

## Deposition and *in-situ* Plasma Doping of Plasma-Polymerized Thiophene Films Using PECVD

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**Abstract:** Highly transparent, thin polythiophene (PT) films were successfully synthesized by the plasma polymerization of thiophene. These films were doped with O<sub>2</sub> plasma by *in-situ* doping technique. The plasma polymerized PT films were deposited at about 50 to 340 nm/min, depending on the temperature and plasma power. A resultant transparency as high as 85% was achieved. The plasma polymerized PT films exhibited the characteristics of an insulator or semiconductor ( $10^{10-12} \Omega/\square$ ,  $10^{-7}$  S/cm). The conductivity was immediately increased up to  $10 \Omega/\square$  and  $10^{-2}$  S/cm, when doped with O<sub>2</sub> plasma. The plasma-doped PT films exhibited an increased surface roughness resulting in a decreased contact angle. However, the thickness of the PT layer was partially decomposed and/or etched with increasing voltage above 40 W.

**Keywords:** polythiophene, plasma polymerization, plasma doping, PECVD.

### Introduction

$\pi$ -Electron conjugated polymers have attracted considerable attention in the last few decades because of their electronic/physical properties and potential application in electronics devices.<sup>1-4</sup> These nano-layered films are known to play important roles in opto-electronic devices such as electro-luminescence, organic transistor, and antistatic coatings.<sup>1,5,6</sup> In particular, polythiophene (PT), which consists of five-numbered heterocyclic rings, has attracted much attention because of its environmental stability and heat resistance of the intrinsically conductive polymers, and PT is also known for its high and stable conductivity with doping.<sup>7-9</sup> However, the fabrication of nano-layered films from conducting polymers has been a big challenge. These conducting polymers can be prepared either through chemical oxidation or electro-chemical of the monomer or, in rare cases, photo-polymerization or vapor-phase polymerization, both of which involve electron transfer. These PT films prepared by the above mentioned conventional polymerization methods have been doped with suitable dopants such as iodine, FeCl<sub>3</sub>, BF<sub>4</sub> or AsF<sub>6</sub>, etc. The nano-layered thin films having a high uniformity and without defect were not easy to obtain from these methods.

Plasma polymerization is well known to be a useful process to produce polymer films, which are formed by reactions in gas phase without introducing any chemical oxidants.

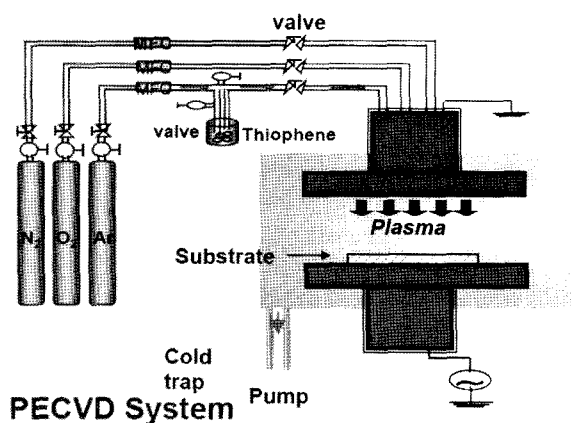
Plasma polymerization is also a solvent-free, low temperature process that can be used to form rapidly deposited thin polymer layers onto a wide variety of substrates.<sup>10</sup> In plasma polymerization, a neutral monomer gas or vapor in a low pressure reactor is subjected to an electric field. The monomer is fragmented into reactive species, which subsequently recombine, forming a polymer. The big advantages of plasma polymerization are the deposition of ultra-thin, pin-hole-free homogeneous films on large areas. Furthermore, such films are highly adherent to a variety of substrates including conventional polymer, glass and metal surfaces. In contrast to the chemical polymerization, this process causes the side reactions resulting in branching and cross-linking, which leads to a three-dimensional network and enhances some mechanical properties. Plasma polymerization has been used to synthesize conducting polymer films from pyrrole and thiophene derivatives.<sup>11-19</sup> Especially, Sathir *et al.*<sup>14</sup> reported the plasma polymerized thiophene layer using Ar gas. After doping with iodine, conductivities ranging from  $10^{-6}$  to  $10^{-4}$  S/cm were obtained. Bhat *et al.*<sup>15</sup> also reported that plasma polymerization of thiophene was carried out in a tubular reactor using an RF source and that the electrical conductivity was found to be very low ( $10^{-10}$  S/cm) before doping. Silverstein *et al.*<sup>20</sup> have also reported the molecular structure and electrical properties of plasma polymerized thiophene. The undoped films exhibited non-linear current-voltage behavior typical of Schottky metal-semiconductor barriers with breakdown at reverse bias and ohmic behavior after doping with iodine.

