Polypyrrole Film Synthesis using In-liquid Plasma Assisted-Electrochemical Deposition

H.J. Jang[1], E.Y. Jung[2], J.Y. Kim[1] and H.-S. Tae[1,3]

[1] *School of Electronic and Electrical Engineering, College of IT Engineering, Kyungpook National University, Daegu, South Korea*
[2] *The Institute of Electronic Technology, College of IT Engineering, Kyungpook National University, Daegu, South Korea*
[3]*School of Electronics Engineering, College of IT Engineering, Kyungpook National University, Daegu, South Korea*

Abstract: This study carries out polypyrrole film synthesis using solution plasma assisted-electrochemical deposition in liquid monomer. Additionally, the influence of DC bias voltage, which is one of the key parameter in film formation, is investigated. Polypyrrole films are successfully formed only when a DC bias is applied to the substrate electrode, and the film properties are highly depent on the magnitude of DC bias. Using the proposed polymerization process, polypyrrole film can be selectively deposited on the micro-pattern electrode.

Keywords: Polypyrrole, electrochemical deposition, solution plasma, selective coating.

1. Introduction

Recently, the study on depositing the polypyrrole (PPy) film on a copper surface immersed in liquid pyrrole has been reported in our research group [1]. PPy could be deposited on the copper surface in a single process by generating a plasma in pure liquid pyrrole. This process can be considered plasma assisted-electrochemical deposition, because the ionic precursors are created with the assistance of plasma, and the PPy film is formed on the anode electrode by electron exchange processes. In this study, we investigate the effect of DC bias as a potentiostatic method in the synthesis of PPy film using plasma assisted-electrochemical deposition. The solution plasma (SP) reactor are newly designed with three electrode configuration to independently control AC power and DC bias during the SP generation. Moreover, using the property of being deposited only on the metal surface that can have electrical potential, the selective coating of the PPy film can be demonstrated using micro-scale interdigitated electrodes.

2. Methods

Figure 1 shows a schematic diagram and photographic images of the proposed SP reactor with three electrodes used in this study. The SP reactor consisted of a L-shaped glass container, a quartz capillary for argon gas path, and three electrodes. The three electrodes consists of one pin-type electrode and two surface-type electrodes. A pin-type electrode is made of a tungsten wire (❶), and the SP is generated at the tip of the wire by applying a bipolar pulse with a voltage of 4 kVpp and a frequency of 5 kHz. One of the surface-type electrode is a copper tape (❷) as a counter electrode facing the pin-type electrode, which is attached on the outer wall of the reactor to generate a stable dielectric barrier discharge. Another surface-type electrode is a copper substrate (❸) for film formation, to which a DC bias voltages of 0, 0.5, 1, 1.5 kV (named Case I, Case II, Case III, and Case IV, respectively) are applied. The SP was generated at the tip of the powered electrode and propagated into the solution as shown in the image of side view in Fig. 1.

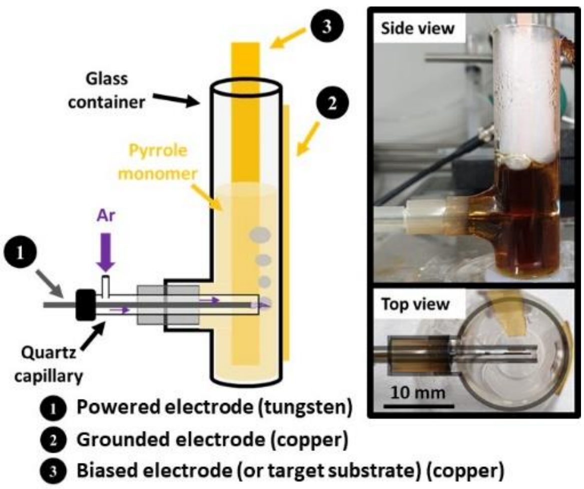

Fig. 1. Schematic diagram and photographs of the proposed solution plasma reactor.

3. Results and Discussion

Basically, positive streamer discharges are easily generated compared to negative streamer discharges due to the difference in generation mechanism [2]. Likewise, the proposed SP reactor follows this discharge aspect in Case I. However, when a DC voltage was applied to the biased electrode, the potential difference between the powered electrode and biased electrode varies depending on the polarity of bipolar pulse. As a result, suppression of positive streamers and enhancement of negative streamers occur under the conditions in which a DC bias was applied to the biased electrode.

The pH values of the SP-processed pyrrole solution under different DC bias conditions were measured for 60 min. In Case I, the pH of the SP-processed pyrrole solution hardly changed as the pH below 8. However, the pH values of the pyrrole solutions processed under the conditions of Cases II, III, and IV, were in the middle of 9. This result means that the SP having the enhanced negative streamer by DC bias conditions (Cases II, III, and IV) actively generated pyrrole anions which were strong basic [3].

