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# TOF-SIMS study on nano size conducting polymer prepared by simple atmospheric pressure plasma polymerization technique for display applications

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## ABSTRACT



We had previously reported on a surface analysis investigation of newly atmospheric pressure plasma (APP) polymerized conducting polymers films, both plasma-polymerized polyaniline and polypyrrole (pPPy). In this study, time of flight secondary ion mass spectrometry (ToF-SIMS) has been used to characterize nano size conducting polypyrrole films between the conventional and novel APP source under room temperature. Specific negative and positive ions from pPPy were effective in monitoring the change in the pPPy content at the surface of the composites. This ToF-SIMS analysis clearly demonstrates that novel APP polymerization source is effective in increasing the surface polymer content and thus confirms previously published X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR), and gas chromatography-mass spectrometry (GC-MS) data based on some necessary assumptions. To check the suitability of the conductive layer for the display application, the resistance variations of the pPPy grown on the interdigitated electrode substrates are examined by doping with iodine.

## KEYWORDS

Atmospheric pressure plasma; nanoparticle; plasma polymerized pyrrole (pPPy); time of flight secondary ion mass spectrometry (ToF-SIMS)

## 1. Introduction

The conducting polymers (CPs) constitute a new class of polymers with particular interest owing to their physical and chemical properties [1]. CPs have been widely used in the field of display applications. Polypyrrole (PPy), one of the most extensively studied CPs, has been recognized for its long-term conductivity stability and ability in forming homopolymers or composites with optimal mechanical properties with low resistance which approaches the conductivity of metals [1–6]. PPy has also good environmental stability and higher conductivity than many other CPs and is currently considered as a preferential material for this type of applications [1]. It is well known that the CPs in display applications can be obtained by low pressure plasma polymerization method [7]. However, the interactions between the use

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of the atmospheric pressure plasma (APP) polymerization technique and the nano size CPs are not well known.

We have recently reported a new polymer synthesis method using novel atmospheric pressure plasma jets (APPJs) [8–10]. The plasma-polymerized pyrrole (pPPy) thin films were reported to be successfully obtained with high quality and single-crystalline characteristics by improving the sufficient fragmentation and recombination of the pyrrole monomer using a novel APPJs technique [9]. However, previous analysis of pPPy thin films requires further examination for the formation of novel pPPy materials. In previous research, Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS) were used to determine the chemical changes introduced by the plasma. Although the FT-IR and XPS were extremely useful in monitoring the changes in the surface composition of pPPy, it was not possible to distinguish between the nitrogen and carbon species arising from pPPy. Thus, the relation proportion of the surface of the conducting pPPy composite was difficult to determine, and some assumptions were made in this regard [2–4]. Accordingly, this study proposes the analysis of flight secondary ion mass spectrometry (ToF-SIMS) on the surface composition of the conducting composites of pPPy where it can detect specific fragments from the materials under test in either the positive or the negative mode of detection. In addition, the use of SIMS is described as a complementary surface analytical technique to our on-going research plan on CPs composites. ToF-SIMS images would reveal interesting structural features of surface morphology of the pPPy films prepared in this work using advanced APPJs. In particular, we examined the resistance variation of the iodine-doped pPPy grown on the interdigitated electrodes in order to check the suitability of the conducting layer for the display application.

## 2. Experiment

The previous research showed that the newly proposed tube and cylindrical insulating substrate holder were introduced to minimize the quenching from ambient air and increase the plasma energy in the nucleation region [8–10]. In the case of a jet whose insulating substrate holder was placed outside the glass tube (Conventional APPJs method), the streamer like short plasmas were only produced in the nucleation region. On the contrary, the strong and intense plasma plumes were produced broadly and extended farther downstream in the case of a jet whose insulating substrate holder was placed inside the glass tube (Novel APPJs method). The argon gas (99.999%) was used as the plasma discharge gas and its flow rate was 1300 standard cubic centimeters per minute (sccm). Liquid pyrrole monomer (Sigma-Aldrich Co.,  $M_w = 67 \text{ g}\cdot\text{mol}^{-1}$ ) was vaporized by means of a glass bubbler, which was supplied by the argon gas, with a flow rate of 130 sccm. A sinusoidal power was applied to the powered electrode with a peak value of 12 kV with frequency of 30 kHz. Our APP polymerization device employed in this research was described in detail in the reference of [8–10]. ToF-SIMS was performed to investigate the surface composition of the polymer. The ToF-SIMS data were obtained using a ToF-SIMS V instrument (ION-TOF GmbH, Germany) equipped with a reflectron analyzer, a bismuth primary-ion ( $\text{Bi}_3^+$ ) source and a pulsed electron flood source for charge compensation. The pressure in the analysis chamber was maintained at less than  $1 \times 10^{-9}$  Torr.  $\text{Bi}_3^+$  (0.5 pA) accelerated at 25 keV were used as the analysis (primary) gun. Negative-ion and positive-ion mass spectra were acquired from a  $500 \mu\text{m} \times 500 \mu\text{m}$  area using a  $\text{Bi}_3^+$  primary-ion beam operating at 25 keV. The mass resolution was typically greater than 8000 at  $m/z = 29\text{Si}$ . Secondary ions were detected in negative ion mode, and a full spectrum from 1 to 1000 amu was acquired. The pPPy films were doped by placing samples in a sealed container containing solid  $\text{I}_2$  (1 g) for the *ex-situ*  $\text{I}_2$  doping, after deposition.

