Preparation of Thin Films of Poly-Thiophene by Atmospheric Pressure Glow (APG) Plasma

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Abstract

A glow discharge can be generated at atmospheric pressure by filling the discharge area with helium gas.[1] Plasma polymers deposited from thiophene by the Atmospheric Pressure Glow (APG) plasma method were analyzed by XPS, FT-IR and SEM. The electric conductivity of plasma polymerized thiophene (PPT) films doped with iodine was measured.

Un-doped PPT films have very low electric conductivity ($\sigma<10^{-16}$ Scm^{-1}). The conductivity of PPT films increased to 10^{-8} Scm^{-1} by doping with I_2. More highly conductive films showed that the atomic composition ratio S/C determined by XPS was coming close to 0.25 which is the monomer value. The results of FT-IR showed that more highly conductive films had more conjugated systems.

1.Introduction

Applications of plasma polymers to electric materials are mainly passive uses: for example, dielectrics of capacitors, resistors and protective films. But, some applications to active uses such as semiconductive materials are expected, so many studies have been carried out. One of the studies reported that plasma polymers whose conductivity is about 10^{-1} Scm^{-1} can be deposited to select a monomer appropriately.[2] These studies, however, adopted the plasma polymerization at low pressure and no study has been done at atmospheric pressure. The APG plasma is the most suitable method to treat the surface of large area films, and if the conductive layer can be deposited on them by this method, we can expect to use it for charge prevention treatment.

To investigate the possibility of deposition of electric conductive polymers, we have chosen thiophene as a monomer for polymerization by the APG plasma and have estimated the PPT films' chemical structure (via XPS and FT-IR analysis) and electric conductivity .

2.Experimental

2.1.Plasma reactor and polymerization

The reactor used for preparation of PPT films is depicted schematically in Fig. 1. The plasma chamber and gas inlet lines were pumped to pressures of less than 1×10^{-4} Torr. The thiophene monomer warmed up at 30°C was bubbled with He (30 cm^3min^{-1}) and then was diluted with a large volume of He (2000 cm^3min^{-1}). The sample gas was introduced between the parallel flat electrodes. The separation between them was 8 mm. Then the pressure in the plasma chamber was restored to atmospheric pressure and the leak valve was opened. After the gas flow rates stabilized, power at a frequency of 3 kHz was applied under a fixed discharge current. A certain discharge time (typically 30 min) deposited a PPT film on the substrate mounted on the lower electrode. During the discharge, the gas inlet lines were warmed up at 80°C without condensation of the monomer. For experiments in which the substrate needed to be heated, it was first heated to the desired temperature and fixed before introducing the sample gas to the chamber. Substrates for XPS and FT-IR were silicon wafers and non-alkali glass plates (Corning 7059) on which gold electrodes were deposited for conduction measurements.

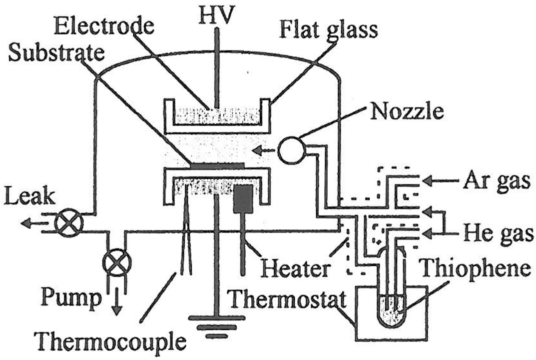

Fig. 1 Schematically diagram of the plasma reactor.

Doping was accomplished by exposing PPT films to a vapor of I_2 at 50°C for 10 min. After being exposed, I_2-doped films were permitted to stand under vacuum (1×10^{-5} Torr) for 1 hour to remove excessive I_2.

2.2.Measurements

XPS spectra gave the atomic composition ratio, S/C, and the peak area ratio, S-C/C-C. C-C bond and S-C bond peak areas were obtained from C_{1S} spectra by dividing them into two peaks (BE 284.6 eV of C-C bond and BE 285.4 eV of S-C bond).

IR spectra of all samples had two relatively sharp peaks: the C-H stretching vibration of methylene at 2924 cm^{-1} and the aromatic plane vibration at 1540 cm^{-1}. The intensity ratio, I(1540 cm^{-1}) / I(2924 cm^{-1}), was determined as an indicator of aromaticity.

The electric conductivity was obtained by measurements of surface resistance and thickness.

3. Results and discussion

3.1. Influence of polymerization parameters

PPT films were usually yellow-brown and semi-transparent. But for some parameters, films became white and granular. Un-doped PPT films deposited during this study showed very low electric conductivity values ($\sigma < 10^{-16}$ Scm^{-1}). This is too low to measure with our instrument, so the exact values were not obtained. Therefore, the correlation between I_2-doped PPT films' conductivity and polymerization parameters was investigated. The doping time was fixed at 10 min.