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The doping of the plasma-polymerized films with chemical under *ex-situ* conditions has been reported.<sup>14-16</sup> However, the conductivity level of the resulting film was low and application of *in-situ* doping was very difficult. In this paper, we report the formation of plasma-polymerized conductive PT films doped by *in-situ* plasma doping technique. Characteristics and the conductivity of these films will also be discussed.

## Experimental

The plasma polymerization was carried out in a commercial parallel-plate electrode, radio frequency (13.56 MHz) plasma reactor (Scheme I). The reactor could be evacuated to 0.03 torr with a rotary pump and the temperature of electrodes was maintained between 25 and 100 °C with circulating cooler. Thiophene monomer of liquid phase (99.95% purity) was attached to one of the reactor inlets. Then, Ar gas (99.999% purity) carried the thiophene into the deposition chamber. Polymerized thiophene films were deposited on PET substrate film or Si wafer at an Ar gas by 13.56 MHz RF power plasma enhanced chemical vapor deposition (PECVD) as shown in Scheme I. The base pressure of the



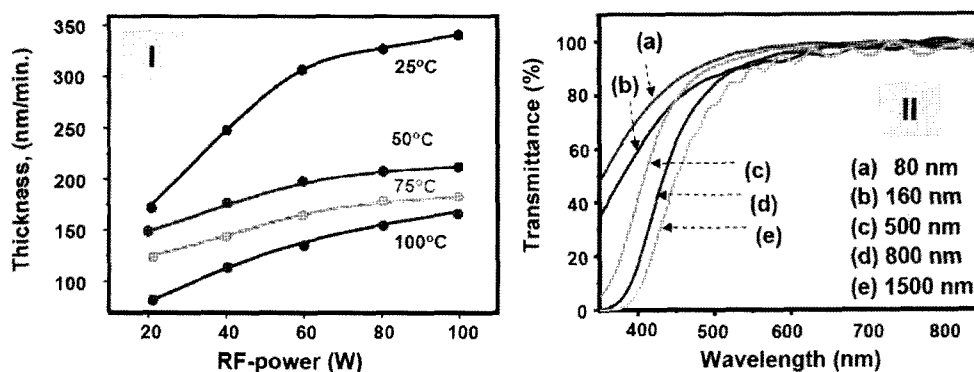
**Scheme I.** PECVD apparatus for plasma polymerization and plasma doping.

reactor was 0.03 torr. Plasma was generated around the substrate holder which is connected to a RF generator (between 20 and 100 W at 13.56 MHz). After the deposition of PT films under various conditions, these films are doped with O<sub>2</sub> plasma by *in-situ* doping technique in the PECVD system. O<sub>2</sub> gas (99.999% purity) is used as an activated doping material and fed into the deposition chamber. The plasma doping was performed between 20 and 60 W DC power at a pressure of 0.4 torr at 25 °C.

