

Copper Electrodeposition on Polyimide Substrate Using Polyaniline Film as a Seed Layer for Metallization of Flexible Devices

Dohyeun Lee¹, Taeho Lim², Hana Lim³, Hyun-Jong Kim^{3,} and Oh Joong Kwon^{1,*}*

¹ Department of Energy and Chemical Engineering, Innovation Center for Chemical Engineering, Incheon National University, 119 Academy-ro, Yeonsu-gu, Incheon 22012, Republic of Korea

² Department of Chemical Engineering, Soongsil University, 369 Sangdo-ro, Dongjak-gu, Seoul 06978, Republic of Korea

³ Surface Technology Center, Korea Institute of Industrial Technology (KITECH), 156 Gaetbeol-ro, Yeonsu-gu, Incheon 21999, Republic of Korea

*E-mail: hjkim23@kitech.re.kr, ojkwon@inu.ac.kr

Received: 19 August 2018 / Accepted: 16 September 2018 / Published: 5 November 2018

The Metallization of flexible printed circuit boards is a key issue for the fabrication of flexible devices. In this study, Cu electrodeposition was performed on a flexible polyimide substrate using polyaniline film as a seed layer for the first time. A conductive polyaniline film was formed on the surface of the polyimide substrate by dip and spin coating methods. It was revealed that the spin coating method was advantageous in forming a uniform and continuous polyaniline film because it reduces the secondary nucleation of polyaniline by removing excess reactants from the polyimide substrate. Pd nanoparticles were also introduced onto the polyaniline-deposited substrate to promote Cu nucleation during the Cu electrodeposition process. With the aid of polyaniline film and Pd nanoparticles, a continuous and uniform Cu film was successfully deposited on a polyimide substrate.

Keywords: Flexible printed circuit board, electrodeposition, polyaniline, palladium, seed layer, copper

1. INTRODUCTION

Flexible printed circuit boards (FPCBs) have attracted much attention in the electronics industry, keeping pace with the proliferation of the level of demand for flexible devices in the market. The flexibility of FPCBs is the most attractive property that enables the fabrication of wearable, rollable, and curved devices. They are also advantageous for weight reductions and for minimizing

electronic devices due to their light weight and good stackability in various configurations. FPCBs have the potential to replace conventional rigid printed circuit boards [1, 2].

Polyimide is a typical material for FPCBs due to its excellent flexibility and insulating characteristics [3]. It also has high thermal/chemical resistances and good tolerance to moisture. The metallization of FPCBs is typically accomplished through Cu electro- and electroless deposition processes [4, 5]. Cu electroless deposition refers to a process by which Cu ions in a solution are reduced on a surface by the oxidation of a reducing agent. Therefore, this process is widely used for the formation of conductive pathways (seed layers) for Cu electrodeposition on insulators. However, there are several issues related to the use of Cu electroless deposition. As the deposition solution for Cu electroless deposition contains both Cu ions and a reducing agent, there is always a possibility of solution decomposition caused by a homogeneous reaction between Cu ions and the reducing agent, even when the solution is thoroughly controlled [6, 7]. This difficulty in the area of solution maintenance may affect reproducibility during the manufacturing process. There is also an environmental issue due to the toxic reagents used in the Cu electroless deposition process. Formaldehyde, a representative reducing agent used in the Cu electroless deposition, is known to be toxic [8]. For this reason, many researchers have devoted much effort to the development of environmentally friendly reducing agents as alternatives to formaldehyde. Examples include glyoxylic acid and hypophosphite salt [9, 10]. However, the quality of the Cu films deposited with these reducing agents is not feasible as a seed layer for Cu electrodeposition.