**Table 1.** Selected peaks, and their assignments observed in negative-ion ToF-SIMS spectra of pPPy grown on glass substrate.

Negative ion mass spectrum	
<i>m/z</i>	Possible ion fragment/possible structure
12	C <sup>-</sup>
13	CH <sup>-</sup>
16	O <sup>-</sup>
17	OH <sup>-</sup>
25	C <sub>2</sub> H <sup>-</sup>
26	CN <sup>-</sup>
42	CNO <sup>-</sup>
50	C <sub>3</sub> N <sup>-</sup>

### 3. Results and discussion

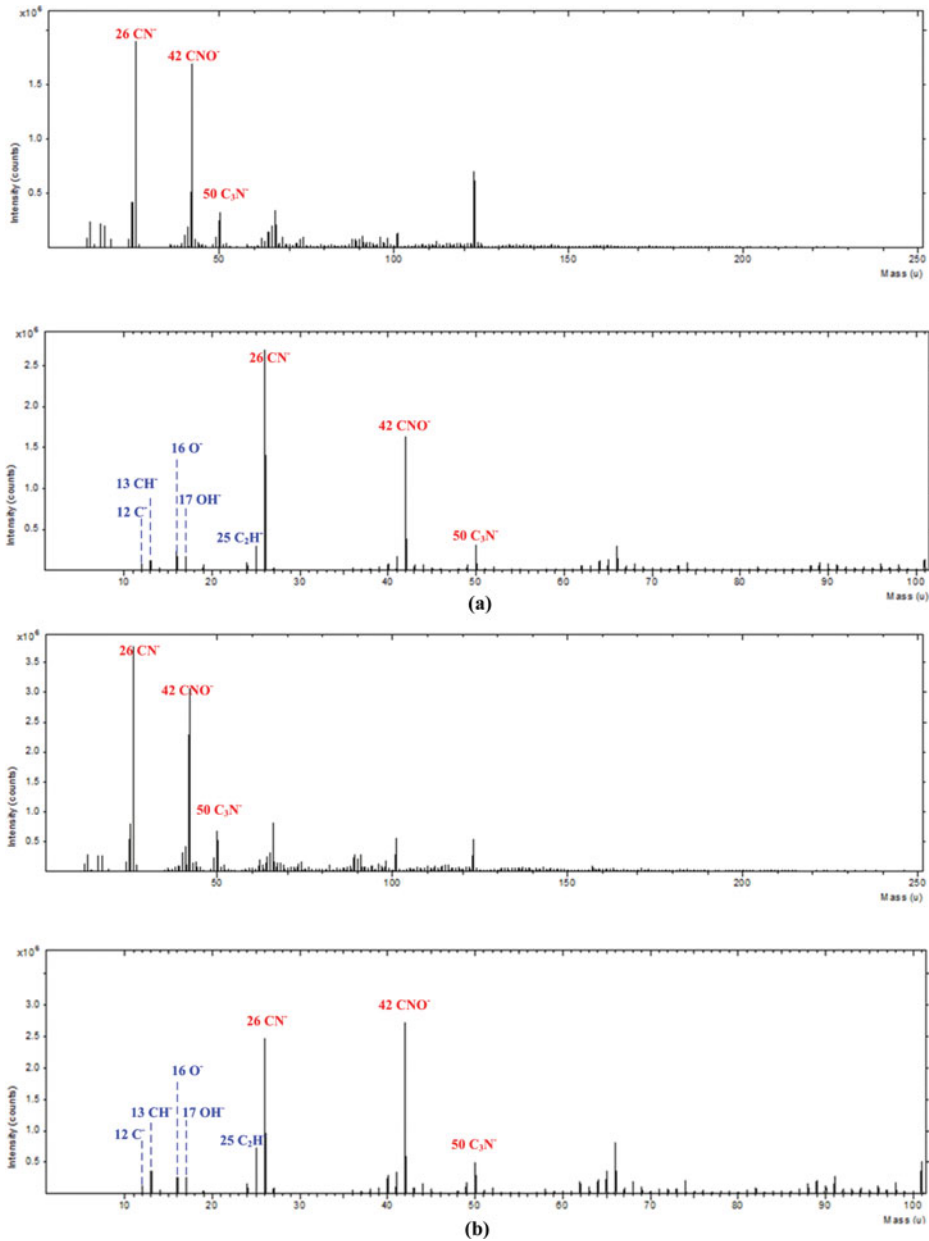
Using ToF-SIMS method, pPPy films were characterized in both positive and negative ion mode in order to determine specific structures due to APP plasma polymerization process. Tables 1 and 2 report the assignment of selected peaks of pPPy grown on glass substrate detected in negative and positive ion mode, respectively.

