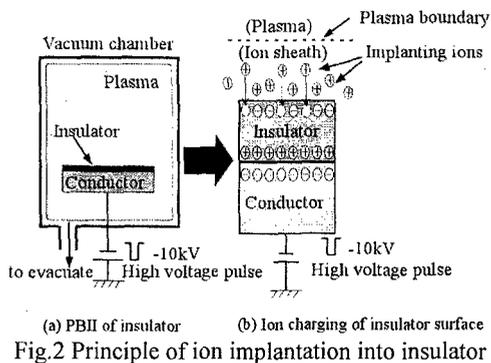


Fig.1 Experimental equipment for plasma-based ion implantation. Plasma is generated by microwave discharge in magnetic field.



This often causes big troubles in the ion implantation processes of mass-production factories for semiconductor devices [7, 8]. However, plasma-based ion implantation that performs the implantation in pulses as shown in Fig.2 resolves this problem. Ion charges accumulate on the sample surface during the on time of the high voltage pulse, resulting in the linear increase of the surface voltage of insulator. Then, during the off time the charges are quickly neutralized by the electrons from plasma as shown in Fig.3. A piece of PET film, 10 mm square in area and 0.1 mm in thickness, is placed on the sample holder in the plasma. The sample holder, which is made of copper, is supplied with negative high-voltage pulses of 10 kV in height and 5 microseconds in width. Since the pulse repetition is 1000 Hz, the duty of the high voltage is 0.5 percent. Just at the instant when the high voltage is supplied to the sample holder, the PET surface facing the plasma is elevated to the same potential as the sample holder, since the capacitance between the back and the front of PET film is much larger than that between the PET front surface and the vacuum-chamber inner surface (grounded). But then, the front-surface potential against the sample holder, V_c , which is determined with the surface charge and the PET film capacitance, increases as positive ions are implanted into PET. The potential-increase rate is proportional to the plasma density. From a simple calculation, it is easily found that in case of the plasma of 10^{11} cm^{-3} in density and 10 eV in electron temperature, the PET surface potential against the holder becomes about 600 V at the end of high voltage pulse. Accordingly, the implant energy varies from 10 keV to 9.4 keV during 5 microseconds of the pulse duration. This value of energy variation does not cause any significant problem to the surface

modification of PET as far as concerned with our purpose described above.

2.2 Characterization of ion-implanted PET films

The samples of PET film used in this experiment are made by biaxial stretching method. Ion implanted PET films are measured by FT-IR spectrometer in order to see how the organic structure of PET is destroyed by ion irradiation. Since the modified layer is very thin, we use ATR (attenuated total-reflection type) FT-IR spectrometer (Perkin Elmer, 1650PC-DC). The prism (or internal reflection element) material is KRS-5. Infrared absorption spectra of surface-modified PET films are shown in Fig.4. In this figure, the peaks at the wave numbers, 1714, 1250, 1120, 1046 and 726 cm^{-1} are specific for PET. The absorption spectrum obtained by ATR method is generally considered lacking quantitatively, since the signals are very changeable depending on the contact conditions between the prism and the sample surface. Thus, in order to get a relative comparison of the absorption spectra we have to mount each sample on the instrument under the same contact conditions as possible. From Fig.4 we can see the tendency that the specific absorption peaks decrease with dose.

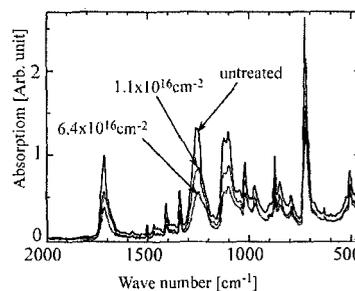


Fig. 4 ATR-FTIR spectra of surface-modified PET films.

Then, the same samples are measured by a laser Raman spectrometer (Jusco, NRS-1000). The wave length is 532 nm. Figure 5 shows the Raman spectra of the ion implanted PET films with different doses of (a) 1.1×10^{15} , and (b) 1.1×10^{16} . It shows that the Raman spectrum changes over the dose of 10^{16} cm^{-2} . The spectrum of (b) has an asymmetric broad peak around 1550 cm^{-1} . Those with asymmetric broad distributions are often seen on the ion plated carbon deposit that is called amorphous carbon or DLC [9]. From the spectra we can see that PET molecules in the modified layer are completely changed into DLC, if we take the above-mentioned results from ATR FT-IR spectrometry into account.