These issues are avoidable if Cu electrodeposition is directly performed on a polyimide surface using other seed layers, with the exception of a Cu seed layer formed by electroless deposition. We undertook Cu electrodeposition on polyimide by introducing polyaniline as a conducting layer. Polyaniline is a conductive polymer that has relatively high conductivity [11]. This conducting polymer is widely used in various fields, including lithium ion batteries, gas sensors, and solar cells, owing to its excellent thermal/chemical resistances and its good eco-compatibility [12-14]. Polyaniline can be synthesized via two routes: chemical and electrochemical polymerization [13, 15-17]. In chemical polymerization, aniline monomers are polymerized in an acidic environment by an oxidizer, such as ammonium persulfate and hydrogen peroxide. Polyaniline can also be electrochemically synthesized by applying an oxidative electrical potential. The physical/chemical properties of polyaniline strongly depend on its oxidation state, and there are three idealized oxidation states of polyaniline, leucoemeraldine, emeraldine, and pernigraniline [18, 19]. It has been reported that the polyaniline structure composed of oxidized and reduced aniline monomer at the same ratio is the most useful form due to its high stability at room temperature [21, 22]. This is referred to as the emeraldine base form. The emeraldine base form of polyaniline shows high conductivity upon doping with an acid (protonation); the protonated emeraldine base is referred to an emeraldine salt [16, 20]. We adopted the emeraldine salt form of polyaniline as a new seed layer for Cu electrodeposition, removing the Cu electroless deposition step from the metallization process of FPCBs. Although polyaniline is electroconductive, its conductivity is not strong enough to facilitate Cu nucleation on polyimide. Thus, Pd catalysts were also introduced onto the polyaniline film to facilitate the nucleation process at the initial state of Cu electrodeposition and to improve the film adhesion because Pd catalysts can serve as nucleation centers for Cu electrodeposition when a substrate is highly resistive [23]. To the best of our

knowledge, this is the first trial to use a conductive polyaniline film as a seed layer for Cu electrodeposition on a polyimide substrate.

2. EXPERIMENTAL

2.1. Polyaniline coating on polyimide substrate

Two solutions were prepared for the polyaniline coating: one (monomer solution) is the aqueous solution containing 0.2 M aniline hydrochloride (99%, Alfa Aesar) and 0.1 M hydrochloric acid (HCl; Samchum chemicals), while the other (initiator solution) was composed of 0.25 M ammonium persulfate (APS; Sigma-Aldrich) and 0.1 M HCl. The two solutions were mixed right before the polyaniline coating because the mixing initiates the polymerization of aniline. The degree of the polymerization was observed by measuring the mixture temperature using a thermocouple (JX-G, HAEDONG). The coating was performed by two methods, dip coating and spin coating. In dip coating, a polyimide substrate (1.5 cm × 1.5 cm, Isoflex) was simply immersed in the freshly-mixed solution for a certain period of time. Meanwhile, the mixed solution was coated on a polyimide substrate by spin coater (Spin-1200D, MIDAS) in the spin coating method. The solution volume used in the spin coating was 0.6 ml. After the coating process, the polyimide substrate was rinsed with 0.2 M HCl and acetone. The rinsed polyimide substrate was then immersed in 0.2 M aniline hydrochloride for 30 min to terminate the polymerization process and rinsed again with acetone to remove residual chemicals. Brittle cover glasses (Marienfeld) were also used as substrates for the thickness measurement of deposited polyaniline films. Before the coating process, all substrates were rinsed with 0.1 M potassium hydroxide (Daejung Chemicals & Metals) for 30 min to remove any impurities on the surface.

2.2. Formation of Pd nucleation centers on the polyaniline-coated substrate

Pd nanoparticles were synthesized and deposited on a polyaniline-coated substrate to promote the nucleation process in Cu electrodeposition. For the synthesis of Pd nanoparticles, oleylamine was used as a stabilizing agent. A PdCl_2 solution was prepared by mixing 4 mM PdCl_2 and 36 mM oleylamine in 25 ml of diglyme. Subsequently, 25 ml of diglyme solution containing 12 mM NaBH_4 was added dropwise to the PdCl_2 solution. The combined solution was stirred overnight. The synthesized Pd nanoparticles were then separated by centrifugation at 10,000 rpm for 15 min after the addition of ethanol. The precipitates were re-dispersed in n-hexane and separated by the centrifugation again with the ethanol addition. The second precipitates were mixed with cyclohexane and then freeze-dried by liquid nitrogen. The separated Pd nanoparticles were finally dispersed in toluene (Pd ink). The Pd ink was sprayed on a polyaniline-coated substrate to form Pd nucleation centers. The Pd loading was $1 \text{ mg}_{\text{Pd}}/\text{cm}^2$. The substrate was then annealed at 190°C for 7 hours in a N_2 atmosphere to remove residual oleylamine which was used as dispersing agent.