Figure 1 shows the changes in the negative-ion ToF-SIMS spectra (0–250 amu) and narrow range spectra (0–100 amu) for the pPPy thin films grown on glass substrates when using the conventional APPJs and novel APPJs methods. As shown in Fig. 1(b), when using novel APPJs method, the almost native-ion spectra peaks were observed to be higher than that in the conventional APPJs method. Figure 1 displays two peaks at 16 and 17 amu, corresponding to O<sup>-</sup> and OH<sup>-</sup>, respectively. In addition, major ions of pPPy can be detected at *m/z* 26, 42, and 50 amu and attributed to CN<sup>-</sup>, CNO<sup>-</sup>, and C<sub>3</sub>N<sup>-</sup>, respectively, which were characteristic pPPy fragments. Weak signals were recorded at 24 and 25 amu, probably due to low carbon contamination species. The assignment of selected peaks was shown in Table 1.

Figure 2 shows the changes in the positive-ion ToF-SIMS spectra (0–250 amu) and narrow range spectra (0–100 and 100–200 amu) for the pPPy thin films grown on glass substrates when using the conventional APPJs and novel APPJs methods. As shown in Fig. 2(b), when using novel APPJs method, the almost positive-ion spectra peaks were observed to be higher than that in the conventional APPJs method. In addition to the PPy features, some characteristic peaks from the polymer chain were also detected. Selected peak assignments are listed in Table 2. These show a series of hydrocarbon fragments arising from PPy, such as

**Table 2.** Selected peaks, and their assignments observed in positive-ion ToF-SIMS spectra of pPPy grown on glass substrate.

