Preparation of carbon related thin films
using atmospheric non-thermal plasma jet

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This paper describes the preparation of carbon related films using atmospheric non-thermal plasma jet generated by dielectric barrier discharge with radio frequency power. The results showed that the deposition of the films could be performed where a mixture of ethylene and argon was used for the plasma gas. The deposition rate was affected by time, power, and ethylene flow rate. Contact angle measurement and thermo gravimetric results indicated that the film was different from polyethylene. FT-IR spectrum without substrate heating had a peak assigned to C-H bond. By heating a substrate, it disappeared and peaks indicating C≡C were observed. The effects of substrate temperature were also observed in Raman spectra, showing that the films without substrate heating had a strong luminescence. With increasing substrate temperature, the luminescence was weakened and two peaks assigned to graphitic sp^2 bonding appeared. SEM images showed that the surface was changed from smooth to rough by heating substrate. These results suggested that dehydrogenation and thermal decomposition took place with increasing substrate temperature.

Key words: Carbon related film, Atmospheric non-thermal plasma, Chemical vapor deposition, Dehydrogenation

1. INTRODUCTION

Plasma assisted chemical vapor deposition (PACVD) having many parameters to control conditions such as gas composition, flow rate, power, pressure, substrate temperature etc. has expanded significantly over the past several decades. Films produced by PACVD are successfully applied for corrosion protection and diffusion barrier. Non-thermal plasma is appropriate for thin film deposition techniques because of its low temperature [1]. Non-thermal plasma is usually obtained under reduced pressure, however the space is limited by the dimensions of the vacuum chamber due to the requirement of a vacuum system. Therefore, the deposition process under atmosphere is preferable to diminish such facilities. One of the techniques to obtain atmospheric non-thermal plasma is a dielectric barrier discharge (DBD) which has been used for ozone generation for many years. This discharge is also applied to flue gas cleaning, surface treatment of plastic foils and films. A homogeneous DBD called atmospheric pressure glow discharge (APGD) was also developed by Okazaki et al. in a plane electrode with He or other gases [2].

In this work, carbon related thin films were deposited with ethylene using the homogeneous glow discharge obtained at atmospheric pressure.

2. EXPERIMENTAL DETAILS

Experimental set-up is shown in Fig. 1. Cylindrical quartz reactor (diameter: 6mm) has a tungsten rod for inside electrode and Stainless steel foil for outside electrode. Gas introduced consisted of a mixture of argon and ethylene. Carbon related thin films were deposited on glass or silicon wafer substrates.
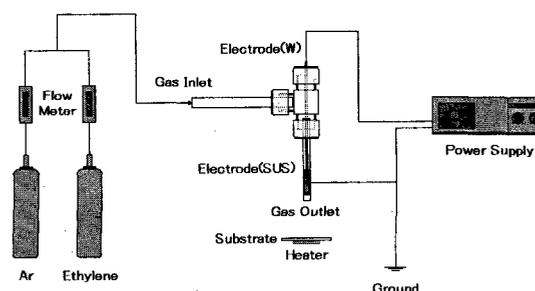
Fig. 1. Experimental equipment

Deposit conditions are summarized in Table I, where the parentheses show standard conditions. The power supply provided radio frequency power (40-120W) at a frequency of 800 kHz in all the experiment. The distance between electrode and substrate was varied between 8 and 22 mm. The carrier Ar gas (8ℓ/min) was mixed with ethylene gas (0.2-1.2ℓ/min), and then fed to the reactor. The substrate temperature was changed from 110°C to 360°C by heating the bottom of the substrate with a sheet type heater.

The discharge was diagnosed with an optical emission spectroscope. The thickness of the films was measured with stylus method to evaluate the deposition rate. The contact angle of the films and the thermogravimetry were also measured. Furthermore, the films were characterized with X-ray photoelectron spectroscope (XPS), micro laser-Raman spectroscope, transmit Fourier transform infrared spectroscope (FT-IR) and scanning electron microscope (SEM).