2.3. Cu electrodeposition

The Cu electrodeposition was performed on the polyaniline-coated substrate after the Pd nanoparticle deposition using a lab-made polytetrafluoroethylene holder. The exposed area of the working electrode (polyaniline-coated substrate) was 1 cm^2 . The counter and reference electrodes were a Cu rod and Ag/AgCl (3.8 M KCl), respectively. The deposition electrolyte was consisted of 0.25 M $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 1.0 M H_2SO_4 . The deposition potential was -1.0 V vs. Ag/AgCl and the total deposition charge was 3 C/cm^2 . All electrochemical experiment was performed at room temperature using a potentiostat (VersaSTAT 3, Princeton Applied Research).

2.4. Material characterization

The sheet resistances of the films were measured using a 4-point probe (CMT-2000N, AIT). The surface and cross-sectional morphologies of the films were observed by optical microscope (OM; BX1, Olympus) and field-emission scanning electron microscope (FE-SEM; JSM-7800, JEOL).

3. RESULTS AND DISCUSSION

The oxidative polymerization of aniline is an exothermic process, increasing the reaction medium temperature. Therefore, the temperature change of the reaction medium is an indicator of the intensity of oxidation [24, 25]. Fig. 1 shows the temperature changes of mixture of the monomer and initiator solutions according to the reaction time. A reaction time of zero indicates the time when the two solutions were mixed. The initial solution temperature was 20°C, and it was maintained for almost 3 min. During this period (induction period), the intermediates of aniline oxidative polymerization slowly began to form in the reaction mixture.

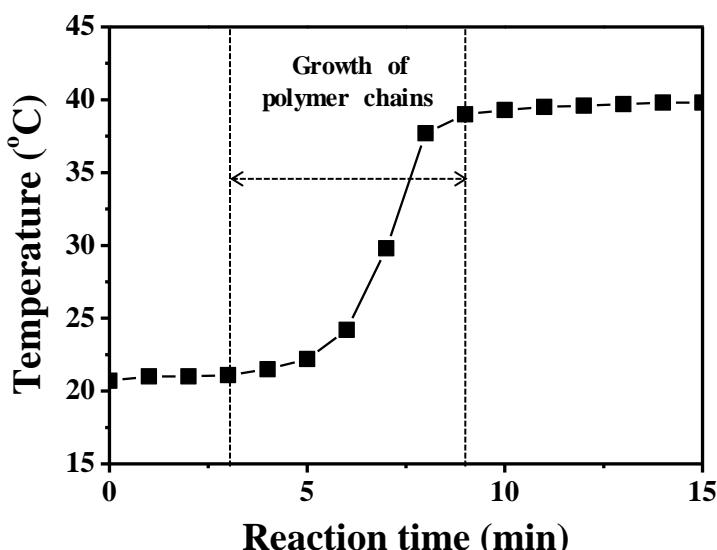


Figure 1. Temperature change of the reaction mixture with reaction time.

During this process, the colorless mixture turned blue, which is an indicator showing that the homogeneous polymerization became heterogeneous. The rapid oxidative polymerization of aniline began with the dramatic increase in temperature due to the auto-acceleration of aniline oxidation by the produced polyaniline [24]. In this stage, the growth of polyaniline chains mainly occurs, forming high-molecular-weight polyanilines. The color of the reaction mixture turned dark blue gradually, and dark green polyaniline precipitates were formed. As the aniline monomer in the solution was consumed in the reaction mixture, the rate of temperature increase of the mixture slowed down in the later stage. During this period, the polymerization process was nearly terminated.

