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Amorphous carbon layer deposition on plastic film by PSII

S. Watanabe[a], M. Shinohara[a], H. Kodama[a], T. Tanaka[a,*], M. Yoshida[b], T. Takagi[a]

[a]*Department of Electronics and Photonic Systems Engineering, Hiroshima Institute of Technology, 2-1-1 Miyake Saeki-ku, Hiroshima 731-5193, Japan*

[b]*Mitsubishi Heavy Industry, Ltd., Hiroshima Research Center, 6-22, 4-Chome, Kan-On-Shin-Machi, Nishi-ku, Hiroshima 733-8553, Japan*

Abstract

Plasma-source ion implantation (PSII) is successfully employed without an external radio frequency plasma source to form a thin amorphous carbon layer on the surface of polyethylene terepthalate (PET) film by applying pulsed high negative voltage ($\sim$10 μs pulse width, 300–900 pulses/s, −10 kV) to a sample immersed in C_2H_2 gas with and without Ar. This pulsed voltage condition is found to itself generate a plasma surrounding the substrate and PET film to form a thin carbon layer. The oxygen barrier characteristics of the PET were improved remarkably by this PSII processing, and laser Raman, X-ray photoelectron and Fourier-transform infrared spectroscopy spectra revealed that the thin amorphous carbon layer was found to consist primarily of graphite crystal with the characteristics of diamond-like carbon. The ratio of sp^2 (graphite) to sp^3 (diamond) populations was found to vary according to the gas pressure of C_2H_2 and the addition of Ar, which affects on the oxygen barrier characteristics.

Keywords: Oxygen transmission rate; Diamond-like carbon; X-ray photoelectron spectroscopy

1. Introduction

Improvement of the oxygen and carbon dioxide barrier effectiveness of thin films has recently attracted much attention for plastic materials, such as polyethylene terepthalate (PET) and E7 films. New approaches have been studied and implemented for the fabrication of plastic films and bottles with good gas-barrier properties [1–5].

The surface modification of plastic films and bottles with amorphous diamond-like carbon (DLC) is a promising technique for improving the oxygen barrier because of the high oxygen barrier performance, low processing cost, and recyclability. To date, the largest reduction in oxygen transmission has been achieved by applying a carbon film by radio frequency (r.f.) plasma-assisted chemical vapor deposition, with transmission reduction of $\sim 1/30$ [6]. However, the crystal structures of such carbon layers require further refinement in order to realize better oxygen barriers for industrial use, and the adhesion and flexibility characteristics of films produce by such deposition methods could be improved.

Plasma-source ion implantation (PSII) is a rapidly advancing surface-modification technique that has been shown to be an effective method for modifying the crystal characteristics of thin layers and mixing layers [7]. In PSII, the target is typically immersed in externally generated plasma and pulse biased with high negative voltage, resulting in the implantation of ions into the target over all surfaces at normal incidence. As such, this technique is highly useful for the surface treatment of 3D workpieces [8–10].

In particular, this method may prove highly useful for the modification of the internal surface of PET bottles, which is not possible using conventional beam-line techniques. Therefore, in this study we examine the possibility of modifying PET films by PSII using C_2H_2 gas without an external r.f. plasma source, utilizing only the corona discharge produced by pulse biasing the target to high negative voltage. In such a system, the ions generated in the corona-discharge plasma sheath are accelerated toward the target. This process is generally considered to be useful for higher gas pressures and higher bias voltages, since the applied bias could generate a corona discharge around the substrate [11]. However, the use of the PSII process under conditions of high negative voltage and high gas pressure has not been investigated with respect to its utility for forming

*Corresponding author. Tel.: +81-82-921-3121; fax: +81-82-921-8971.

E-mail address: tanaka@cc.it-hiroshima.ac.jp (T. Tanaka).

