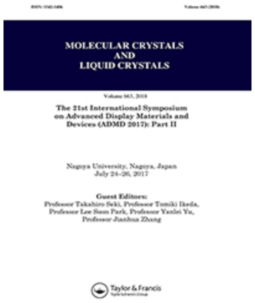

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Experimental study on atmospheric pressure plasma polymerized conducting polymer under coupling and remote conditions

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ABSTRACT
This article has analyzed conducting polymer from the viewpoint of material properties, which is polymerized under atmospheric pressure condition for coupling and remote conditions, respectively. The experimental results show that the atmospheric pressure plasma polymerized pyrrole (pPPy) exhibits similar characteristics from the viewpoint of crystallinity, but the shapes and roughness of the particles are significantly distinguished. In the case of coupling condition, a uniform and flat layer like a thin film was obtained. However, in the case of remote condition, the deposited layer had more rough nanoparticles compared to that of coupling condition. The pPPy surface characteristic and morphology changes are discussed by using field emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM), and X-ray diffraction (XRD) results. Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS) analysis are used to determine the chemical changes introduced by the atmospheric pressure plasma for coupling and remote conditions. The both pPPy materials, which were obtained by coupling and remote conditions, are expected to be applied to various fields, especially for designing the thin conducting electrode layer of polymer light emitting diode (P-LED) or for improving the efficiency by inserting conducting polymer powder on hole injection layer.

KEYWORDS
Atmospheric pressure plasma polymerization; coupling condition; electrode materials; P-LED; pyrrole; remote condition

1. Introduction

Recent interest in conducting polymer, and especially its potential applications in the display industry, has fueled the growth of a once limited field of materials science [1, 2]. However, most of the studies, which were previously reported, are about solution process technique for polymerization [3]. The conventional solution technique has many advantages, such as low cost, large area processing ability and simple manufacturing process [4, 5]. However, due to the constraints of organic solvents, these methods have limitations in implementing various laminated structures. Unlike the studies made extensively on solution process technique,

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a little attention was given to plasma polymerization as a 'dry' process for polymer light emitting diode (P-LED). Especially, as a 'dry' process, atmospheric pressure plasma polymerization is recognized as another important method to easily obtain the various polymer thin films in complex structures [6, 7]. The polymer films obtained by the latter method are pin-hole free with a high degree of cross linking density and adhere well to the most substrate [8, 9]. In addition, plasma polymerization technique is a solvent-free and room temperature process that can be used to deposit the polymer thin films onto a variety of substrates [10]. Recently, we have reported that the synthesis of atmospheric pressure plasma polymerized pyrrole with single crystalline characteristic, which was analyzed from the perspective of atmospheric pressure plasma [11]. However, the polymeric material produced as an effect of direct contact between the substrate and the plasma plume has not been extensively studied from the viewpoint of polymer structures. Therefore, in this experiment, we examine that the detailed polymer structures are investigated by using the atmospheric pressure plasma polymerized material via the coupling and remote conditions. The coupling condition means the direct contact between the plasma and the substrate, and the remote condition means the remoteness of the substrate from the intense and broadened plasma.

2. Experiment set-up

A copper tape with a length of 10 mm was rolled at a point 10 mm from the end of the device composed of three glass tubes configured in a triangular shape. Plus, we installed guide glass tube and polytetrafluoroethylene (PTFE) bluff body at the end of the three glass tubes to generate intense plasmas and to prevent external quenching effect. Three glass tubes of bundle had inner diameter of 1.5 mm, outer diameter of 3 mm, and length of 13 cm, respectively. The guide glass tube, which had an inner diameter of 20 mm with length of 60 mm, constituted a chamber where the pyrrole monomers were decomposed by the intense argon (Ar) plasma. The decomposed monomers and radicals were polymerized and deposited on the glass substrate. The detailed experimental system on device structure and other instruments in this study has been described as those in [11] except for gas flow rates and applied power. The high purity Ar gas (99.999%) was used as the discharge gas for plasma generation with a flow rate of 2000 standard cubic centimeters per minute (sccm). Liquid pyrrole monomer (Sigma-Aldrich Co., Mw = 67 g·mol^{-1}) was vaporized by the Ar gas, with a flow rate of 200 sccm. Then, a voltage of peak-to-peak 18 kV was applied through the copper electrode. All photographs of the devices and plasma plumes were taken with a DSLR camera (Nikon D5300) with a Macro 1:1 lens (Tamron SP AF 90 mm F2.8 Di). The field emission scanning electron microscopy (FE-SEM, HITACHI SU8220) and atomic force microscopy (AFM, Park Systems NX20) were used to analyze the surface and cross section image and morphology. The X-ray diffraction (XRD, MP-XRD DS109) was used to estimate the dependence of the film crystallinity and check the surface morphology. Fourier transform infrared spectroscopy (FT-IR, PerkinElmer Frontier) was measured by a Perkin-Elmer Frontier spectrometer between 400 cm^{-1} and 4000 cm^{-1}. The X-ray photoelectron spectroscopy (XPS) was carried out on a ESCALAB 250XI surface analysis system. FT-IR and XPS analyses were used to measure the chemical bonding structures introduced by the Ar plasma.