Polyaniline coating was then conducted with the reaction mixture considering the reaction mechanism, as noted earlier. Polyaniline coating generally involves the adsorption of intermediates (and/or aniline oligomers) on a substrate surface (primary nucleation) and subsequent polyaniline chain growth during the induction and chain growth periods, respectively (Fig. 1) [25, 26]. During the induction period, small clusters of intermediates are formed simultaneously in the solution and on the substrate surface, acting as nuclei for the polymerization of aniline. Polyaniline chain growth then takes place around these nuclei. In the later stage, aggregates of polyaniline granules formed in solution phase also adsorb on the substrate surface, participating in the formation of polyaniline film (secondary nucleation). Figs. 2a and b show surface OM images of the polyaniline-coated polyimide substrates prepared by the dip- and spin-coating processes, respectively. When using the dip coating, the color of the surface changed from yellow, which is the color of the polyimide substrate, to green as the dipping time (reaction time) was increased. The green color is a typical characteristic of the emeraldine salt form of polyaniline, indicating that the polyaniline was uniformly coated over the surface [19]. Polyaniline also covered the surface of the polyimide substrate uniformly when using the spin coating, turning the yellow polyimide substrate to brown. The green color was not observed in this case because the thickness of the polyaniline film deposited by spin coating was thinner than that by dip coating.

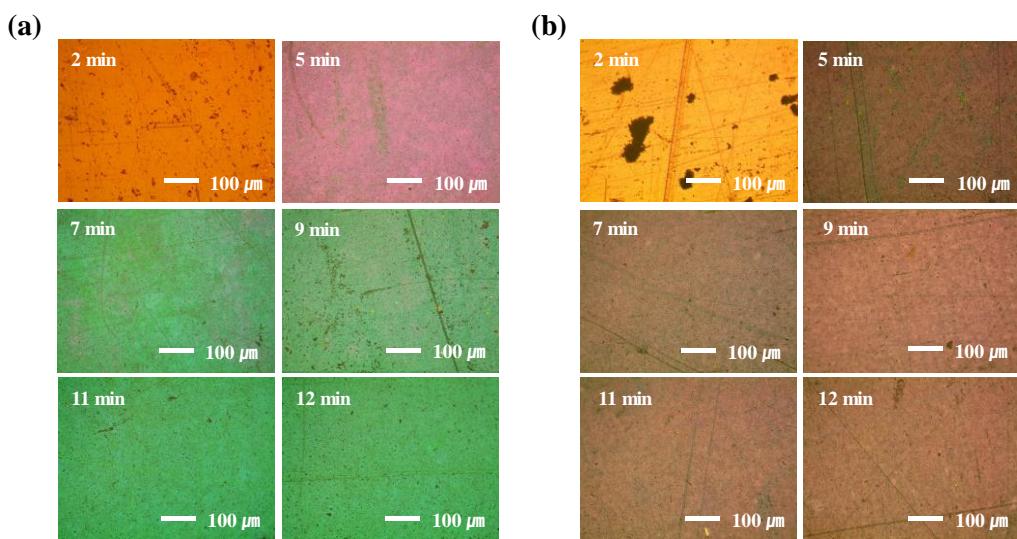


Figure 2. Surface OM images of polyimide substrates after polyaniline coating with reaction time, (a) dip coating and (b) spin coating.

The thickness of the polyaniline film was measured on a glass substrate using cross-sectional FE-SEM images. Fig. 3 shows the thickness of the polyaniline films according to the reaction time. The thickness was increased with the reaction time regardless of the coating method. Using the dip coating, a polyaniline film approximately 600 nm thick could be obtained, but its surface uniformity was poor due to the deposition of aggregated polyaniline granules in the solution phase [26]. These aggregates formed polyaniline stalagmites, leading to large uncertainties in the thickness measurements when the film was thick (Fig. 3a inset). However, thin polyaniline films of less than 200 nm were deposited by spin coating. This was attributed to the limited amount of monomers and APS; not only is a small amount of reaction mixture used in the spin coating, but it is also swept away during the process. The deposition of aggregated polyaniline granules was notably suppressed, as shown in the inset of Fig. 3b. Spin coating can effectively inhibit the adsorption of these aggregates by sweeping away aggregated polyaniline granules which form in the solution phase.