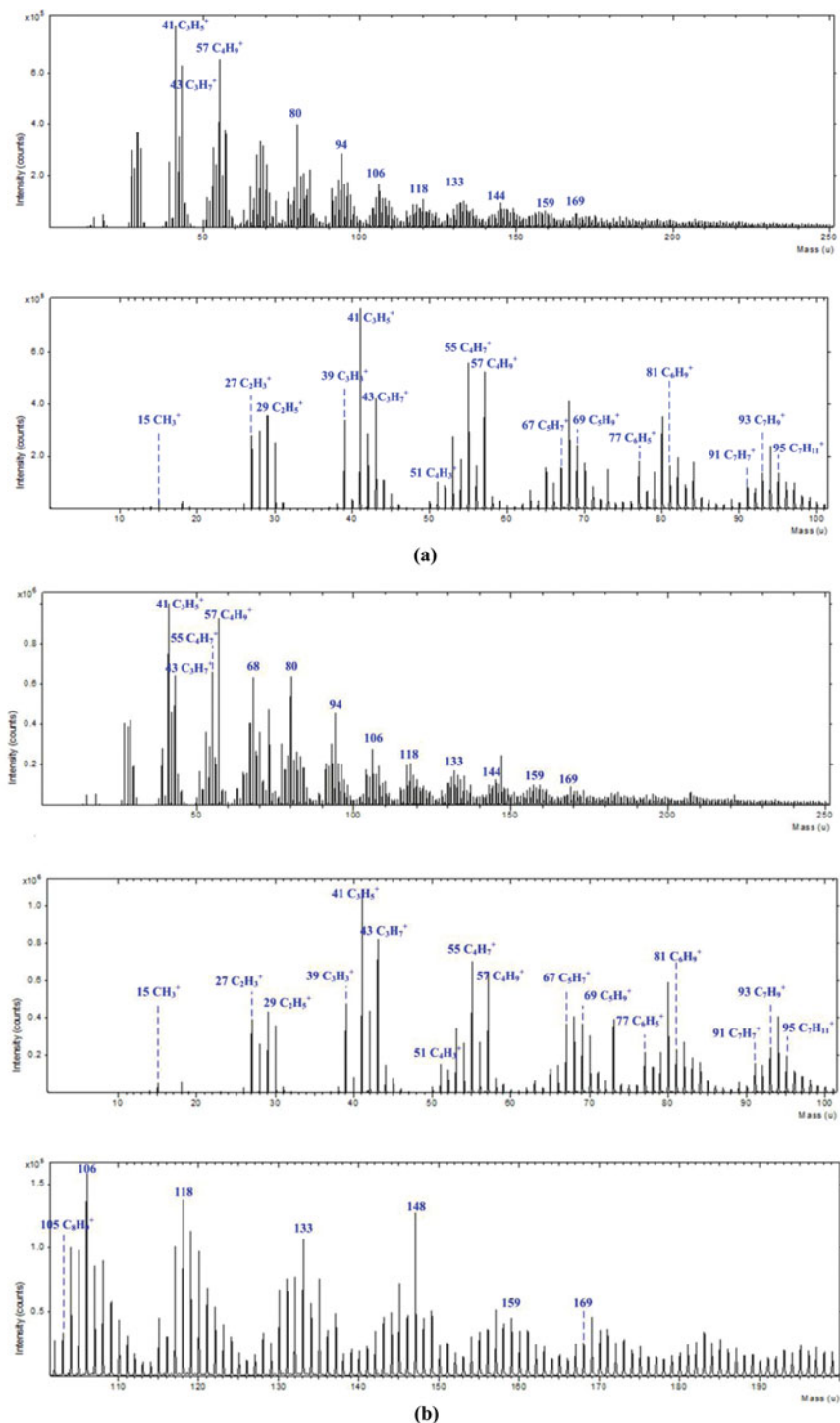
Positive ion mass spectrum	
<i>m/z</i>	Possible ion fragment/possible structure
12	C <sup>+</sup>
15	CH <sub>3</sub> <sup>+</sup>
27	C <sub>2</sub> H <sub>3</sub> <sup>+</sup> /CH <sub>2</sub> -CH <sup>+</sup>
29	C <sub>2</sub> H <sub>5</sub> <sup>+</sup> /CH <sub>3</sub> -CH <sub>2</sub> <sup>+</sup>
39	C <sub>3</sub> H <sub>3</sub> <sup>+</sup> /CH <sub>2</sub> -C-CH <sup>+</sup>
41	C <sub>3</sub> H <sub>5</sub> <sup>+</sup> /CH <sub>2</sub> -CH-CH <sub>2</sub> <sup>+</sup>
43	C <sub>3</sub> H <sub>7</sub> <sup>+</sup> /CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> <sup>+</sup>
55	C <sub>4</sub> H <sub>7</sub> <sup>+</sup> /CH <sub>2</sub> -CH-CH <sub>2</sub> -CH <sub>2</sub> <sup>+</sup>
57	C <sub>4</sub> H <sub>9</sub> <sup>+</sup> or C <sub>3</sub> H <sub>7</sub> N <sup>+</sup>
67	C <sub>5</sub> H <sub>7</sub> <sup>+</sup>
69	C <sub>5</sub> H <sub>9</sub> <sup>+</sup>
91	C <sub>7</sub> H <sub>7</sub> <sup>+</sup>
93	C <sub>7</sub> H <sub>9</sub> <sup>+</sup>



**Figure 1.** Negative-ion ToF-SIMS spectra (0–250 amu) and narrow range spectra (0–100 amu) of pPPy film grown on a glass substrate when using (a) conventional APPJs and (b) novel APPJs methods.

