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Application of an ECR Plasma for the Deposition of Transparent and Semiconducting Carbonaceous Films

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The effect of pressure on the deposition of transparent and semiconducting carbonaceous films from pure methane plasma on the fused silica substrate in the ECR apparatus at pressures from 10^{-2} Pa to 1 Pa was studied. The transparent and semiconducting polymer film was deposited at the pressure of 10^{-2} Pa on the fused silica substrate that was negatively biased at about −50V. With increasing pressure, the electron temperature, ion density and degree of ionization decreased and the deposit changed to polyethylene-like polymer film. As the degree of ionization was few percent at the pressure of 10^{-2} Pa, the transparent and semiconducting film is prepared by the impingement of carbonaceous ions on the negatively biased substrate at low pressure. The electric field strength decreased with increasing pressure in the ECR discharge. Thus lowering pressure is necessary to the polymer film deposition with the application of negative bias voltage.

Key words: ECR plasma, pressure effect, transparent and semiconducting carbonaceous film.

1.INTRODUCTION

We have studied the preparation of carbonaceous thin films using the ECR plasma apparatus as shown in Fig. 1 with pure methane as carbon source at pressure of $4x10^{-2}$ Pa [1]. In this case, the difference between the plasma potential and the floating potential on the wall of the chamber reached to 45 V at ECR resonant point and the wall was negatively self biased. Transparent and semiconducting polymer-like carbonaceous thin films were deposited on the fused silica substrate placed at the ECR resonant point on the wall of the fused silica discharge tube inserted into the chamber of the ECR apparatus. Small amounts of carbonaceous ions formed in the center of plasma would drift to the wall by the potential gradient and the three dimensional cross linked polymer including graphite was deposited. The approximately the same polymer thin films were also deposited from pure methane plasma on the fused silica substrate mounted on the holder, on which a negative bias voltage of −50V was applied, and it was inserted into the ECR plasma chamber (Fig. 1) [2]. The latter case, a deposit on the substrate without an application of negative bias voltage is characterized as polyethylene-like polymer. In summarizing up the results, the ion bombardment on the substrate achieves the deposition of transparent and semiconducting thin films [2].

ECR plasma has the capability to operate at lower pressures than 1 Pa and to create higher plasma densities, with corresponding higher degrees of ionization. In some cases, following data are given: an ion density; 10^{12} cm^{-3}, degree of ionization; 10% [3]. We have estimated that the electron temperature (kTe) and the ion density (n_i) has the maximum value of around 15 eV and an order of magnitude of 10^{11} cm^{-3} , respectively, at the ECR resonant point in the center of the cavity. The degree of ionization was estimated to be a few percent at the pressure of 10^{-2} Pa. CH_x^+ and $C_2H_x^+$ ions were taken in the plasma by means of quadrapole mass analysis (QMA). The degree of ionization was also esimated as few percent. Therefore, the plasma prepared in the ECR plasma apparatus at the pressure of $4x10^{-2}$ Pa would be decided as the ECR plasma [2].

Though the reported number is a little, some papers according to the effect of pressure on the ECR plasma have been reported. Pelletier reported that the electron temperature and the plasma potential decreased with increasing pressure [4]. Moreover, Asmussen found that, when gas pressure is increased, there is a transition from ECR heating to collisional heating of the electron gas [5]. The investigation of the dependence of the plasma parameters on pressure is the one of the method of the clarification of the advantage of the ECR plasma. In the present paper, the effect of the pressure on the plasma parameters and the properties of deposits in the ECR plasma is investigated.

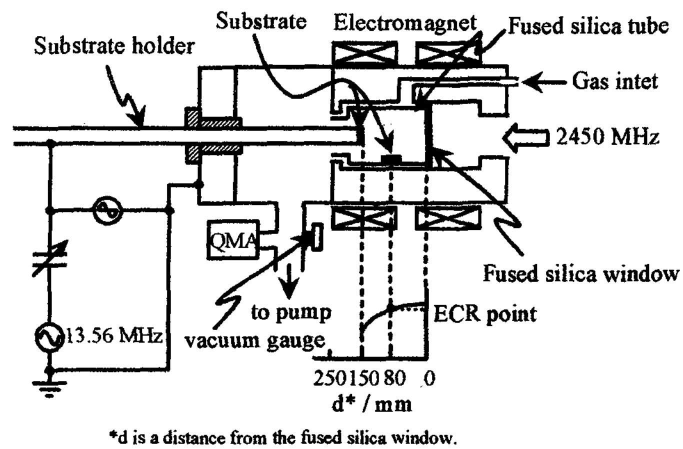

Fig. 1 Schematic diagram of the ECR plasma apparatus.