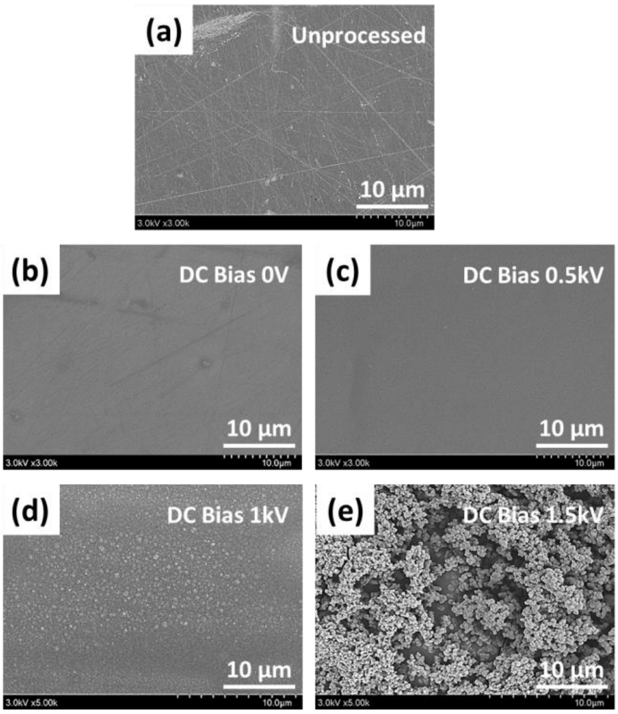

Fig. 2. FE-SEM images of biased electrodes after SP-processing for 60 min depending on DC bias conditions: (a) for an unprocessed, processed with DC (b) 0 V, (c) 0.5 kV, (d) 1 kV, and (e) 1.5 kV

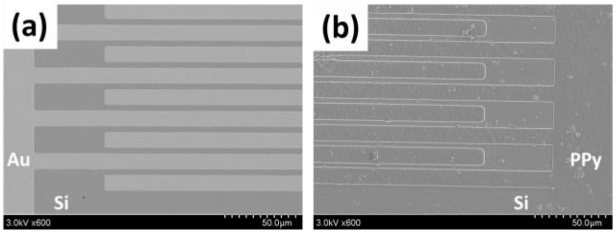

Fig. 3. FE-SEM images of (a) pristine IDE substrate and (b) IDE substrate after SP-process using DC 0.5 kV condition.

Under only these in-liquid discharge conditions, PPy films were formed on the biased electrode. PPy films on the biased electrode were observed using FE-SEM as shown in Fig. 2. As shown in Fig. 2(a), several scratches were observed on the surface of unprocessed biased electrode. The copper electrode processed in Case I had less scratches and a smoother surface (Fig. 2(b)). The surface morphology of the resulting film in Case II was smooth and flat (Fig. 2(c)). It was observed that the film produced in Case III had a bumpy surface composed of PPy grains (Fig. 2(d)). In Case IV, where the strongest DC bias was applied, nanoparticles/nanofibers were excessively deposited on the smooth film surface, resulting in cracks in some places (FIG. 2(e)). These morphological differences of resulting films affected the surface gloss properties depending on DC voltage condition. The resulting film with a smooth and flat surface could be obtained when using the proper DC bias (here 0.5 kV).

Using the material-selective property of this synthetic process, we demonstrated the selective deposition of PPy films onto interdigitated electrode (IDE) patterns. As shown in Fig. 3(a), the width of the IDE used in this study is 10 μm, and adjacent IDEs are separated by 4 μm from each other. A PPy film was coated on the IDE during SP polymerization, which appeared black in the FE-SEM images. As shown in Fig. 3(b), it was observed that the PPy film was coated along the IDE pattern. The PPy film coated on the IDE was observed to be 12.75 μm, covering about 1 μm more at each edge of the IDE width. Therefore, this process enables selective coating of PPy with a resolution of several micronmeters.

4. Conclusion

In summary, the SP reactor with three electrodes ignited the streamer discharge in liquid pyrrole by introducing high voltage AC power. The characteristics of the SP were controlled by applying the DC bias voltage via the biased electrode immersed in the solution. As the DC bias voltage increases, negative streamers were enhanced and positive streamers were suppressed. In this case, the pH value of the solution was increased after SP processing. At the same time, the film was deposited on the biased electrode with the anodic potential, and it was confirmed that the film was made of PPy. In addition, selective deposition on micro-sized-patterned electrodes could be obtained under the condition where the PPy film was the flattest among the studied cases (Case II). This process is an eco-friendly method that uses only a single monomer material and electricity, and is also an innovative method that enables micro-sized deposition to large area deposition for industrial field in a single step without complicated preparation process.

5. References

[1] H. J. Jang, B. J. Shin, E. Y. Jung, G. T. Bae, J. Y. Kim, and H.-S. Tae, Appl. Surf. Sci., **608,** 155129 (2023).

[2] A. Sun, C. Huo, and J. Zhuang, High Volt., **1(**2), 74-80 (2016).

[3] A.R. Katritzky, A.F. Pozharskii, “Reactivity of heterocycles” in *Handbook of Heterocyclic Chemistry*, 2nd. MA, USA: Academic Press, pp. 377–379 (2000).