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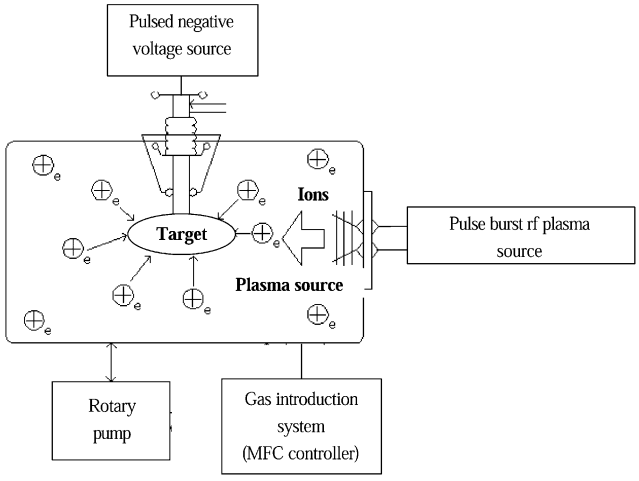

Fig. 1. Experimental apparatus.

an amorphous carbon layer with good oxygen barrier characteristics.

The process is performed using C_2H_2 and C_2H_2+Ar (30%) gases [12–14], and the characteristics of the amorphous carbon layer on the modified PET films are examined with respect to the differences between this process and a PSII process using an external r.f. plasma source.

2. Experimental

Fig. 1 shows a schematic diagram of the PSII apparatus. The chamber is grounded electrically and has the dimensions of 450 mm in height, 590 mm in width, and 470 mm in depth. Two series of experiments were performed for comparison, PSII with an external plasma source and PSII without an external plasma source. The external plasma source was an inductively coupled plasma (ICP). The r.f. antenna for the ICP source was wound on the inside of the upper lid of the plasma chamber, with one end grounded. The antenna itself was a 5-turn copper coil, approximately 250 mm in diameter and operating at 222 kHz.

The PET film target was set in the center of the chamber on the end of a conducting copper rod that was insulated from the chamber. The entire area of the PET film was held in contact with the copper rod. The treatment area of the PET film was a circular area 50 mm in diameter. The copper rod was set on a stainless steel (SUS) electrode, to which the high negative bias was applied. For some measurements, a carbon layer was deposited directly onto Si (1 0 0) wafers of thickness 0.5 mm and lateral size 10×10 mm^2.

A pulsed negative voltage of up to -11 kV was applied to the target at a pulse width of 10 μs by a high-voltage pulse modulator that was capable of approximately 8 A current. The target chamber was evacuated by diffusion pump to a base pressure of 4.0×10^{-4} Pa, and after filling the chamber with the appropriate gas, the gas pressure was held at 5.0–11.0 Pa during ion implantation. The condition of PSII processing are listed in Table 1.

The oxygen transmission rate (OTR) was measured as an index of the oxygen barrier effectiveness of PET films using a MOCON instrument (OX-TRAN 2/20). In OTR measurement, the film was installed so as to separate two sealed chambers, and both chambers were purged with dry N_2 gas for 10 h. All measurements were conducted under ambient conditions (27–30 °C, 48–51% relative humidity).

The chemical bonding characteristics of the carbon layers were examined by X-ray photoelectron spectroscopy (XPS), and the structure was characterized by laser Raman spectroscopy using Ar^+ laser light (514.5 nm). The integrated C–H stretching absorption was measured by Fourier-transform infrared spectroscope (FT-IR). The compositional depth profiles were obtained by Auger electron spectroscopy (AES) using the Si-wafer samples.

3. Results and discussion

3.1. Discharge properties

Fig. 2 shows examples of the waveforms of the pulsed negative bias and current, and for the external plasma source, the r.f. voltage, for the processing conditions in Table 1. In the case of the external plasma source, the bias rises relatively slowly ($\sim$5 μs), indicating that the plasma produced by the r.f. voltage lowers the impedance of the plasma as a result of the implantation of ions. It should be noted that bias rise time without the r.f. discharge is much shorter (0–1 μs) and that the pulse current rises to 8 A. This implies that the applied bias rapidly establishes a corona discharge and stable plasma sheath for the duration of the pulse. The relationship between peak current and voltage of $I\propto V^2$ reveals that the applied bias produces a plasma