2. EXPERMENTAL

The apparatus used for deposition of the carbonaceous films was the ECR apparatus as schematically shown in Fig. 1 [1]. The substrates, fused silica and silicon wafer, were placed at two positions, on the negatively biased sample holder placed in the center of the discharge tube and on the wall of the discharge tube at the ECR resonant point where the substrate was negatively self-biased. After the chamber was evacuated below $1x10^{-3}$ Pa, CH_4 was introduced into the chamber and the pressure in the chamber was maintained at desired values between 10^{-2} Pa and 1Pa. Microwave power of 200W at 2450MHz was transferred to the chamber. The discharge was continued for the period of 1 h. The deposits on the substrates were characterized by means of several characterization methods, such as UV/vis absorption spectroscopy and ellipsometry. The electrical conductivity was measured using conventional four probe method. The electric single probe and double probe methods, quadrapole mass analysis, and optical emission spectroscopy were applied to diagnose the plasmas.

3. RESULTS

(1) Pressure effect on the plasma parameters

In OES spectra, several species due to dissociation of methane were identified. The dependence of the band and line head intensities on the pressure is given in Fig. 2. CH radicals and CH^+ ions decreased with increasing pressure, while the intensity due to hydrogen atoms were almost independent with pressure. Large amounts of methane molecules could dissociate and ionize at lower pressures. By means of electric double probe

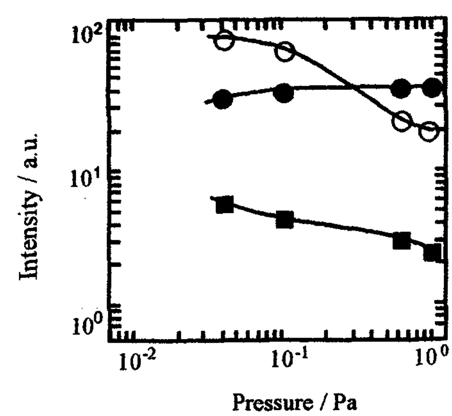

Fig. 2 Normalized intensities of band and line heads in the plasma vs. pressure. (O:CH,● :H,■:CH^+)

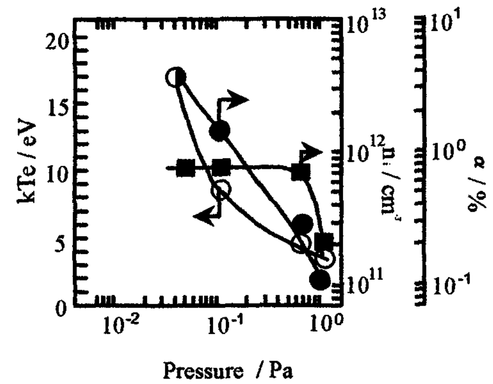

Fig. 3 Electron temperature (O), ion density (■) and degree of ionization (●)vs. pressure.

methods, the dependence of electron temperature (kTe) and the ion density (n_i) in the plasma on the pressure is studied. Results obtained are shown in Fig. 3. The kTe considerably decreased with increasing pressure. On the other hand, the ion density did not depend on the pressure up to 1 Pa. Thus the degree of ionization of species in the plasma was few percent at 10^{-2} Pa and decreased with increasing pressure as also shown in Fig. 2. The dependence of the plasma potential and the floating potential measured by means of the electric single probe method on the pressure are shown in Fig. 3. The plasma potential decreased with increasing pressure. On the other hand, the floating potential of the surface of the discharge tube increased with increasing pressure. As a result, the difference between plasma potential and the floating potential, which corresponds to the self bias voltage of the sample placed on the wall of the discharge tube decreased with increasing pressure.

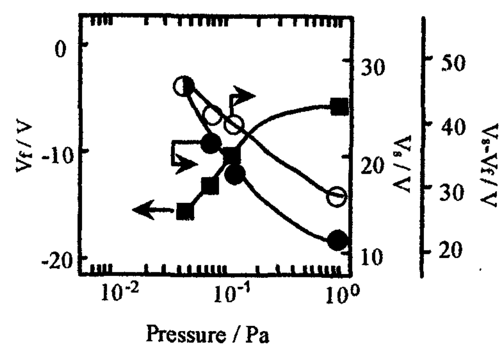

Fig. 4 Plasma potential (○), floating potential (■) and difference between plasma potential and floating potential (●) vs. pressure.

(2) Dependence of the deposits on the pressure

The plasma parameters were affected with pressure as mentioned above. On the other hand, we reported that unique transparent and semiconducting carbonaceous film was obtained only on the substrate, on which the bias voltage of −50 V was applied at the pressure of 10^{-2} Pa [2]. Thus the dependence of the properties of deposit on the pressure was investigated in the deposition on the substrate applied the bias voltage of −50 V. Two kinds of samples, which were mounted on the holder biased negatively at −50 V and on the negatively self-biased wall of the discharge tube, were selected.