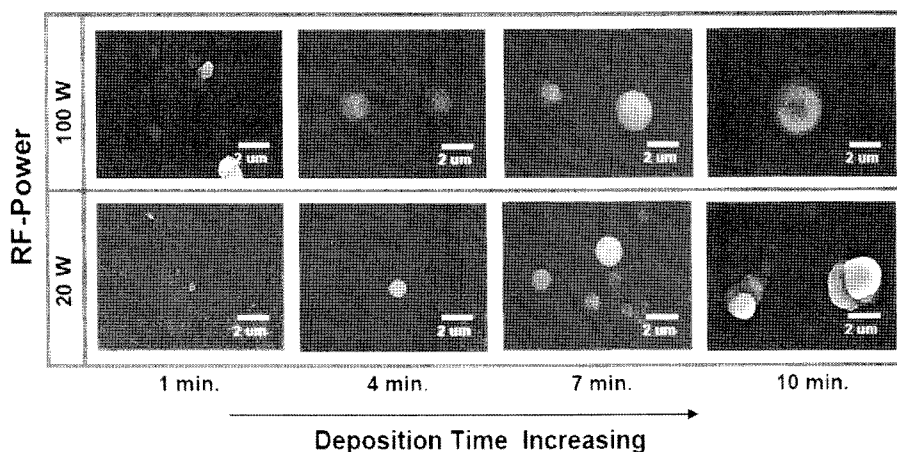
The thickness and the conductivity of conductive PT thin films deposited on the substrates were measured with ellipsometer (SE-800, SENTECH) and standard 4-probe technique (Loresta-GP, Mitsubishi Chemical), respectively. Atomic force microscopy (AFM: Nanoscope IIIa DI, USA) and SEM (JSM-633F, Jeol) was used in order to characterize the surface morphology of plasma polymerized PT films. FT-IR and UV/Vis spectrophotometers are used for structural analysis and XPS measurements of the characteristics of plasma deposited PT films or doped PT films were performed using a model ESCA 2000 by VG. The contact angle was measured from the Goniometer model 13-200-0 by ERMA. After pure water was dropped onto the surface of the plasma polymerized or doped PT films, the contact angle of water on the films was immediately measured by means of the advanced angle method at 25 °C.

## Results and Discussion

The plasma polymerization that occurred under a low energy flux resembles conventional polymerization method. In general, the deposition factors of a plasma polymerization are determined by the following parameters: the geometry of the system, the reactivity of the monomer and its flow rate, addition of the carrier gas, the working pressure in the chamber, the plasma power, and temperature of the substrate, etc.. Figure 1(I) shows the growth of PT films as a function of RF power during the plasma polymerization of thiophene. Deposition was carried out at range from 20-100 W power, 0.4 torr, and the argon is used as a carrier gas. Ar gas



**Figure 1.** The growth of PT deposited films as a function of RF power under the plasma polymerization (I) and light transmittance versus thickness of films (II).



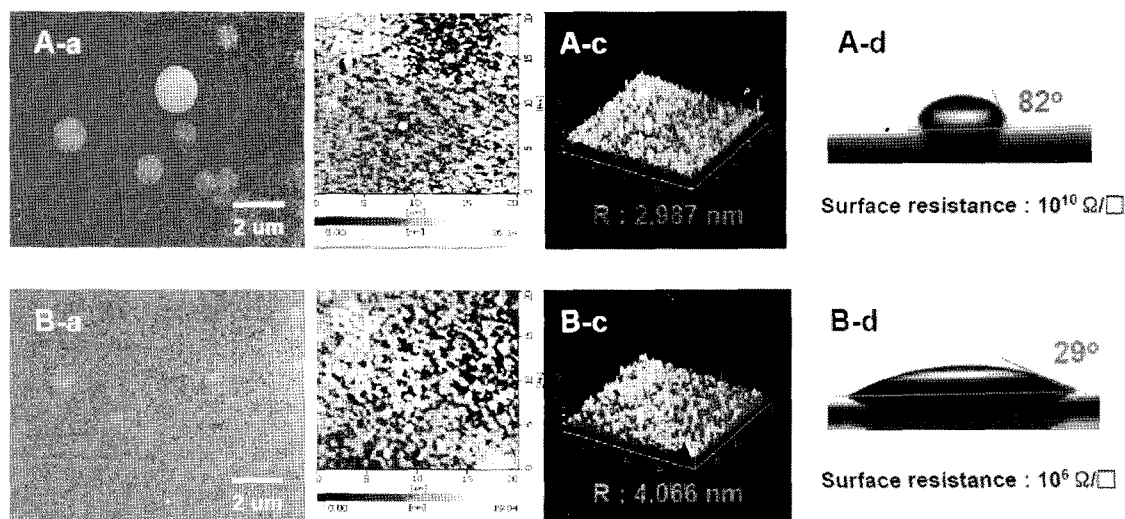
**Figure 2.** SEM morphologies of the PT films deposited under the conditions of 20 and 100 W power/25 °C for 1, 4, 7, and 10 min.