Table 1
Experimental conditions of PSII process

Conditions	
Pulse width (μs)	10
Pulse delay (from r.f. pulse) (μs)	50
Pulse rate (pulses/s)	300
Pulse voltage (peak) (kV)	~-11
Pulse current (peak) (A)	8
Gas	C_2H_2, C_2H_2+Ar (30%)
Gas pressure (Pa)	5.7 (C_2H_2)
Deposition time (min)	15
PET film thickness (μm)	38
RF power (W)	0–374
RF pulse (μs)	20 (afterglow $\sim$50 μs)

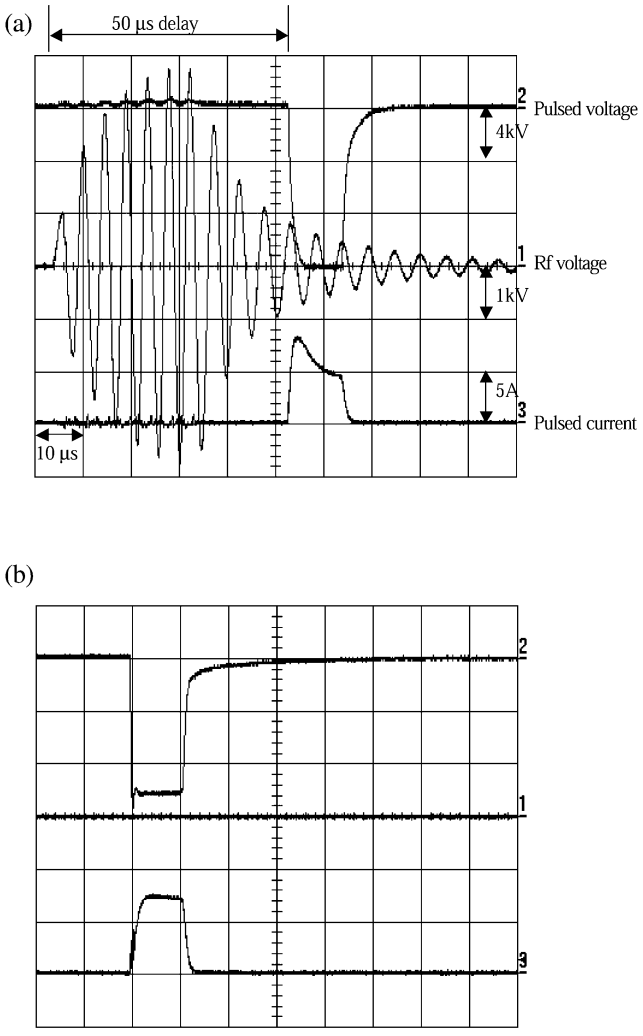

Fig. 2. Waveforms for PSII (a) with r.f. discharge (b) without r.f. discharge.

on its own, without the need for an externally generated plasma source, in addition to performing its regular function of driving ion implantation.

Moreover, the glow discharge plasma generated by the pulsed bias is stable at high gas pressure (>1 Pa). At such high pressures, the effect of etching is suppressed through increased ion–ion collisions, which decreases kinetic energy of incident ions to the target [15]. This is allowing implantation to become the dominant process.

3.2. Carbon layer properties

3.2.1. XPS spectra

Fig. 3 shows the XPS spectrum of a carbon layer on a PET film. The spectrum shows the C1s regions, representing the inter-atomic bonds of the carbon layer. This band can be resolved into three peaks, attributable to C–C (sp^3) and C=C (sp^2) bonds, an sp^2 satellite peak, and a minor peak due to C=O bonds [14]. It should be noted that the sp^2 peak also includes a contribution from C–H bonding.

These XPS data reveal that the carbon layer deposited on PET film without r.f. discharge has primarily sp^2 character, indicative of C–H bonding (285.0 ± 0.2 eV). The ratio $sp^3/(sp^2$ and C–H) is close to that for ICP PSII using C_2H_2 gas [7]. In this case, the ratios are 0.12 for C_2H_2 and 0.45 for $C_2H_2 + Ar$ (30%). The carbon layer is therefore primarily amorphous carbon as desired. Bombardment by Ar ions has the effect of enhancing the sp^3 character or decreasing the proportion of C–H bonds in the amorphous carbon layer.