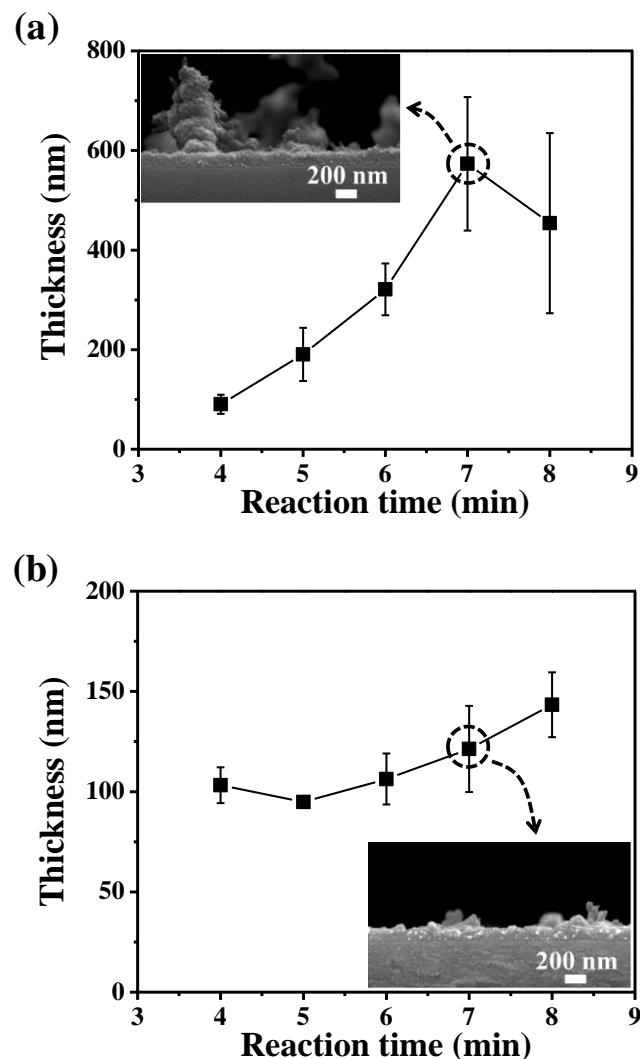


Figure 3. Thickness of polyaniline film prepared by (a) dip coating and (b) spin coating according to the reaction time. Insets are cross-sectional SEM images of polyaniline films deposited on glass substrates for 7 min of reaction time.

The changes in the sheet resistance of the polyaniline films with the reaction time are shown in Fig. 4. The sheet resistance tended to decrease with an increase in the reaction time when using both coating methods because the thickness of the conductive polyaniline film was increased.