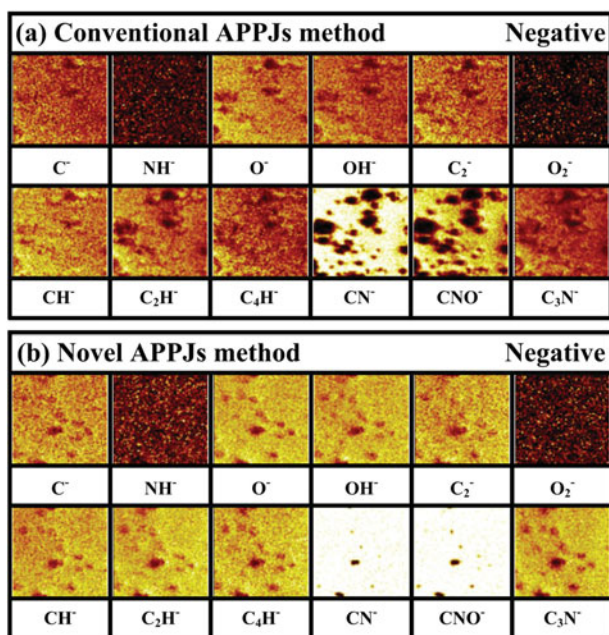
$C_2H_5^+$ ,  $C_3H_5^+$ ,  $C_3H_7^+$ , and  $C_4H_7^+$ . These clusters of peaks at 39, 41, 43, 53, 55, 57, 69, and 71 amu are typical aliphatic hydrocarbon fragments of the form  $C_nH_{2n-3}$ ,  $C_nH_{2n-1}$ , and  $C_nH_{2n+1}$ , arising from the PPy chain. It is to note that they are more intense than those arising from the conventional APPJs method.

Figure 3 shows the changes in the ToF-SIMS negative-ion maps showing distributions of  $C^-$ ,  $NH^-$ ,  $O^-$ ,  $OH^-$ ,  $C_2^-$ ,  $O_2^-$ ,  $CH^-$ ,  $C_2H^-$ ,  $C_4H^-$ ,  $CN^-$ ,  $CNO^-$ , and  $C_3N^-$  on the surface of the pPPy thin films when using the conventional APPJs and novel APPJs methods. The brightest and lightest color intensity correspond to the highest surface concentration of ions on the surface. As shown in Fig. 3(b), when using novel APPJs method, the all negative-ion

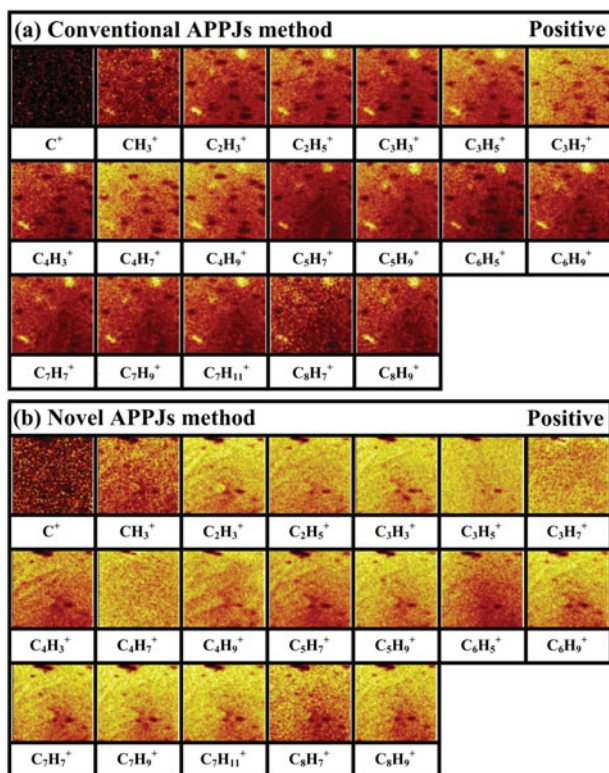


**Figure 2.** Positive-ion ToF-SIMS spectra (0–250 amu) and narrow range spectra (0–100 and 100–200 amu) of pPPy film grown on a glass substrate when using (a) conventional APPJs and (b) novel APPJs methods.





**Figure 3.** ToF-SIMS negative-ion maps showing distribution of C<sup>-</sup>, NH<sup>-</sup>, O<sup>-</sup>, OH<sup>-</sup>, C<sub>2</sub><sup>-</sup>, O<sub>2</sub><sup>-</sup>, CH<sup>-</sup>, C<sub>2</sub>H<sup>-</sup>, C<sub>4</sub>H<sup>-</sup>, CN<sup>-</sup>, CNO<sup>-</sup>, and C<sub>3</sub>N<sup>-</sup> on the surface of pPPy film when using (a) conventional APPJs and (b) novel APPJs methods.