These results demonstrate that the surface of PET film can be successfully modified to DLC by PSII using C_2H_2 or $C_2H_2 + Ar$ gas, without the need for an external plasma source. However, further analysis by methods such as elastic recoil detection analysis (ERDA) will need to be carried in order to clarify the compositional ratio of C–H. The sp^2 satellite peak should also be examined in detail.

3.2.2. Laser Raman spectroscopy

Fig. 4 shows the typical Raman shift spectra of the thin carbon layer produced from C_2H_2 and $C_2H_2 + Ar$ (30%) by PSII without r.f. discharge with baseline subtracted. Sharp peaks at 1300, 1600 and 1700 cm^{-1}, characteristic of the PET film, are removed for clarity, and the spectra can be fitted by two Gaussian functions corresponding to a graphite-like peak (G-bond) at 1550–1600 cm^{-1} and a disorder peak (D-bond) at 1400 cm^{-1}. These two broad peaks are characteristic of DLC [12–14,16], confirming the formation of a thin DLC layer on the treated PET film.

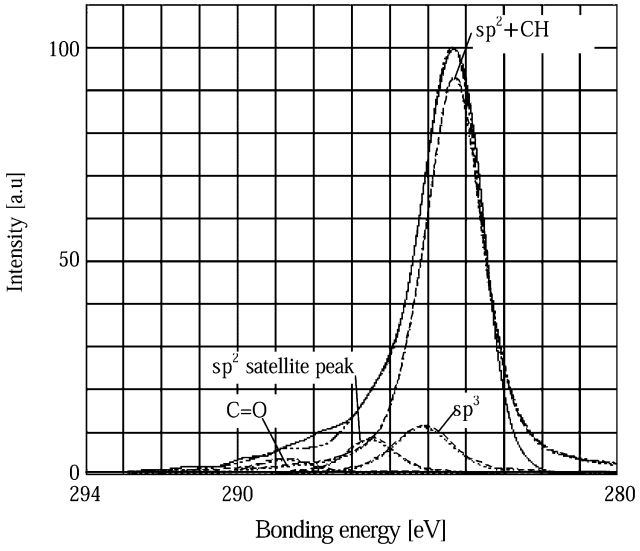

Fig. 3. XPS spectra for typical carbon layer with fitted curves for various chemical bonds. sp^2: 284.5 eV; sp^3: 285.3 eV; sp^2 satellite peak: 286.6 eV; C=O: 287.9 eV; C–H: 285.0 ± 0.2 eV.

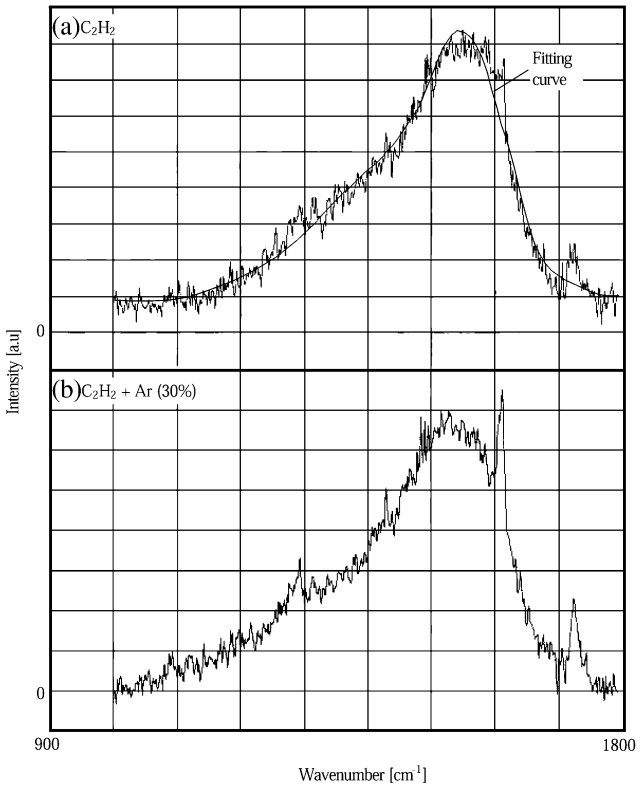

Fig. 4. Raman spectra of the PET film with and without treatment by PSII process. Characterizing D and G band by Gaussian type functions. (a) Coated using C_2H_2 with fitting curve; (b) Coated using $C_2H_2 + Ar$ (30%).