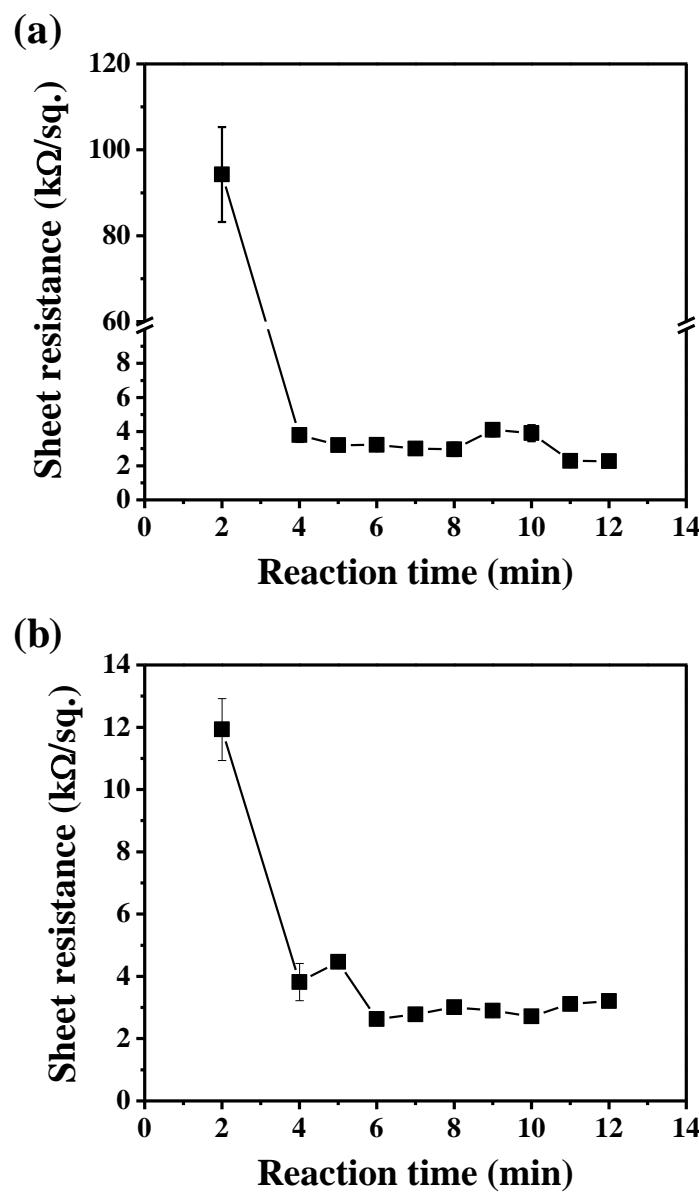


Figure 4. Sheet resistance of polyaniline film prepared by (a) dip coating and (b) spin coating according to the reaction time.

However, it should be noted that the measured sheet resistance was similar after a reaction time of 4 min regardless of the coating method used, though the polyaniline thickness was thinner when using spin coating as compared to dip coating (Fig. 3). This indicates that a uniform and continuous polyaniline film was formed by spin coating as compared to that by dip coating. The uniformity of the film strongly depends on the nucleation step, during which intermediates of aniline polymerization and/or aniline oligomers nucleate on a heterogeneous polyimide substrate due to adsorption. During the nucleation step, the intermediates (and/or aniline oligomers) form islands on the substrate; these

islands do not affect the sheet resistance because they are not connected to each other. It has also been reported that these intermediates are non-conductive [25]. The islands then grow and become connected to each other during the polyaniline chain growth step, constituting a polyaniline film which is conductive. Therefore, a uniform and continuous polyaniline film can be formed at thinner thickness levels when the nucleation density is higher. The sheet resistance measured at a reaction time of 2 min clearly shows the difference in the nucleation density between the dip- and spin-coating processes. The sheet resistance was 94.3 k Ω /sq. for dip coating, whereas a smaller value by 88% (11.9 k Ω /sq.) was determined with spin coating. This demonstrates that the spin coating formed a continuous and conductive polyaniline film earlier than the dip coating due to the high nucleation density, despite the fact that the film thickness was thinner. The suppression of secondary nucleation may have also a positive influence on the formation of uniform, continuous polyaniline films. Therefore, it can be concluded that a polyaniline film prepared by spin coating is more suitable as a seed layer for Cu electrodeposition than by dip coating in terms of both film uniformity and sheet resistance.

The Pd nanoparticles synthesized with oleylamine were then deposited onto polyaniline films prepared by both the dip- and spin-coating approaches. The reaction time was 7 min for both methods, which is the time when the sheet resistances of both films reached 3.0 k Ω /sq. and 2.8 k Ω /sq., respectively.