Regarding the measurement by ATR FT-IR spectroscopy as shown in Fig.4, the specific peaks for PET decrease with dose. Up to the dose of $6.4 \times 10^{16} \text{ cm}^{-2}$, there is no indication that the specific peaks would become zero with further higher doses. However, this does not mean that a lot of complete organic structures remain in the ion-implanted layer. Because the modified layer thickness is much thinner than the penetration depth of the evanescent wave used for the measurement. The mean projected range of 10 keV N_2^+ ions that are

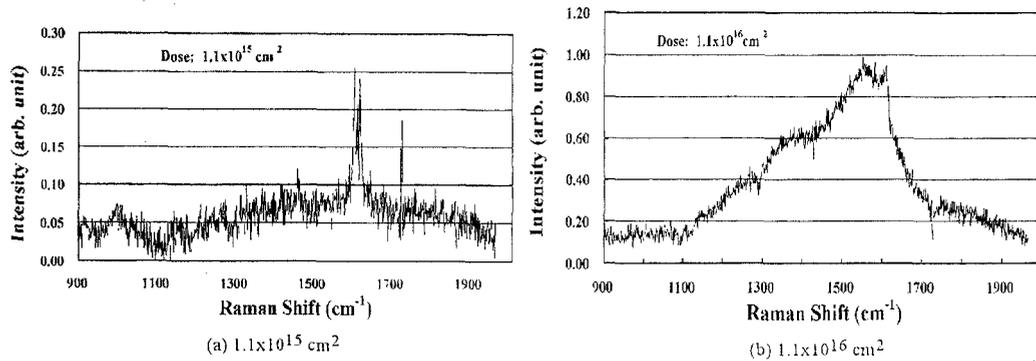


Fig.5 Laser Raman spectra of surface-modified PET films. DLC is formed at the dose of over 10^{16} cm^{-2}

implanted into PET is calculated with the simulation software TRIM-98 to be about 0.04 micron, assuming the PET density of 1.33 g/cm^3 as shown in Fig.6. As mentioned above, implanted ions contain a lot of N^+ ions with same energy. Therefore, the modified-layer thickness will be about 0.1 micron, if we take the mean projected range of N^+ ions and their standard deviation into account.

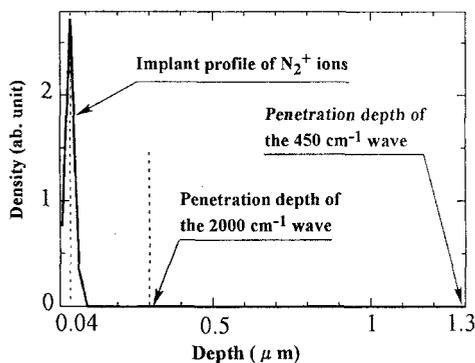


Fig.6 Implanted-ion profile calculated with the simulation software TRIM-98.

On the other hand, the penetration depths of the evanescent waves differ with their wave numbers, that is, the depth is inversely proportional to the wave number. Typically, the penetration depth for the wave number of 1000 cm^{-1} is 0.6 micron, which is about 6 times as large as the ion-implanted layer thickness. Thus, the absorption spectra in Fig.4 are considered to be the summation of those from the ion implanted layer and from the

un-implanted part beneath the implanted layer. The power density P of the evanescent wave inside PET is expressed as a function of the depth z as follows;

$$P = P_0 \cdot \exp(-z / d_p) \tag{1}$$

where P_0 is the wave power density on the PET surface, and d_p , the penetration depth of the wave power. Since the wave power density is concentrated near the surface area, the ratio of spectrum signals from the two parts is determined not by the depths ratio but by the ratio of the depth integrations of equation (1). Therefore, as far as we observe only the ion-implanted layer, a considerable proportion of PET molecules is destroyed. The result by a laser Raman spectroscopy as shown in Fig.5 confirms this speculation. The Raman spectrum is very similar to those of typical DLC's, which are made by plasma PVD or ion plating using hydrocarbon gases such as methane, ethane or ethylene. Since the wave length in the laser Raman spectrometer (532 nm) is roughly one order shorter than that in the FT-IR, the penetration depth is considered sufficiently smaller than the thickness of ion implanted layer.

2.3 Gas barrier characteristics of ion-implanted PET films

O_2 and CO_2 gases that are permeating through PET sheets are measured at room temperature with the apparatus for gas permeability measurement (Jusco, Gasperm-100). Figure7 shows the measured permeability coefficients for O_2 and CO_2 Nitrogen ion implantation with 10 keV in energy and $6 \times 10^{16} \text{ [ions/cm}^2\text{]}$ in dose