3. Results and discussion

Figure 1 shows the plasma discharge images of pPPy film grown on glass substrates for 20 min. for coupling and remote conditions. In the case of coupling condition, the more

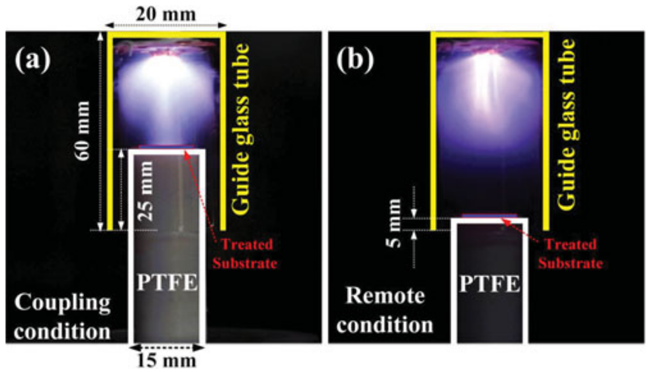

Figure 1. The plasma discharge images of guide glass tube in APPJs as variations of the distance between plasma plume and substrates with respect to PTFE bluff body: (a) coupling and (b) remote conditions.

intense plasma plume was observed compared to that of remote condition. Because the plasma plume is closer to the substrate than the remote condition, the plasma path is connected thereby generating more intense plasma channel between plasma plume and substrate. On the other hand, in the case of remote condition, which is in the floating state, positioning the substrate away from the plasma, a broadened plasma was formed, but it was not connected to the glass substrate, as previously reported [12]. In addition, the surface temperatures of the substrates on both conditions were about 65 °C and 35 °C, respectively.

Figure 2 shows the SEM images of pPPy films grown on glass substrates for 20 min. for coupling and remote conditions. In the case of coupling condition with cross-sectional view images, the deposited pPPy film was uniformly grown presumably due to the direct contact between substrate and plasma plume caused by producing the plasma channel in Fig. 1.