flow was 29 sccm, and the dynamic rate was 160 nm/min at the 20 W/25 °C conditions. The mass and thickness of plasma-polymerized PT films are almost linearly deposited with deposition time and the deposition rates. Especially, the deposition rates have been related to the ratio of plasma power to monomer mass flow rate. Transparent, yellowish PT films were deposited at a relatively low deposition rate. The deposition rate was increased with increasing power as a 340 nm/min at 100 W and the film growth rate at low temperature was faster than that at high temperature. Especially, at high temperature conditions, the deposition rate relatively slow because the thiophene monomers activated by plasma are partially decomposed under  $\text{Ar}^+$  plasma of high temperature. The PT layer obtained by the plasma polymerization was a light brown colored transparent film and these films were deposited at 50 to 340 nm/min rate depending on the power and/or temperature. PT films did not show the electrical property as a conductor or semiconductor. The light transmittance of films as a function of the PT thickness is shown in Figure 1(II).

Plasma polymerization of thiophene resulted in homogeneous and pinhole-free layers, as can be seen in Figures 2 and 3. Figure 2 shows SEM morphologies of the PT films deposited at the condition of 20 and 100 W power/25 °C for 1, 4, 7, and 10 min, respectively. The thickness of PT layer was linearly grown with the increase of deposition time; the thickness was 140, 470, 800, and 1,120 nm, respectively, in the case of 20 W power and 320, 900, 1600, and 2,200 nm, respectively in the case of 100 W power. However, the morphologies of films deposited on substrates show very uniform structure but the films have the aggregated or condensed PT form of globular shape from place to place as shown in Figure 2. The size of the globules increases with the time of deposition and power. The films deposited for 10 min showed a globular size up to 2  $\mu\text{m}$ , and the numbers of globules were also increased. Similar results have been observed from plasma-polymerized thiophene film deposited on glass

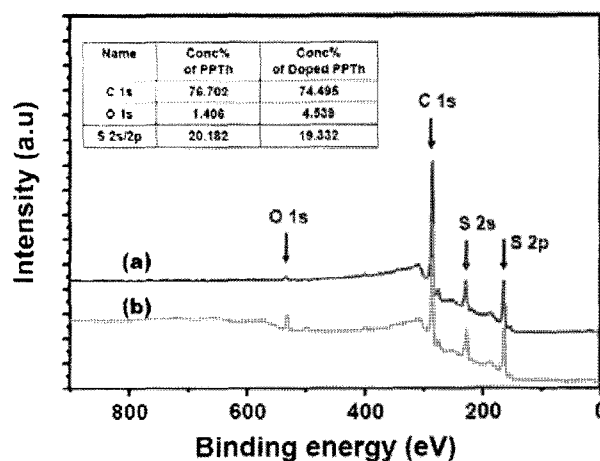
and aluminum plates by N.V. Bhat *et al.*<sup>15</sup> They have reported that the films deposited for 10 min showed a globular size ranging from 1 to 1.2  $\mu\text{m}$  whereas those deposited for 45 min revealed variation from 8 to 10.2  $\mu\text{m}$ . In addition, the numbers of globules observed were higher. According to the Cruz *et al.*,<sup>21</sup> these globules can be originated by the presence of oligomers trapped between the layers of the polymer. The size of these can be also determined by external growth due to polymerization as well as agglomeration of the particles formed during the polymerization process.<sup>22</sup> The size and number of globules were increased with the RF power increases.<sup>15</sup> However, the decrease in both RF power and polymerization time can increase the smoothness of the plasma-polymerized thiophene film surface.