Table I. Deposit conditions

Power [W]	40 - 120 (80)
Frequency [kHz]	800
Deposition time [min]	2 - 17.5 (8)
Ar flow rate [ℓ/min]	8
Ethylene flow rate [ℓ/min]	0.2 - 1.2 (0.4)
Substrate temperature [°C]	110 - 360 (110)
Distance between electrode and substrate [mm]	8 - 22 (8)

( ): Standard conditions

3. RESULTS

3.1 Discharge Diagnostics

Optical emission spectroscopy (OES) was used to diagnose and monitor the plasma discharges generated in ethylene and Ar gas at atmosphere [3]. This technique is an effective tool in determining the gas intermediate species participating in the reaction mechanisms.

The OES spectrum had CH, C and H_β peaks as shown in Fig. 2. The spectrum presents the emission peaks corresponding to CH (390 nm and 431 nm), C (427 nm and 392 nm) and H_β (486 nm). It indicates that ethylene molecules are changed into active species and some hydrogen atoms are produced through the dissociation of ethylene.
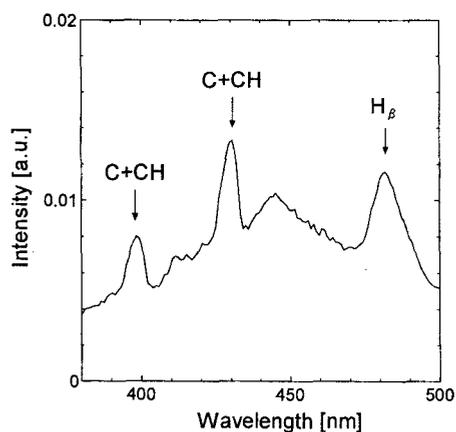
Fig. 2. OES spectrum from Ar-ethylene plasma

3.2 Film Growth

Effects of powers, deposition times, ethylene flow rates, and distance between electrode and substrate on film thickness are shown in Figs. 3-6.

As shown in Fig. 3, the thickness almost linearly increases with deposition time, suggesting that the film can be formed both on the substrate and on the deposited film. Fig. 4 shows that the thickness also increases with power. It indicates that the increasing power results in more activation of ethylene molecules. Fig. 5 shows that the film thickness decreases with ethylene flow rate increased. It suggests that at low ethylene flow rate, ethylene molecules can obtain enough energy to form film because more energy is put

into fewer molecules compared with the case at high ethylene flow rate. On the other hand, at high ethylene flow rate, electron energy is dispersed for numerous ethylene molecules and their activities are weakened. Fig. 6 shows that the film thickness is almost independent of the distance between electrode and substrate, suggesting that active species can keep its activity for a while after the plasma zone.
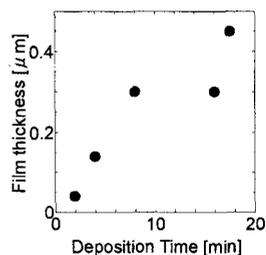
Fig. 3. Film thickness at different deposition times
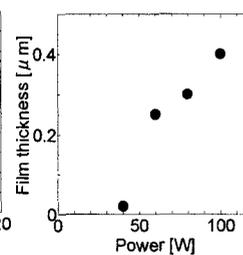
Fig. 4. Film thickness at different powers
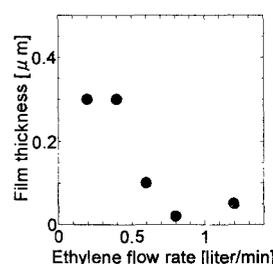
Fig. 5. Film thickness at different ethylene flow rates
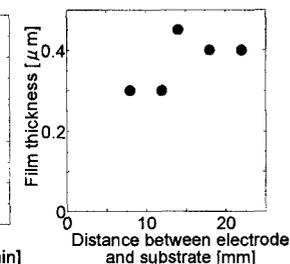
Fig. 6. Film thickness at different distance between electrode and substrate

3.3 Mechanical Properties

3.3.1 Contact Angle Measurements

The contact angle of adhesive dropped onto a material indicates the material's wetability. Lower contact angle indicates hydrophilic surface. The results are listed in Table II. The static contact angle of water droplets on the deposited film surface reveals approximately 80°. This value is less hydrophilic than the untreated glass substrate surface (63°±2°). The contact angle of polyethylene (PE) film has been reported as 94° [4]. Thus, there are some differences between deposited film and polyethylene film.