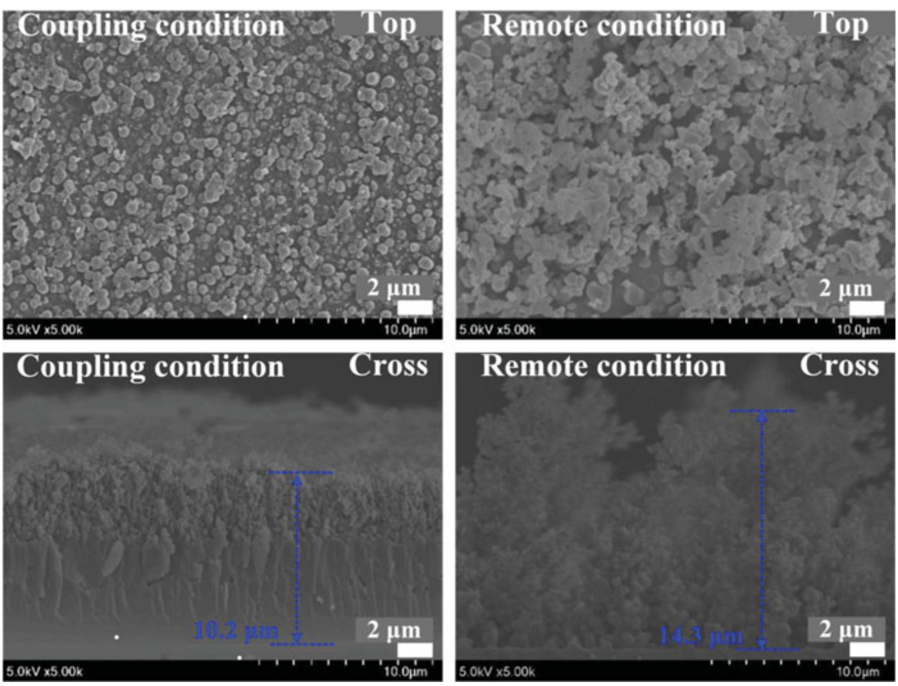

Figure 2. Top and cross-section views of SEM images of pPPy film prepared on glass substrates for 20 min. under coupling and remote conditions.

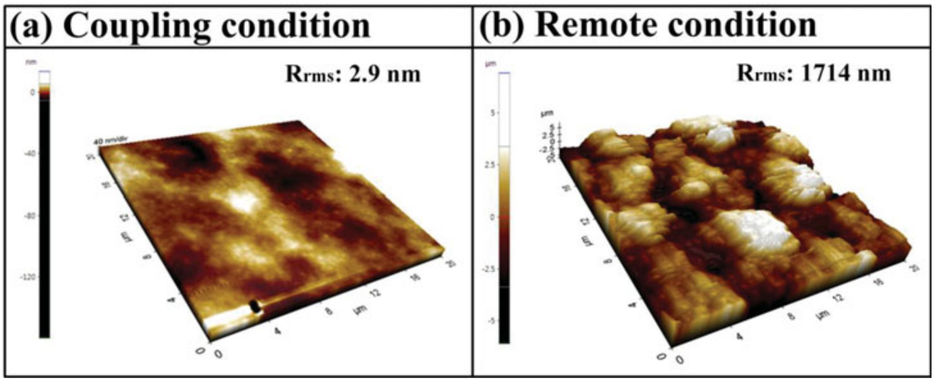

Figure 3. AFM images with roughness of pPPy film prepared on glass substrates for 20 min. under (a) coupling and (b) remote conditions.

In other words, much denser and more uniform pPPy film, which was strongly bonded, could be obtained in coupling condition. Whereas, in the case of remote condition, the deposited layer was shown more rough nanoparticles in the form of a "dry" powder (or a powder form). Noticeably, in the previous experiments, polymer films were uniformly deposited under the remote condition, being presumed that these polymer synthesis methods were greatly affected by the gas flow rate and applied voltage [12].

Figure 3 shows the AFM images of pPPy film grown on glass substrates for 20 min. for coupling and remote conditions. As shown in Fig. 3, the roughness of the pPPy film is significantly affected by the distance between the substrate and the plasma. The root mean square roughness (r_{rms}) data in coupling and remote conditions were 2.9 nm and 1714 nm, respectively. In the case of coupling condition, the film roughness was extremely reduced compared to that of remote condition due to the direct contact between substrate and plasma plume thereby causing the uniform ion bombardment with thermal effect in Fig. 2. Thus, direct contact between plasma and substrate in coupling condition affects the high quality of uniform surface morphology of the plasma polymerized pyrrole under certain conditions. These results are in good agreement with SEM results.

Figure 4 shows the XRD patterns of the pPPy film grown on glass substrates for 20 min. for coupling and remote conditions. The XRD data on previously reported in solution process was observed at a broad peak about 23° with the polymerized pyrrole peak [13, 14]. In our

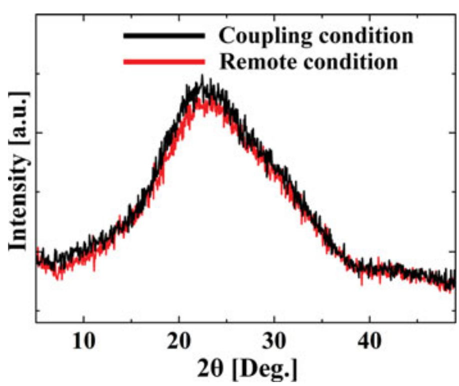

Figure 4. XRD patterns of pPPy film prepared on glass substrates for 20 min. under coupling and remote conditions.