The surface of polymerized PT films was studied by the method of AFM to obtain more insight into the structure and morphological features. Figure 3(A-b and A-c) shows the two- and three-dimensional AFM images (scale 20  $\mu\text{m} \times 20 \mu\text{m}$ ) of the PT layer surfaces deposited at 20 W for 10 min along with SEM image (A-a) obtained from the same sample. As shown in AFM image of Figure 3, the morphological features of the surface shows very uniform structure and the AFM rms surface roughness was 2.987 nm. These PT film layer also showed the characteristic as almost insulator having sheet resistance of  $10^{10} \Omega/\square$ . The contact angle of water on the films was 82° when pure water was dropped onto the surface of the plasma polymerized PT films. In order to produce the characteristic as conductor or semiconductor, these films are doped with  $\text{O}_2$  plasma by *in-situ* doping technique into PECVD system. Then,  $\text{O}_2$  gas is used as an activated doping material into the deposition chamber. The plasma doping was performed between 20 and 60 W DC power at a pressure of 0.4 torr under 25 °C. Figure 3(B) shows the SEM (B-a) and AFM (B-b and B-c) images of the PT layer surfaces when these films are doped with  $\text{O}_2$  plasma at 20 W power for 10 min. With plasma doping, the size of the globules decreases with the time of dop-



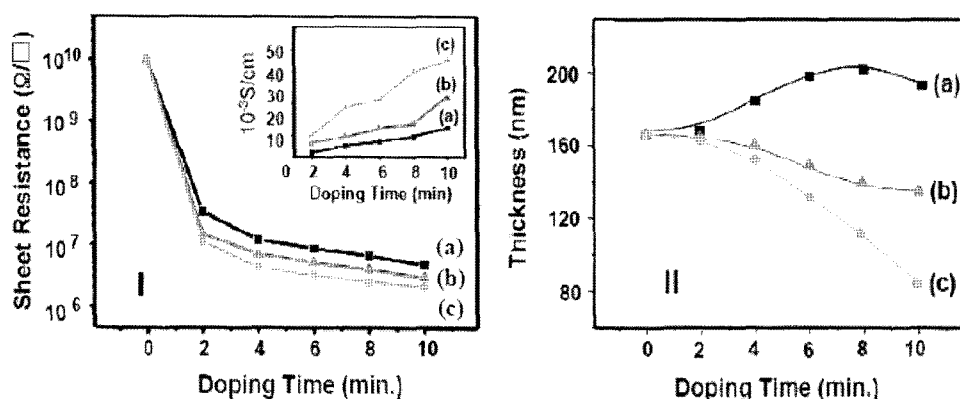
**Figure 3.** Two- and three-dimensional AFM images (b and c) of the PT layer surfaces deposited at 20 W for 7 min along with SEM images (a) obtained from the same sample: A (plasma polymerized PT film), B ( $O_2$  plasma doped PT film). (d) the contact angle of water on the films when pure water was dropped on to the surface of the films.

ing as shown in Figure 3(B-a) but the surface roughness values of  $O_2$  plasma-treated PT films were increased to 4.066 nm (Figure 3, B-c). The combined results indicate that the roughness value is decreased with increasing the contact angle. The decrease of the contact angle may be explained by the increase in the total surface energy of PT films due to the increase in surface area induced by roughening as well as the creation of new binding states by plasma treatment. In general, correlations between various surface properties need to be investigated since plasma treatment can generate radicals and new functional groups on surfaces and can increase surface roughness. Characterization of surface chemical bonding states, relative surface energy, and surface morphology was carried out using XPS, contact angle measurements, and AFM, respectively. These plasma doped PT film layer also showed the characteristic as semiconductor having surface resistance of  $10^6 \Omega/\square$  and then the contact angle of water on the films was  $29^\circ$  (Figure 3, B-d). Moreover, these reduction in contact angle indicates the increased surface hydrophilicity, which may have been caused by the introduction of new polar groups, such as carboxyl and hydroxyl, on the surface.<sup>23</sup> Figure 4 is the XPS spectra obtained from the surface of plasma-doped PT films (b) and before doping (a), respectively. The presence of the plasma-doped PT film is indicated by a large increase in the oxygen atom peak intensity at 532 eV, and a relatively small decrease in the carbon and sulfur peak intensities. Especially, the peak area ratio for the oxygen and carbon, corrected by the elemental sensitivity factors, is 4.539: 74.495 in plasma-doped PT films. On the other hand, that in untreated bare PT film is 1.406: 76.702. In here, the oxygen atom largely increased in plasma-doped polymers is attributed to  $O_2$  plasma treatment and it can be considered as