Table II. Contact angles

Glass	Films	PE
63°±2°	80°±3°	94°

3.3.2 Thermal Properties

Thermal properties of the films were measured by thermo gravimetric / differential thermal analysis equipment (TG-DTA), and the spectrum is shown in Fig. 7.

The spectrum of PE film shows specific vaporizing point around 450°C. On the other hand, that of deposited film has more gradual slope. It shows that thin film has wide range for vaporization, which assigned to be amorphous structure of the film. The film didn't vaporize completely even over 700°C.
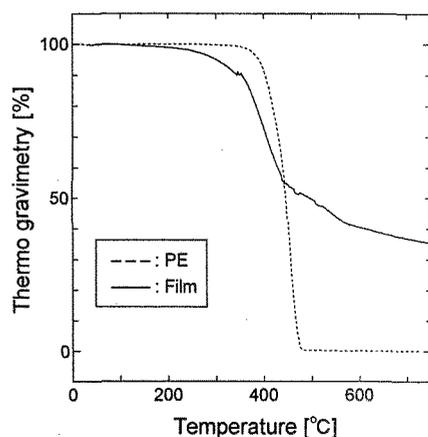
Fig. 7. TG of the deposited film and polyethylene

3.4 Chemical Composition

XPS is widely used for the analysis of polymer surfaces. With this technique, we can obtain information on the chemical content of the surface up to a few nanometer depth of the polymer. Wide scan spectra of XPS were used to determine to identify and to estimate the amount of the elements present on the surface.

The obtained XPS spectrum for the film deposited at standard condition shows that carbon and oxygen are contained in the thin film as shown in Fig. 8. Considerable oxygen can be detected caused by oxygen adsorbed on the film surface. However, as indicated by FT-IR spectra shown in Fig. 9, some oxygen have a bond such as O-H in the film. The contamination of oxygen was caused because deposition area was open to atmosphere without replacement by the inert gas. The replacement with Ar-ethylene gas in deposition area is necessary, if we need to reduce the contamination.
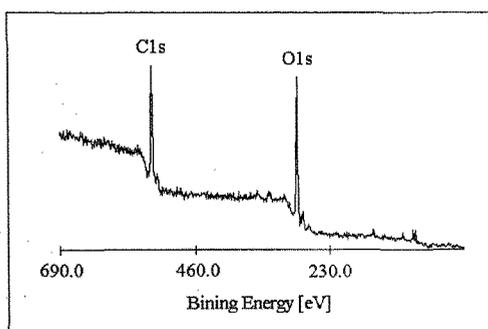
Fig. 8. XPS spectrum of the deposited thin film
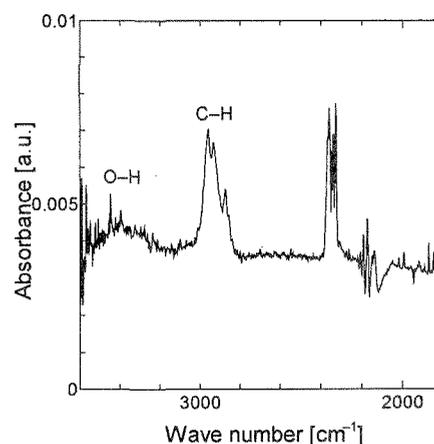
Fig. 9. FT-IR spectrum of the deposited thin film

3.5 Structure Transformation with Various Substrate Temperatures

3.5.1 FT-IR Spectroscopy

It has been reported that deposition temperatures have influenced on the thin film structure especially at the case of carbon related films [5]. In this work, some samples were deposited on the heated silicon wafer substrates, and characterized by transmit FT-IR (Fig. 10).