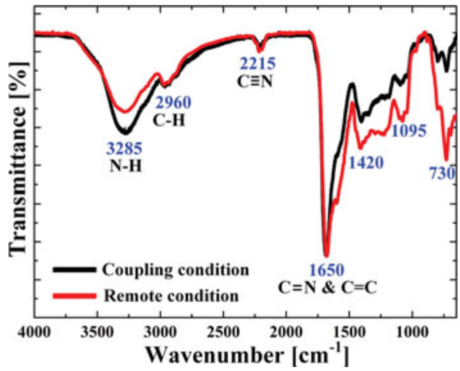

Figure 5. FT-IR spectra of pPPy film prepared on glass substrates for 20 min. under coupling and remote conditions.

experiment, in both coupling and remote conditions, the obtained XRD data also exhibited broad peak at 23°. In addition, we calculated that the value of interplanar spacing was about 0.38 nm for the broad peak at $2\theta = 23°$. Although the film surface characteristics of polymerized pyrrole in coupling and remote cases were different in Figs. 2 and 3, polymerized materials exhibit similar properties in terms of crystallinity characteristics in Fig. 4.

FT-IR and XPS measurements were used to determine the chemical changes introduced by the plasmas for coupling and remote conditions. Figure 5 shows the FT-IR spectra of pPPy film grown on glass substrates for 20 min. for coupling and remote conditions. The FT-IR spectra of these polymers films were measured between 650 cm^{-1} and 4000 cm^{-1}. For both coupling and remote cases, the broad and sharp peaks located at 3285 cm^{-1} corresponding to N-H stretching with hydrogen bonded, aliphatic C-H bonds at 2960 cm^{-1}, multiple bonds of C≡N peak at 2215 cm^{-1}, and C=C/C = N peaks at 1650 cm^{-1}, were clearly observed [15]. The first two peaks of 3285 cm^{-1} and 2960 cm^{-1} indicated that some of the pyrrole rings in the polymer chain were well decomposed, and the last two peaks of multiple bonds at 2215 cm^{-1} and 1650 cm^{-1},which had π electrons, could be an evidence of films with a better electric conductivity by using halogen dopants [7, 12]. As shown in Fig. 5, in the case of coupling condition, the N-H stretching band was increased compared to that of remote condition. Whereas, in the case of remote condition, different absorptions peaks at 1420 cm^{-1}, 1095 cm^{-1}, and 730 cm^{-1}, which meant the reflected broken pyrrole rings, were more significantly increased than coupling condition [6, 7]. These results imply that the interaction between substrates and plasma plume plays an important role in atmospheric pressure plasma polymerization.

Figure 6 shows XPS spectrum of pPPy film grown on glass substrates for 20 min. for coupling and remote conditions. The XPS survey spectrum of pPPy nanoparticles is shown in Fig. 6(a). The high resolution C1s, O1p, and N1s peaks were deconvoluted in detail, as presented in Figs. 6(b), (c), and (d), respectively [16]. Figure 6(b) illustrates the component fitting of the C1s energetic distribution. The binding energy scale was calibrated by setting the C1s peak at 285 eV. The peak at 285.0 eV can be attributed to C-H or C-C bonds, whereas the peak at 286.5 eV corresponds to C−N or C-O bonds [6, 17]. In the case of coupling condition, the peak at 285.0 eV, which reflected C-H or C-C peaks, was decreased compared to that of remote condition, whereas, the peak at 286.5 peak corresponding to C−N or C−O bonds were slightly increased. On the other hand, in the case of remote condition, the peak at 286.5 were decreased, while 285.0 peak was increased compared to that of coupling condition. The N1s peak, which was set to 400.0 eV, was deconvoluted as shown in Fig. 6(d). In the case of coupling condition, the peak at N-H bond at 400.0 eV was increased compared to that of