**Figure 4.** XPS spectra of plasma-doped PT films (b) and before doping (a).

introduced to new functional groups, such as carboxyl and hydroxyl, on the surface. According to Clark *et al.*,<sup>24</sup> the O1s peak at 532 eV is explained to the position of which suggests the oxygen in carbonyl groups. Existence of oxygen in the polymerized samples has also been supported by the result of the infrared spectroscopy. From infrared spectrum, the  $1650\text{--}1700\text{ cm}^{-1}$  band assigned to the carbonyl C=O stretching is measured in  $O_2$  plasma-treated PT films. But, the typical IR absorption bands of PT film can not be obtained from plasma polymerized PT and its plasma doped film samples. The IR bands of plasma polymerized PT film are especially wide, reflecting that the molecular structure of a polymer originates in the random assembly of molecular fragments. The lack of these bands has been explained because exposure to the plasma partially opened the



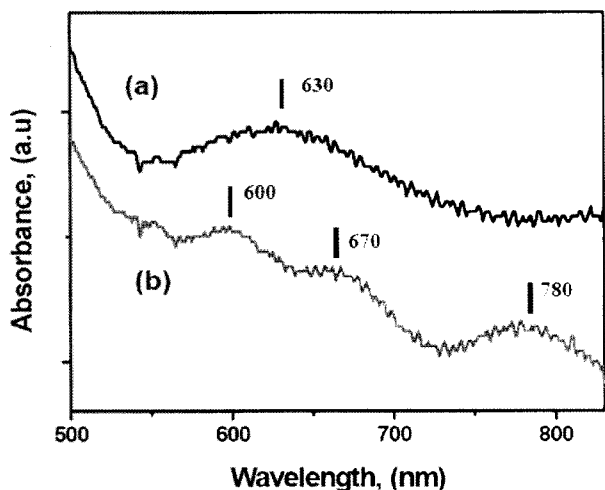
**Figure 5.** Changes of conductivity (I) and thickness (II) on PT layer as a function of the doping time. (a) 20 W, (b) 40 W, and (c) 60 W RF power.

thiophene rings.

Electrical properties are very important because many applications are based on electrical behavior. Conducting polymers are prepared by several methods, and their electronic states can be reversibly changed between insulating and conducting states by redox reactions. Conductivity is the product of two important factors: the number of carrier electrons or holes and carrier mobility, which in a loose sense is the case in which a carrier moves through a material. The electrical conductivities of most conductive polymers are in the same range as those of inorganic semiconductors, but there is some difference according to the degree of crystallinity, purity, and a lack of defects in these materials. In this work, we obtained PT films that are very homogeneous and pinhole-free by plasma polymerization and *in-situ* plasma doping, and their electrical properties are observed. Figure 5(I) shows the doping time dependence of the conductivity of PT layer between 2 and 10 min at power of 20, 40, and 60 W, respectively. At the initial state, before doping, PT film layer exhibited the characteristic as almost insulator having sheet resistance value of  $10^{12} \Omega/\square$ , but the sheet resistance was decreased with increasing doping time and reached  $10^6 \Omega/\square$  after 10 min doping. The conductivity is  $10^{-7} \text{ S/cm}$  at the initial state, before doping and up to  $10^{-2} \text{ S/cm}$  at over 10 min of doping. However, in the case of high-voltage conditions, the behavior of the conductivity increase is higher and faster than that observed at lower-voltage doping as shown in Figure 5(I). The thickness of PT layer was decreased as a function of voltage when voltage was increased more than 40 W as shown in Figure 5(II). PT layer seems to be etched at high-voltage conditions. The reduction of thickness at the high-voltage condition might be attributed to the fact that the plasma doped-PT materials are partially decomposed under plasma and high-vacuum at high-voltage conditions. But, the thickness of PT layer was not decreased at low-voltage less than 30 W. Actually, thickness increases at first up to 8 min and then decreases with further increase in doping time (Figure 5(II-a)). This is con-