3.1.1. Influence of discharge current

Without heating of substrate, the discharge current was varied between 0.5 to 3.0 mA to study the effect of current on the polymerization. No remarkable changes of S/C and S-C/C-C with current were observed. So the compositions of PPT films were not so different. However, FWHM of S-C and C-C peaks was increased as the current was increased. And Fig. 2 shows that I(1540 cm^{-1}) / I(2924 cm^{-1}) is decreased as the current is increased. So we think that increasing discharge current breaks the structure of the monomer in the films and decreases the aromaticity. The electric conductivity decreasing as the current increases in Fig. 3 supports that opinion.

3.1.2. Influence of substrate temperature

The substrate temperature was varied between 40 and 120°C, while the discharge current was fixed at 1.0 mA. SEM photographs showed that PPT films deposited at low temperature had disordered structure and looked like aggregations of particles, while those deposited at higher temperature had more homogeneous structure. In general, the electric conductivity is decreased in granular films by the effect of grain boundaries and becomes larger in more homogeneous films. However, Fig. 4 shows

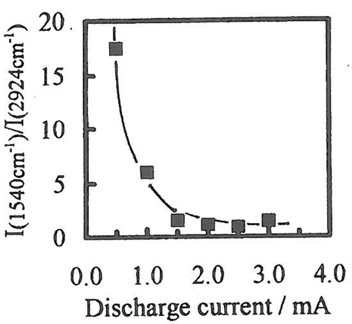

Fig. 2 Absorbance at 1540 cm^{-1} / absorbance at 2924 cm^{-1} as a function of the discharge current without heating the substrate.

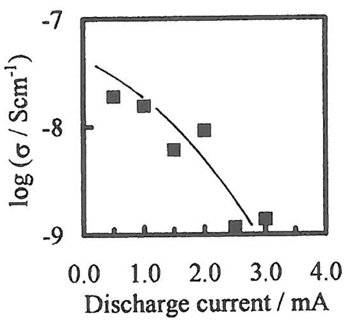

Fig. 3 The electric conductivity as a function of the discharge current.

that it is decreased as the substrate temperature is increased.

We suggest two reasons why improvement of the electric conductivity with uniformed films' shape was not observed. First, figures 5 and 6 show that the number of sulfur atoms and the aromaticity in PPT films are decreased as the substrate temperature is increased. Therefore, one reason is that the decrease of the electric conductivity by the effect of breaking the monomer structure is bigger than its increase by the effect of making the films' shape uniform. Next, owing to doping by exposing to iodine vapor, the effect of doping becomes greater on larger surface areas of the film. So we suppose that PPT films deposited at lower temperatures had larger surface areas due to granular shape and that the electric conductivity was increased by that reason even without homogeneous shape.

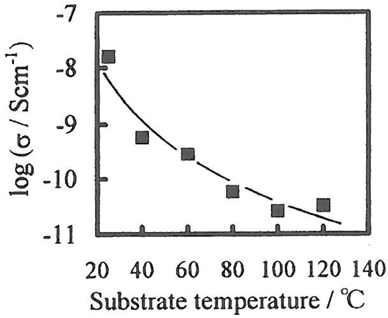

Fig. 4 The electric conductivity as a function of substrate temperature with the discharge current of 1.0 mA.

3.2.Influence of He

For APG plasma to occur, metastable He (2^3S_1) which has a very long lifetime (6×10^5 s) must be present.[1] And this metastable He has quite a high energy (19.82 eV). In the discharge field, electrons may excite the He atoms present much more than monomers, and then these excited He atoms would excite monomers. So the influence of He on plasma polymerization was investigated.

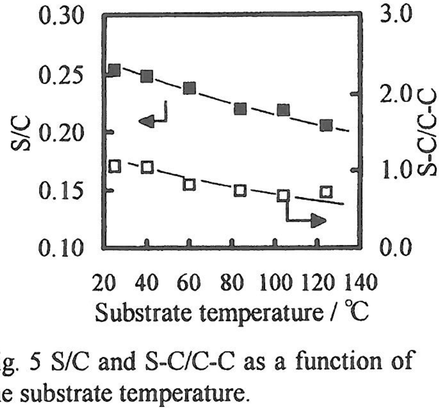

Fig. 5 S/C and S-C/C-C as a function of the substrate temperature.

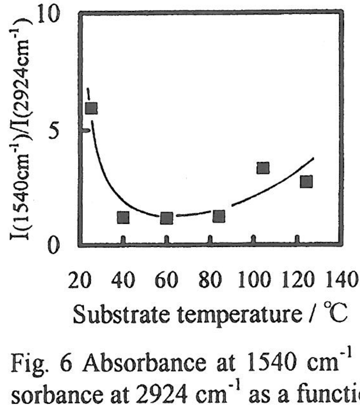

Fig. 6 Absorbance at 1540 cm^{-1} / absorbance at 2924 cm^{-1} as a function of the substrate temperature.

3.2.1.The effect of Ar addition on APG plasma

T.Fujii et al. found that Ar addition into He plasma decreases the number of excited He atoms and the electron temperature at low pressure.[3] If this can also be applied to APG plasma, a lowering of the destruction of the monomer structure is expected. Then He/Ar mixture gas which the total flow rate was 2000 $cm^3 min^{-1}$ was used to diluent gas and the deposition of PPT was carried out under various Ar contents.