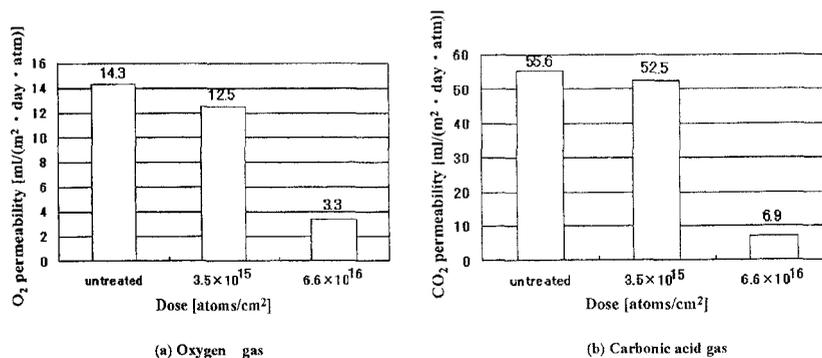


Fig.7 Gas permeability of ion-implanted PET films

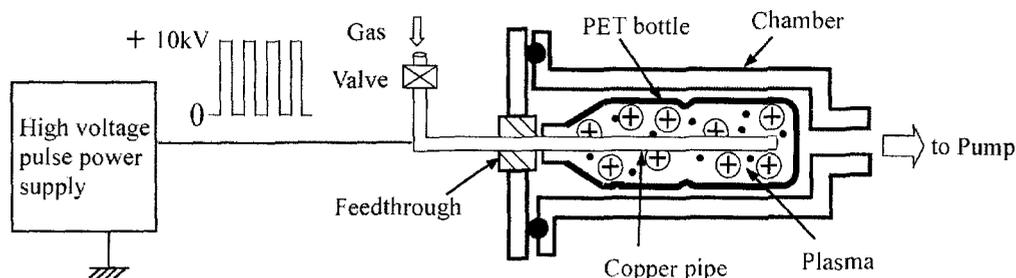


Fig.8 A new equipment for modifying the inner surface of PET bottle to DLC.

reduces CO₂ and O₂ permeability values down to 1/10 and 1/6 of times the values for the untreated films, respectively.

3. ION IMPLANTATION INTO AN INNER SURFACE OF A PET BOTTLE

In the above-mentioned preliminary experiment a sample of PET film was placed in a microwave plasma. However, during the experiment we found that plasma of considerable density was easily generated only by the high voltage pulses at a pressure of around 1 Pa, where PBII was carried out. Therefore, we constructed a new equipment for modifying the inner surface of PET bottle without using any microwave power supply. Figure 8 shows the schematic drawing of the equipment as well as the new method to implant ions into the inner surface of bottle [10]. The sample of PET bottle was made by biaxial stretch-blow molding method. The wall thickness is 0.5mm. An electrode that is supplied with positive high-voltage pulses differently from negative ones as in the preliminary experiment is inserted into the bottle. Since the plasma potential is kept close to that of the electrode, positive ions are accelerated to bombard the inner surface with the kinetic energy corresponding to the pulse voltage. The surface charging by ions is neutralized by electrons from plasma during the pulse off time. The inner surface of the PET bottle is investigated by both ATR FT-IR and Laser Raman spectroscopy, too. The result shows that the new method can also perform surface modification of the PET-bottle inner surface similarly to the previous experiment for PET film. Figure 9 shows the Laser Raman spectrum of the ion implanted inner surface of a PET bottle.

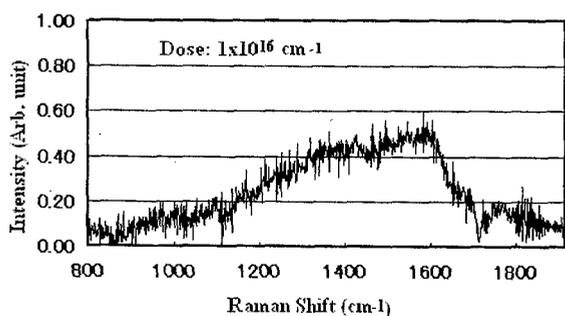


Fig.9 Laser Raman spectrum of inner surface of an ion-implanted PET bottle

4. DISCUSSIONS AND CONCLUSION

In order to enhance the barrier characteristics of PET film against CO₂ and O₂ gases, a new technique for surface modification was investigated. PBII of nitrogen plasma was proved to be able to change PET-film surface into DLC that is similar to those made by plasma PVD or ion plating. Since the technique is basically the materials modification by ion implantation differently from coating, there will be no peeling problems. Regarding the gas barrier characteristics, the measurement of PET-film sample has shown a remarkable gas-permeability reduction of roughly 1 order. We consider that they will be at least comparable to those tested with plasma-coating technique by a European company [1], because the thickness of the ion-implanted PET layer by the new technique is almost same as or slightly larger than their deposited DLC and the Raman structure is very close to those of the typical DLC's. For PET bottle modification a new method that applies positive high-voltage pulses to the electrode inserted into the bottle is proved to be effective. Since the pressure at which the modification is carried out is in the range from one to several Pa, the evacuation time from atmospheric pressure will be within 1 minute when a high-speed dry pump is used.

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