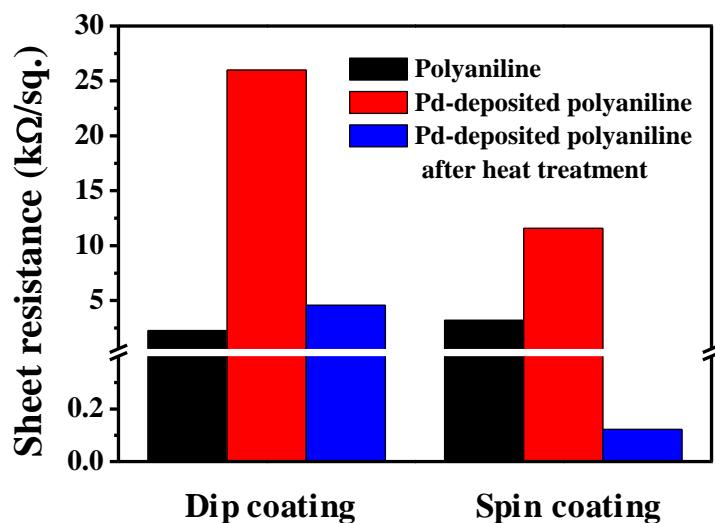


Figure 5. Sheet resistances of Pd-deposited polyaniline films before and after the heat treatment.

Pd nanoparticles facilitate the Cu nucleation process when Cu electrodeposition is performed on a highly resistive substrate [23]. A seven-hour heat treatment was also conducted at 190°C for 7 hours to remove any oleylamine adsorbed onto the surfaces of the Pd nanoparticles. Fig. 5 shows the change in the sheet resistance of the Pd-deposited film before and after the heat treatment. Oleylamine attached to Pd nanoparticles increased the sheet resistance because oleylamine molecules surrounding Pd nanoparticles are not conductive. The sheet resistance was decreased greatly after the heat treatment, which removed the oleylamine from the Pd nanoparticles. With regard to spin coating, the

polyaniline film showed the lowest sheet resistance ($0.12\text{ k}\Omega/\text{sq.}$) after a heat treatment. It is assumed that the uniform polyaniline film deposited by spin coating led to the low sheet resistance. Therefore, the spin coating (reaction time: 7 min) was selected as the optimum condition for the deposition of polyaniline film as a seed layer. Cu electrodeposition was then performed on the Pd-deposited polyaniline film which was prepared by spin coating. Fig. 6 shows the surface morphology of the electrodeposited Cu film. A uniform and continuous Cu film was successfully formed on the polyaniline film.

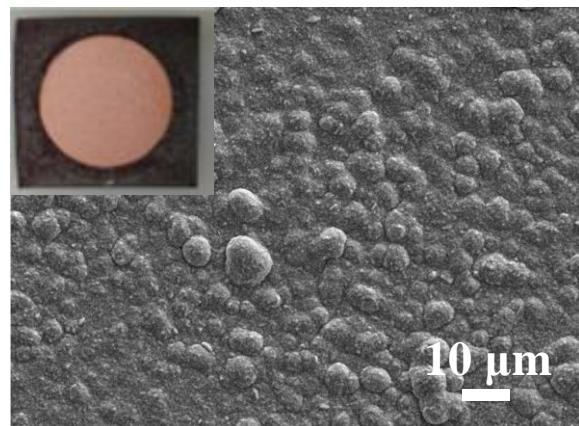


Figure 6. Surface SEM image of the electrodeposited Cu film. Inset is the photo of the polyimide substrate after Cu electrodeposition.

4. CONCLUSION

Direct Cu electrodeposition was performed on a polyimide substrate using polyaniline film and Pd nanoparticles as a seed layer and nucleation promoter. A uniform and conductive polyaniline film was formed on a polyimide substrate through spin coating, which reduces the adsorption of the polyaniline aggregates which form in the solution phase. Synthesized Pd nanoparticles, nucleation promoters for Cu electrodeposition, were then deposited onto the polyaniline-coated polyimide substrate via a spraying method. The subsequent Cu electrodeposition step successfully resulted in a uniform and continuous Cu film on the substrate.