No remarkable changes of S/C and S-C/C-C with Ar content were observed. The electric conductivity was increased slightly as Ar content was increased, whereas Fig. 7 shows that the ratio I(1540 cm^{-1}) / I(2924 cm^{-1}) has a peak at 20 % and then decreases to its initial value. However, in IR spectra of PPT deposited with He/Ar mixture gas, several new peaks which were due to the aromatic plane vibrations were observed. One of them at 1190 cm^{-1} was selected; the intensity ratio, I(1190 cm^{-1}) / I(2924 cm^{-1}), is plotted in Fig. 8. No significant decrease over 20 % was considered to mean that the structure of PPT had varied to the more aromatic structure. Therefore, the destruction of the monomer was decreased by Ar addition and we think that the higher aromaticity increased the electric conductivity.

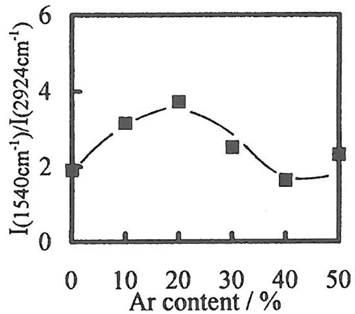

Fig. 7 Absorbance at 1540 cm^{-1} / absorbance at 2924 cm^{-1} as a function of Ar content.

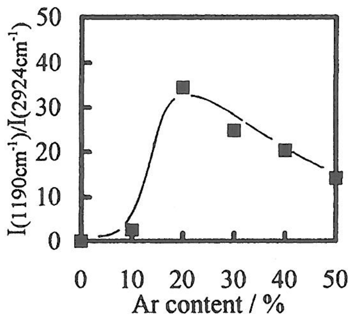

Fig. 8 Absorbance at 1190 cm^{-1} / absorbance at 2924 cm^{-1} as a function of Ar content.

3.2.2.The effect of He addition on low pressure plasma

For experiments of low pressure plasma polymerization, the total pressure was 1.0 Torr and the partial pressure of He was varied between 0 and 0.8 Torr. Figures 9 and 10 show that both S/C and I(1540 cm^{-1}) / I(2924 cm^{-1}) are increased as the partial pressure of He is increased to 40 % and that they are decreased later. That the discharge voltage was decreased as the He content was increased suggests that the aromaticity is increased as the power per molecule is decreased. But over 40 %, the reason why the aromaticity is decreased is that the decrease of the aromaticity due to the effect of breaking the monomer structure with He is bigger than its increase due to the effect of the power per molecule.

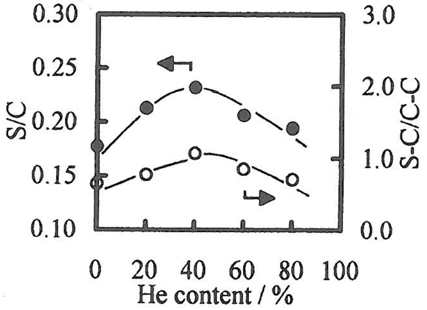

Fig. 9 S/C and S-C/C-C as a function of He content with the discharge current of 1.0 mA and no heating of the

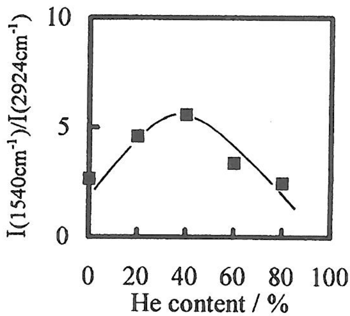

Fig. 10 Absorbance at 1540 cm^{-1} / absorbance at 2924 cm^{-1} as a function of He content.

The plasma polymerization at atmospheric pressure is not easily compared to that at low pressure. If the same tendency is happening at atmospheric pressure, the monomer structure should be almost destroyed in an APG plasma in which the volume ratio of He is more than 99 %.

4.Conclusions

In this study, the highest electric conductivity was obtained under the following parameters: discharge current, 1.0 mA, and the substrate temperature, room temperature; and the conductivity value was 1.93×10^{-8} Scm^{-1}. Considering the mechanical strength, we think the substrate must be heated to a certain extent. And the decrease of the electric conductivity under those conditions may be improved by increasing the amount of dopants or using some method such as ion injection.

We think that the destruction of the monomer structure by excited He is very great. But the destruction doesn't deny completely the possibility of using He-APG plasma for polymerization of electric conductive polymers. In fact, the effect of Ar addition acted as an excited He getter. And only I_2.doping changes PPT films from insulators to semiconductors.

References

[1] S. Kanazawa, M. Kogoma, T. Moriwaki and S. Okazaki, J. Phys. D, 21, 838 (1988)
[2] A. Kruse, A. Baalmann and M. Hennecke, ISPC-11th, vol.3 (1993)
[3] T. Fujii, Thesis, Yamaguchi University (1994)