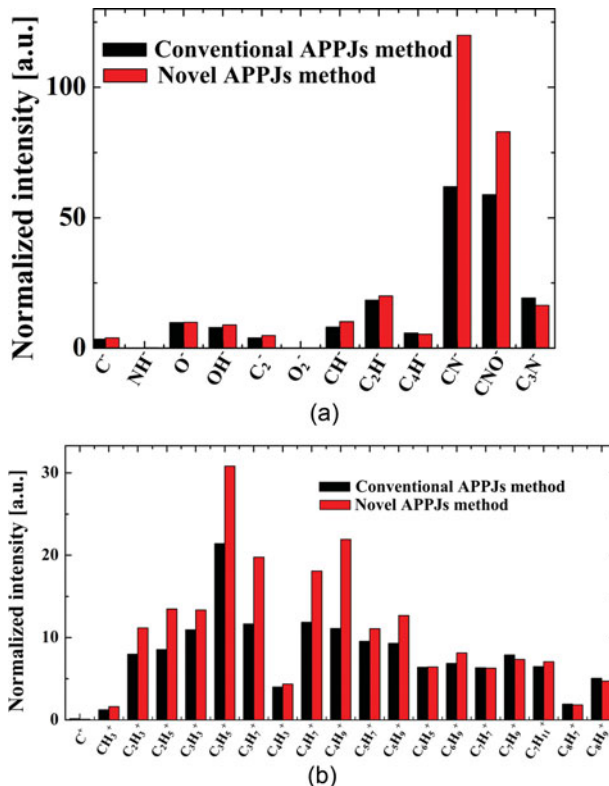


**Figure 4.** ToF-SIMS positive-ion maps showing distribution of C<sup>+</sup>, CH<sub>3</sub><sup>+</sup>, C<sub>2</sub>H<sub>3</sub><sup>+</sup>, C<sub>2</sub>H<sub>5</sub><sup>+</sup>, C<sub>3</sub>H<sub>3</sub><sup>+</sup>, C<sub>3</sub>H<sub>5</sub><sup>+</sup>, C<sub>3</sub>H<sub>7</sub><sup>+</sup>, C<sub>4</sub>H<sub>3</sub><sup>+</sup>, C<sub>4</sub>H<sub>7</sub><sup>+</sup>, C<sub>4</sub>H<sub>9</sub><sup>+</sup>, C<sub>5</sub>H<sub>7</sub><sup>+</sup>, C<sub>5</sub>H<sub>9</sub><sup>+</sup>, C<sub>6</sub>H<sub>5</sub><sup>+</sup>, C<sub>6</sub>H<sub>9</sub><sup>+</sup>, C<sub>7</sub>H<sub>7</sub><sup>+</sup>, C<sub>7</sub>H<sub>9</sub><sup>+</sup>, C<sub>7</sub>H<sub>11</sub><sup>+</sup>, C<sub>8</sub>H<sub>7</sub><sup>+</sup>, and C<sub>8</sub>H<sub>9</sub><sup>+</sup> on the surface of pPPy film when using (a) conventional APPJs and (b) novel APPJs methods.

maps were observed to be brighter than that in the conventional APPJs method, which means that a considerable amount of  $C^-$ ,  $NH^-$ ,  $O^-$ ,  $OH^-$ ,  $C_2^-$ ,  $O_2^-$ ,  $CH^-$ ,  $C_2H^-$ ,  $C_4H^-$ ,  $CN^-$ ,  $CNO^-$ , and  $C_3N^-$  particles were fragmented and formed on the substrates. Therefore, the results in Fig. 3(b) confirmed that the fragmentation and formation of the polymer on the substrates were effectively produced when using novel APPJs method.