siderable that the oxide layers are generated or un-reacted monomers remained on plasma deposited PT film under  $\text{O}_2$  plasma of low RF power. The thickness decrease of PT layer is also relatively very slow at low RF power because the plasma deposited PT film is almost not decomposed at low applied power. However, as the results,  $\text{O}_2$  plasma treatments can be usefully used as a doping process of conjugated polymer, but the film surface of a few nanometer levels can be also modified and/or decomposed with high applied power.

The FT-IR spectroscopy was used for the identification of PT layer grown or deposited on substrate film. The characteristic IR absorption of PT film can be seen at 1440, 1050, 830, and 700  $\text{cm}^{-1}$ , respectively. These peaks can be assigned to polythiophene, ring C-C and/or C-S stretch, symmetrical C-H in-plane bend, and ring deformation, respectively. Additionally, the aliphatic characteristic IR absorption bands are also observed at 2950 and 2200  $\text{cm}^{-1}$  due to the probable existence of methyl and methylene groups. According to Tanaka *et al.*,<sup>25</sup> the absorption peak at 2950  $\text{cm}^{-1}$  can be assigned to the stretching of methyl and methylene groups, and 2200  $\text{cm}^{-1}$  peak is due to C-C bond of a fragment generated from the opened thiophene ring. This result shows that a considerable amount of fragmentation of hydrogen atoms bonded to aliphatic carbons occurs in the plasma polymerized PT layer. The source of aliphatic hydro carbons structure might be the fragmentation of the thiophene rings in the plasma atmosphere. The absorption spectrum for the plasma polymerized PT film itself and after plasma treatment/doping are seen in Figure 6. In spectrum (a), the absorption band near 630 nm and increasing in absorption at low wavelength is typical of plasma polymerized PT film, in particular, 630 nm peak is due to the  $\pi-\pi^*$  transition.<sup>26</sup> This absorption spectrum of PT film (a) is changed to spectrum (b) with  $\text{O}_2$  plasma treatment/doping. The relatively small peaks at higher wavelengths are appeared and represent energy states within the gap due to defects. Thus, these can be charged defects that participate in conduction or structural defects that cre-



**Figure 6.** Electronic absorption spectra of plasma-polymerized PT films (a) and doped with plasma (b).

ate localized energy states. These peaks at lower energy could indicate the presence of bipolarons created by plasma doping.<sup>16</sup>

The self-assembly of molecules or small clusters, that is, the spontaneous association of atomic or molecular building blocks under plasma conditions, is emerging as a successful chemical strategy to form well-defined morphological structures of nanometer dimensions, with potential applications in many areas of nanotechnology. Especially, the self-organizing, functional system is also the ultimate aim of bottom-up fabrication. This bottom-up approach of synthesis is a promising way to design novel nanoscale functional materials with atomic precision. By the above-mentioned experimental method, we simply synthesized PT nano-layer by depositing thiophene monomer using PECVD without any additional catalyst. The doping of the PT is also achieved *in-situ* with O<sub>2</sub> plasma. This time, O<sub>2</sub> plasma seems to be acted as a dopant of gas phase.

## Summary

Highly transparent PT layers with conductivities in the range of antistatic applications have been obtained by plasma polymerization of thiophene and doping with O<sub>2</sub> plasma. These plasma polymerized PT films, deposited at about 50~340 nm/min, had the homogeneous and pinhole-free layers, depending on the temperature and plasma power. In order to realize the conductivity, these films are doped with O<sub>2</sub> plasma by *in-situ* plasma doping technique and their conductivity was immediately increased up to 10<sup>-2</sup> S/cm. On the other hand, the thickness of PT layer was partially decomposed and/or etched with increasing voltage above 40 W. It is to be noted that the plasma polymerization and plasma doping do seem to be an appropriate technique

to obtain conductive layers for applications requiring semiconductor.

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