3.2.3. Oxygen transmission rate

Table 2 lists the typical preparation conditions and the results of OTR measurements. The OTRs of the treated samples are ~100 times lower than that of the untreated PET film. The OTR per unit layer thickness (normalized to 300 nm) is proportional to the ratio of intensities of the D and G peaks in the Raman spectra (I_D/I_G). From this relationship, carbon layers with smaller I_D/I_G afford better oxygen barrier characteristics per unit thickness. In our PSII process without r.f. discharge, the gas pressure controls the ratio I_D/I_G. The

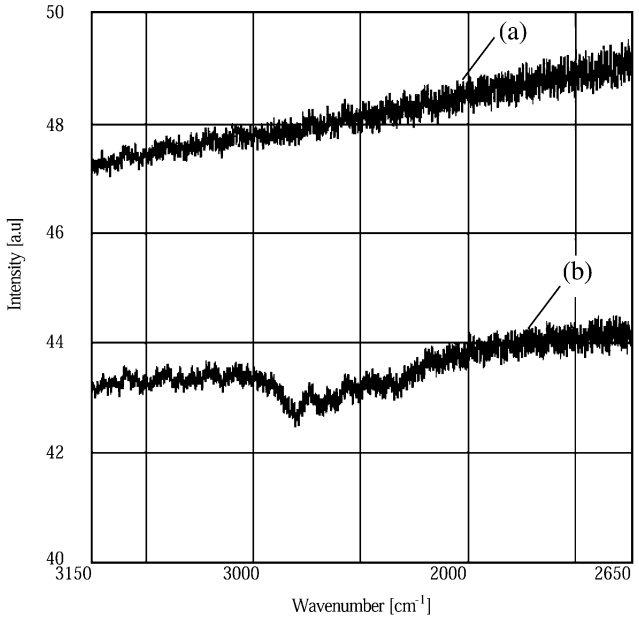

Fig. 5. FT-IR reflection spectra for samples treated by PSII (a) with r.f. discharge and (b) without r.f. discharge.

OTR per unit thickness also changes by a small amount according to the ratio $sp^3/(sp^2$ and C–H).

3.2.4. RF plasma

The effect of employing an external r.f. plasma was investigated using the Si substrates to aid measurement. Fig. 5 shows FT-IR spectra for the two cases; with r.f. plasma and without. The C–H chemical bond region is shown. Peaks assigned to sp^3-CH_3 (symmetrical) at 2960 cm^{-1}, sp^3-CH and -CH_2 at 2925 cm^{-1}, and sp^3-CH_3 (symmetrical) at 2865 cm^{-1} were observed for the sample prepared without r.f. discharge, whereas none of these peaks were present for the r.f.-discharge sample. This result implies that the C_2H_2 molecules are more dissociated in the r.f.-discharge plasma, which reduces the proportion of C–H bonds in the carbon layer [17].

Fig. 6 shows the compositional depth profile of the carbon layers as determined by AES. The interfacial layer between the carbon and the substrate is ~400 nm

Table 2
PSII processing conditions and film characteristics

	Sample 1	Sample 2	Sample 3	Sample 4
Gas	Untreated	C_2H_2	$C_2H_2 + Ar$ (30%)	C_2H_2
Pressure (Pa)		5.7	7.1	8.5
Pulse volt (kV)	Untreated	10.0	7.0	6.0
Pulse current (A)		8.0	8.0	8.0
Deposited layer thickness (nm)	Untreated	290	320	70
sp^3/sp^2	Untreated	0.12	0.45	0.11
I_D/I_G	Untreated	0.656	0.517	0.282
OTR ($cm^3/(m^2/day)$) (per unit thickness)	63.3 ± 0.1 (–)	0.4 ± 0.01 (0.39)	0.4 ± 0.01 (0.43)	0.5 ± 0.01 (0.12)