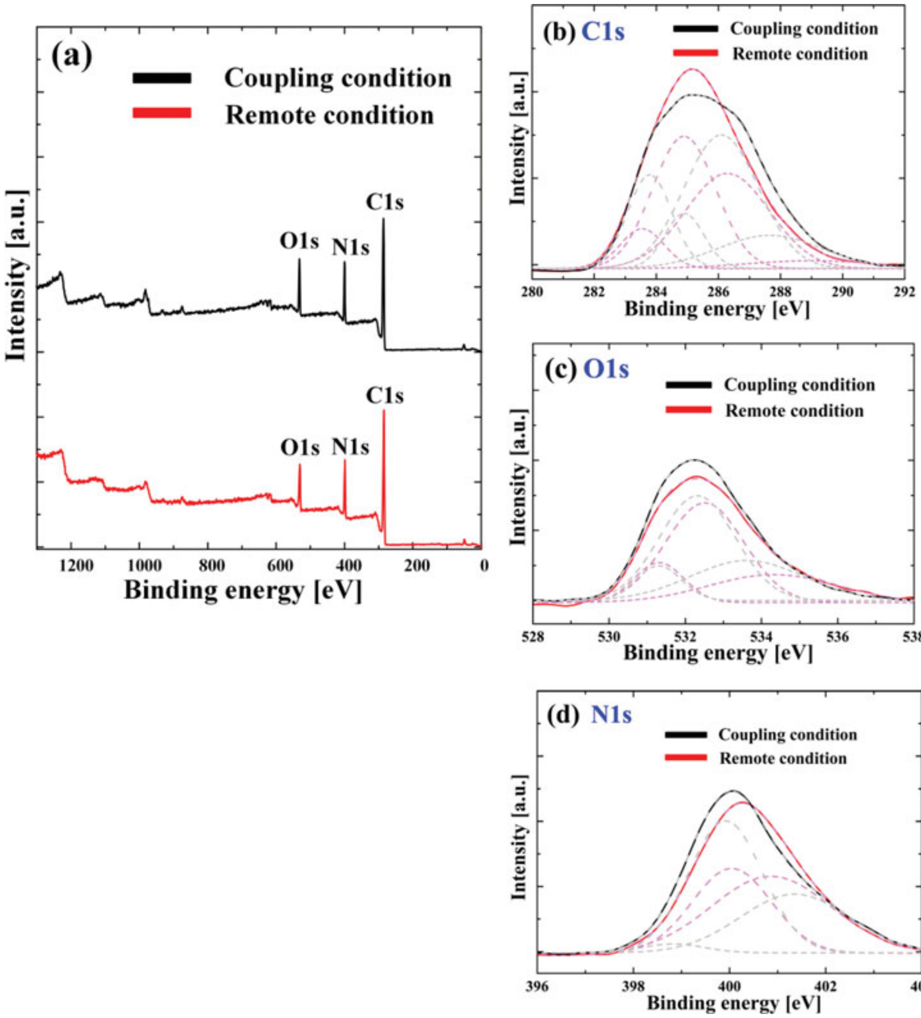

Figure 6. (a) XPS survey spectra and (b) C1s (with narrow scan); (c) O1s (with narrow scan), and (d) N1s (with narrow scan) spectra of pPPy film prepared on glass substrates for 20 min. under coupling and remote conditions.

remote condition, this is the same as the result of FT-IR in Fig. 5 [6]. Thus, the FT-IR and XPS analyses are in good agreement.

In Table 1 and Fig 6(c), the percentage of elements identified from XPS spectrum are presented. In the case of coupling condition, O1s element was detected at a higher rate than that of remote condition. This is presumably due to high process temperature and direct contact between substrate and strong plasma plume.

Table 1. Atomic percentage by XPS survey spectra about plasma polymerized pyrrole (pPPy) film prepared on glass substrates for 20 min. under coupling and remote conditions.

Composition, %	C1s	O1s	N1s
Coupling condition	72.9	10.1	17.0
Remote condition	73.3	9.8	16.9

4. Conclusions

In summary, we have investigated the influence of distance between substrate and plasma on the atmospheric pressure plasma polymerized pyrrole from the viewpoint of material properties for coupling and remote conditions, respectively. In the case of coupling condition, much denser and more uniform pPPy film, which was strongly bonded, was obtained in coupling case. Whereas, in the case of remote condition, the deposited layer showed more rough nanoparticles in powder form measured by FE-SEM, AFM results. On the other hand, the XRD data showed similar properties in terms of crystallinity characteristics, however, FT-IR and XPS analyses showed that the pPPy nanoparticles had a little change of polymer chemical structures for coupling and remote conditions, respectively. The both pPPy materials, which are obtained by coupling and remote condition, are expected to be applicable to various fields, especially polymer light emitting diode (P-LED) as a thin conducting layer or materials used to increase the efficiency by inserting conducting polymer powder on hole injection layer of P-LED.

Funding

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