ACKNOWLEDGEMENT

This work was supported by Incheon National University Research Grant in 2016.

References

1. T. Tsutsu and K. Fujita, *Adv. Mater.*, 14 (2002) 949.
2. K. Jain, M. Klosner, M. Zemel and S. Raghunandan, *Proc. IEEE*, 93 (2005) 1500.
3. E. Sugimoto, *IEEE Electr. Insul. M.*, 5 (1989) 15.
4. C.F. Coombs, *Printed Circuits Handbook*, 6th ed., McGraw-Hill, (2008) New York, NY, USA.

5. J.W. Dini and D.D. Snyder, *Electrodeposition of Copper*, in *Modern Electroplating*, 5th ed., John Wiley&Sons, Inc., (2010) Hoboken, NJ, USA.
6. F. Hanna, Z. A. Hamid and A.A. Aal, *Mater. Lett.*, 58 (2003) 104.
7. F. Inoue, H. Philipsen, A. Radisic, S. Armini, Y. Civale, S. Shingubara and P. Leunissen, *J. Electrochem. Soc.*, 159 (2012) D437.
8. M. Paunovic and R. Arndt, *J. Electrochem. Soc.*, 13 (1983) 794.
9. L. Yu, L. Guo, R. Preisser and R. Akolkar, *J. Electrochem. Soc.*, 160 (2013) D3004.
10. X. Gan, K. Zhou, W. Hu and D. Zhang, *Surf. Coat. Technol.*, 206 (2012) 2405.
11. J. Stejskal, I. Sapurina, J. Prok  s and J. Zemek, *Synth. Met.*, 105 (1999) 195.
12. J.-M. Jeong, B.G. Choi, S.C. Lee, K.G. Lee, S.-J. Chang, Y.-K. Han, Y.B. Lee, H.U. Lee, S. Kwon, G. Lee, C.-S. Lee and Y.S. Huh, *Adv. Mater.*, 25 (2013) 6250.
13. D. Nicolas-Debarnot and F. Poncin-Epaillard, *Anal. Chim. Acta*, 475 (2003) 1.
14. Q. Li, J. Wu, Q. Tang, Z. Lan, P. Li, J. Lin and L. Fan, *Electrochem. Commun.*, 10 (2008) 1299.
15. S. Bhadra, N.K. Singha and D. Khastgir, *J. Appl. Polym. Sci.*, 104 (2007) 1900.
16. G. Fomo, T. T. Waryo, P. Baker and E.I. Iwuoha, *Int. J. Electrochem. Sci.*, 11 (2016) 10347.
17. M.M. El-Deeb, K. Alenezi, H. El Moll, M. El-Masry and Z. Matarneh, *Int. J. Electrochem. Sci.*, 12 (2017) 10140.
18. N.V. Blinova, J. Stejskal, M. Trchov   and J. Prok  s, *Polym. Int.*, 57 (2008) 66.
19. J.G. Masters, Y. Sun, A.G. Macdiarmid and A.J. Epstein, *Synth. Met.*, 41 (1991) 715.
20. A. Ray, A.F. Richter and A.G. Macdiarmid, *Synth. Met.*, 29 (1989) 151.
21. W.-S. Huang, B.D. Humphrey and A.G. Macdiarmid, *J. Chem. Soc., Faraday Trans. 1*, 82 (1986) 2385.
22. J.-C. Chiang and A.G. Macdiarmid, *Synth. Met.*, 13 (1986) 193.
23. J.J. Kim, S.-K. Kim and Y.S. Kim, *J. Electrochem. Soc.*, 151 (2004) C97.
24. I. Sapurina and J. Stejskal, *Polym. Int.*, 57 (2008) 1295.
25. M.A. Shishov, V.A. Moshnikov and I. Y. Spurina, *Chem. Pap.*, 67 (2013) 909.
26. I. Sapurina, A. Riede and J. Stejskal, *Synth. Met.*, 123 (2001) 503.