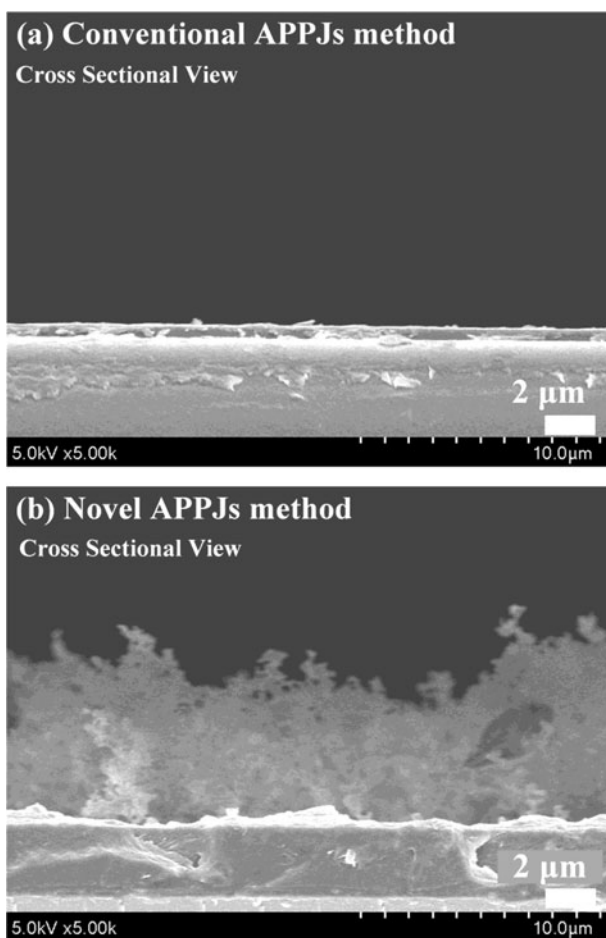
Figure 4 shows the changes in the ToF-SIMS positive-ion maps showing distributions of  $C^+$ ,  $CH_3^+$ ,  $C_2H_3^+$ ,  $C_2H_5^+$ ,  $C_3H_3^+$ ,  $C_3H_5^+$ ,  $C_3H_7^+$ ,  $C_4H_3^+$ ,  $C_4H_7^+$ ,  $C_4H_9^+$ ,  $C_5H_7^+$ ,  $C_5H_9^+$ ,  $C_6H_5^+$ ,  $C_6H_9^+$ ,  $C_7H_7^+$ ,  $C_7H_9^+$ ,  $C_7H_{11}^+$ ,  $C_8H_7^+$ , and  $C_8H_9^+$  on the surface of the pPPy thin films when using the conventional APPJs and novel APPJs methods. As shown in Fig. 4(b), when using novel APPJs method, the all negative-ion maps were observed to be brighter than that in the conventional APPJs method, which means that a considerable amount of  $C^+$ ,  $CH_3^+$ ,  $C_2H_3^+$ ,  $C_2H_5^+$ ,  $C_3H_3^+$ ,  $C_3H_5^+$ ,  $C_3H_7^+$ ,  $C_4H_3^+$ ,  $C_4H_7^+$ ,  $C_4H_9^+$ ,  $C_5H_7^+$ ,  $C_5H_9^+$ ,  $C_6H_5^+$ ,  $C_6H_9^+$ ,  $C_7H_7^+$ ,  $C_7H_9^+$ ,  $C_7H_{11}^+$ ,  $C_8H_7^+$ , and  $C_8H_9^+$  particles were fragmented and formed on the substrates. Therefore, the results in Fig. 3(b) confirmed that the hydrocarbon fragments of the polymer chain on the substrates were effectively produced when using novel APPJs method.

Figure 5 shows the changes in the normalized intensities of negative-ion and positive-ion ToF-SIMS on the surface of the pPPy thin films when using the conventional APPJs and novel APPJs methods. As shown in Fig. 5, when using novel APPJs method, the almost negative-ion and positive-ion polymer contents were observed to be increased than that in the conventional APPJs method. This ToF-SIMS analysis clearly demonstrated that novel APP polymerization method is effective in increasing the surface polymer content. These results suggest that there



**Figure 5.** Normalized intensities of (a) negative-ion ToF-SIMS and (b) positive-ion ToF-SIMS on the surface of pPPy film when using conventional APPJs and novel APPJs methods.



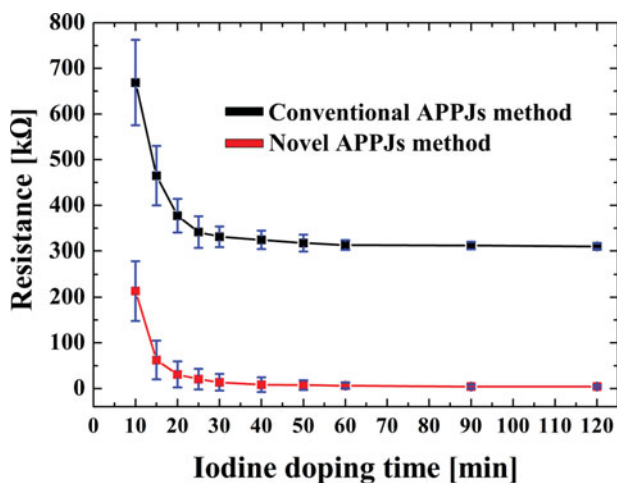


**Figure 6.** Changes in cross-sectional views of SEM images of pPPy film grown on a glass substrate when using (a) conventional APPJs and (b) novel APPJs methods.

are C, N, H, and O atoms in the pPPy thin films; the C, N, and H atoms belong to the pyrrole structure, but the O atom could have originated in the oxidation of the pPPy from the ambient air. This result is in good agreement with previously reported XPS, FT-IR, and gas chromatography-mass spectrometry (GC-MS) analysis of such material [8, 9].