The UV/vis absorption curves measured for two kinds of samples which were deposited varying pressure are shown in Fig. 5. In both samples, approximately the same results were obtained. The deposits at the pressure of 10^{-2} Pa exhibited π-π^* transition due to cojugated double bonds at around 240 nm. By increasing pressure, the absorbance at 240 nm decreased and the curve changed to that due to polyethylene-like polymer. This tendency was also identified by means of infrared absorption spectroscopy. The refractive index of both samples deposited varying pressure was measured with ellipsometry. The refractive index is given in Table 1 with the thickness of the deposits. The refractive index of the deposit at 10^{-2} Pa corresponded with that deposited by ion beam deposition [6]. The refractive index decreased with increasing pressure and reached to that of polyethylene-like polymer at the pressure of 1Pa. Both deposits at the pressure of 10^{-2} Pa were the semiconductors with the conducivity of around 10^{-5} Scm^{-1} as given in Table 2. When the pressure was increased, the deposit changed to the insulator.

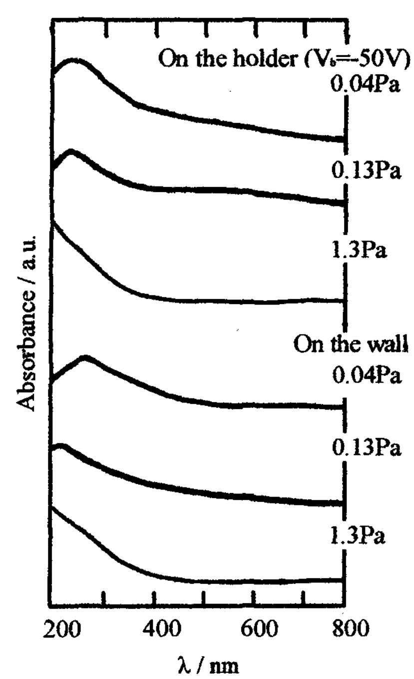

Fig. 5 UV/vis spectra of samples deposited varying pressure.

4. DISCUSSION AND CONCLUSIONS

The mean power absorbed by an electron in the high frequency discharge, $\bar{P}$, is given by

Table 1 Refractive index and film thickness of the samples deposited varying pressure.

Substrate position	Pressure / Pa	n	d / nm
On the holder	0.04	2.07±0.05	136± 2
(d=150mm,V_b=-50V)	0.13	1.99±0.01	122± 3
	1.3	1.58±0.05	130± 5
On the wall	0.04	1.99±0.05	114±19
	0.13	2.01±0.09	154± 3
	1.3	1.56±0.01	159± 9

Table 2 Electric conductivity of the samples deposited varying pressure.

Substrate position	Pressure / Pa	Electric conductivity / Scm^{-1}
On the holder	0.04	7.4×10^{-4}
(d=150mm,V_b=-50V)	0.13	less than 10^{-7}
	1.3	less than 10^{-7}
On the wall	0.04	6.9×10^{-5}
	0.13	less than 10^{-7}
	1.3	less than 10^{-7}

$$\overline{P}=\frac{n_e e^2E^2}{2m_e\nu_e}\left[\frac{\nu_e^{\,2}}{\nu_e^{\,2}+\omega^2}\right] \quad (1) \qquad [5]$$

At very low pressure, the mean free path of electron-neutral and electron-ion collisions becomes very long, $\nu_e \ll \omega_e$, and equation (1) becomes

$$\overline{P}=\frac{n_e e^2E^2}{2m_e\nu_e}\left(\frac{\nu_e}{\omega}\right)^2 \quad (2) \qquad [5]$$

Since the collision frequency, ν_e, is directly proportional to pressure, the lowering pressure gives the increase of the strength of electric field, E, even the $\overline{P}$ of the same value is applied. With increasing pressure, ν_e increased and E decreased. The high degree of ionization that is the characteristic of ECR plasma would be kept at lower pressures [5].

With varying pressure, the plasma parameters were changed. The electron temperature and the degree of ionization decreased with increasing pressure. This exhibited that the collision between particles in the plasma increased with increasing pressure, and positive ions were decreased by the recombination with electrons as shown in Fig. 2. With increasing pressure, the plasma potential and the absolute value of the floating potential decreased. As a result, the difference between the plasma potential and floating potential, which corresponded to the self-bias voltage, was decreased.

With increasing pressure, the deposits changed from the unique transparent-semiconducting films to polyethylene-like films. This was verified by means of UV/vis absorption spectroscopy, IR absorption spectroscopy, ellipsometry, and electrical conductivity measurement. This tendency was observed with decreasing the absolute value of negatively biased voltage at the pressure of 10^{-2} Pa.

By Comparison of the results in the plasma diagnostics and the properties of deposits in the deposition of the carbonaceous films using ECR apparatus, the impingement of large amounts of ions on the negatively biased substrate contributes to the deposition of the unique transparent and semiconducting carbonaceous films at lower pressures. Both conditions, higher degree of ionization and self bias voltage, were obtained in the ECR plasma prepared at the pressures as low as 10^{-2} Pa order of magnitude.

5. REFERENCES

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