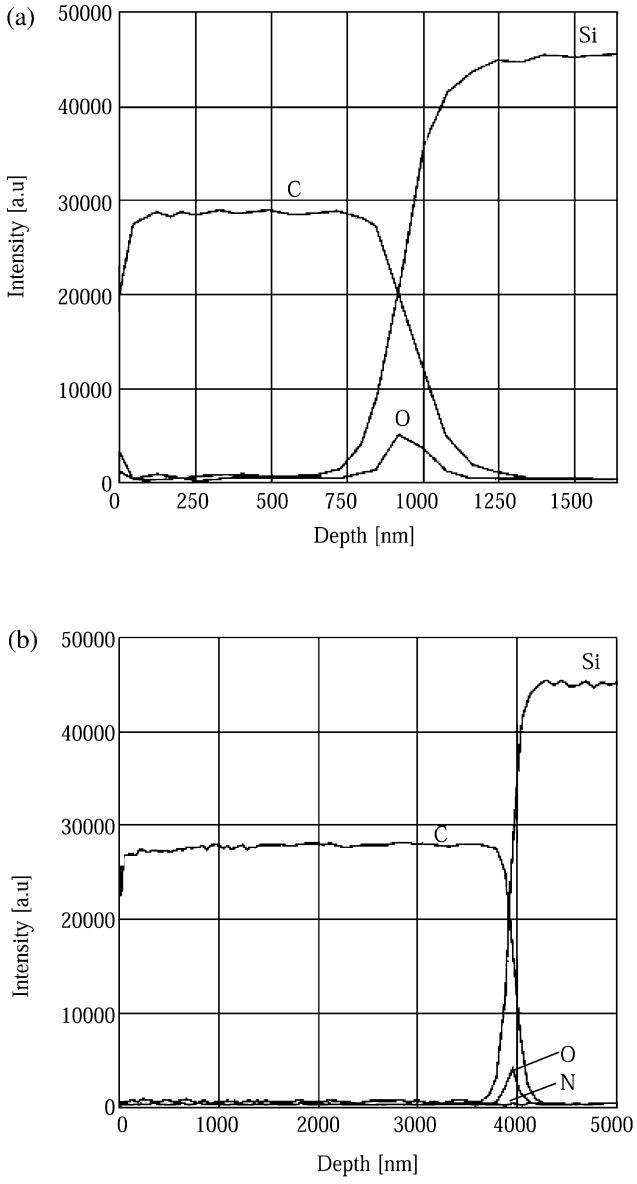

Fig. 6. Compositional depth profiles by AES for samples treated by PSII (a) with r.f. discharge and (b) without r.f. discharge.

for PSII without r.f. plasma, which is thicker than that with r.f. discharge. This indicates that more ions are produced by r.f. discharge, resulting in a higher ion bombardment dose and implantation, indicative of a higher etching rate [15].

The precise mechanism of the deposition process considering the properties of the external plasma and pulsed voltage conditions and ion–ion collision is currently under investigation by both experiment and simulation.

4. Conclusion

A high-pressure (>1 Pa), C_2H_2 PSII method without an external r.f. plasma source was examined as a potentially useful method for modifying the surface of PET films to amorphous carbon, or DLC. Using only pulsed bias at high negative voltage, the PSII technique was successfully used to modify the PET surface to a carbon layer that consisted primarily of graphite crystal and C–H bonding networks. The ratio $sp^3/(sp^2$ and C–H) changes when Ar is added to the plasma gas. The carbon layer is confirmed to have the DLC characteristics from the Raman spectrum.

The OTR of PET films with 70–320 nm carbon layers was reduced by a factor of $\sim$100 times that untreated PET, and the OTR per unit thickness was found to be related to the ratio of intensities of graphite and disorder peaks in the Raman spectra.

The samples prepared using an external r.f. plasma exhibited markedly different C–H bonding characteristics, and it is considered that the deposition rate of the carbon layer treated in this way is slower than the layers prepared without an external r.f. plasma source due to the increased etching rate of the r.f. discharge case. The r.f. plasma effect on the OTR of the carbon layer is under investigation.

Further investigation of the discharge and pulsed bias conditions is necessary in order to realize appropriate conditions and films for industrial application. In addition, quantitative characterization of the DLC and sp^2/sp^3 ratio is necessary in order to further improve the OTR.

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