The spectrum at low substrate temperature (without heating substrate) has a peak around 2900 cm^{-1}, which can be assigned to C-H stretching bond, however it disappears over 175°C. On the contrary, the spectra above 175°C have peaks around 2100~2200 cm^{-1}, indicating triple bond between carbon atoms. This fact can explain that dehydrogenation proceeds with increasing substrate temperature. Moreover the spectra at 300°C and 360°C have a peak around 1050 cm^{-1} respectively. The peak is regarded to C-C bond on account of the graphite structure caused by thermal decomposition after dehydrogenation.
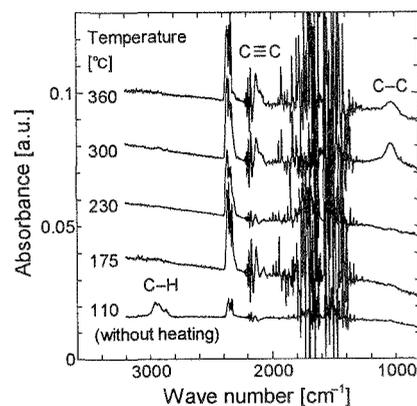
Fig. 10. IR spectra at different temperature

3.5.2 Raman Spectroscopy

Raman spectra of the samples were obtained by micro laser-Raman spectrometer. The effect of substrate

temperature on Raman spectra are shown in Fig. 11 where the interruption from photoluminescence is weakened by increasing substrate temperature and two peaks appear due to graphitic sp^2 bonding called G-peak (1550 cm^{-1}) and D-peak (1330 cm^{-1}) respectively [6]. Although the strong luminescence prohibited characterizing polymer bonds [7], the G and D peaks are very similar to thermal decomposed carbon. Thus, these results also support dehydrogenation and thermal decomposition as well as the observation on FT-IR spectra.
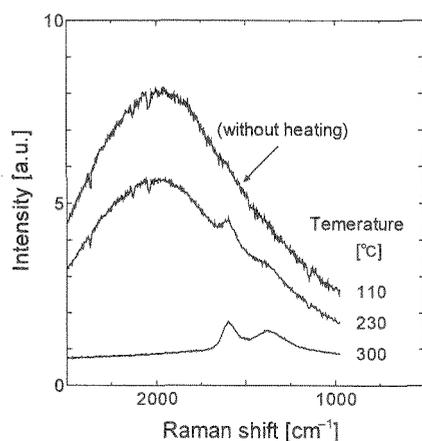
Fig. 11. Raman Shift at different temperature

3.5.3 Surface Observation by SEM

Fig. 12 shows SEM images of film surface. The left image (110°C) at low substrate temperature has very smooth surface, while the right image (175°C) at high substrate temperature has rough surface. It shows that the surface is changed from smooth to rough by increasing substrate temperature. It's considered that rough surface is caused by dehydrogenation and thermal decomposition from the polymer smooth surface.

To identify the thermal degradation of the film as mentioned above, the sample at low substrate temperature was heated at 175°C for 8 minutes. The surface of the heated sample looked rough similarly to film deposited at high substrate temperature, suggesting that the thin films are decomposed after deposition.
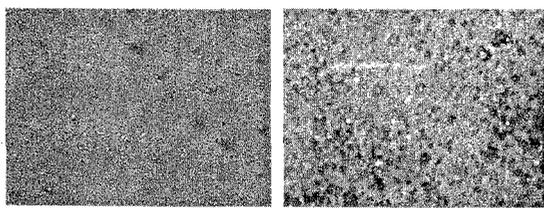
Fig. 12. SEM micrographs (×1000, 20kV) 40 [μm]
(Left: 110°C, Right: 175°C)

4. DISCUSSION

Contact angle measurement and thermogravimetry show that the deposited films are different from polyethylene films. Compared with PE, these films have less wetability and different thermal property. On the other hand, FT-IR spectra have a peak of C-H bond and Raman spectra show luminescence from polymer like carbon. These results indicate that the films have polymer like structure, while the structures are not in order but amorphous structure, this might be caused by various active species formed in the plasma.

For the well-organized structure, we need lower the power put into the plasma zone to generate only one kind of active species.

5. CONCLUSION

In this research, we prepared carbon related thin films using atmospheric non-thermal plasma jet. These films were deposited with varying time, power, distance between electrode and substrate, ethylene flow rate and substrate temperature. By the various characterizing methods including contact angle method, thermogravimetry, XPS, FT-IR, Raman spectrometer and SEM, most of the films were different from polyethylene film and substrate temperature affected the film structure. The high substrate temperature induced dehydrogenation and thermal decomposition of the film.

6. REFERENCES

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