Figure 6 shows the cross-sectional view of the field emission-scanning electron microscopy (FE-SEM) images of the pPPy thin films, grown for 40 min, on glass substrates when using the conventional APPJs and novel APPJs methods. As shown in Fig. 6, no nanoparticles with nanofibers were observed when using conventional APPJs method. Whereas, when using novel APPJs method, many nanoparticles and nanofibers were observed to be linked together in many irregular cross-linked networks. These results are also in good agreement with previously reported SEM and transmission electron microscopy (TEM) analysis [8–10].

Figure 7 shows the changes in the resistance ( $R$ ) of the pPPy thin film on the substrates of interdigitated electrodes under various iodine exposure (doping) times when using the conventional APPJs and novel APPJs methods. The doping with iodine had the objective to introduce charge carriers into the pPPy structures for enhancing its electrical conductive characteristics. The resistance of the pPPy thin film was over the measurement limit of  $2.0 \times 10^7 \Omega$  without iodine doping. As the doping time was increased, when using conventional



**Figure 7.** Changes in resistance of pPPy thin films on substrate of interdigitated electrodes under various iodine exposure (doping) times when using conventional APPJs and novel APPJs methods.

APPJs method, the corresponding resistance decreased sharply, during very short period, that was, 25 min and was also saturated to be about  $3.2 \times 10^5 \Omega$  after 60 min. However, as the doping time was increased, when using novel APPJs method, the corresponding resistance decreased more sharply and also saturated to be about  $4.5 \times 10^3 \Omega$  after 60 min. A detailed parametric study will be carried out to measure electric conductivity characteristics of the plasma polymer for display application with this method in the near future.

#### 4. Conclusions

ToF-SIMS analyses were effective in monitoring the change in surface composition of pPPy film when using the novel APPJs polymerization method. It is clearly demonstrated that novel APP polymerization method is effective in increasing the surface polymer content. In addition, the hydrocarbon fragments of the polymer chain on the substrates were effectively produced when using novel APPJs method. The resistance of the pPPy thin films were about  $4.5 \times 10^3 \Omega$ . Moreover, the resistance of the pPPy thin film prepared using novel APPJs method can be easily controlled by simply doping the iodine under various doping times for the application of future display. Furthermore, we also expect that the new pPPy film grown under low temperature ( $30^\circ\text{C}$ ) process can provide a versatile advantage for gas sensors, molecular electronics, optoelectronics, and bio-nanotechnology.

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#### References

- [1] Nguyen, D. N., & Yoon, H. (2016). *Polymers*, 8, 118.
- [2] Perruchot, C., Chehimi, M. M., Delamar, M., Eccles, J. A., Steele, T. A., & Mair, C. D. (2000). *Synthetic Metals*, 113, 53.
- [3] Teo, L.-L., Sin, S.-L., & Chan, C.-Y. (2010). *Journal of Nanomaterials*, 2010, 385617.

- [4] Prissanaroon-Ouajai, W., Pigram, P. J., Jones, R., & Sirivat, A. (2008). *Sensors and Actuators B*, 135, 366.
- [5] Lisboa, P., Gilliland, D., Ceccone, G., Valsesia, A., & Rossi, F. (2006). *Applied Surface Science*, 252, 4397.
- [6] Prissanaroon, W., Brack, N., Pigram, P. J., & Liesegang, J. (2004). *Current Applied Physics*, 4, 163.
- [7] Ameen, S., Song, M., Kim, D.-G., Im, Y.-B., Seo, H.-K., Kim, Y. S., & Shin, H.-S. (2012). *Macromolecular Research*, 20, 30.
- [8] Park, C.-S., Kim, D. H., Shin, B. J., & Tae, H.-S. (2016). *Materials*, 9, 39.
- [9] Park, C.-S., Kim, D. H., Shin, B. J., Kim, D. Y., Lee, H.-K., & Tae, H.-S. (2016). *Materials*, 9, 812.
- [10] Kim, D. H., Park, C.-S., Kim, W. H., Shin, B. J., Hong, J. G., Park, T. S., Seo, J. H., & Tae, H.-S. (2017). *Phys. Plasmas*, 24, 023506.