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CU ELECTRODEPOSITION ON POLYPYRROLE PRECOAT FOR THE METALLIZATION OF PRINTED CIRCUIT BOARDS

To explore an alternative green metallization strategy for nonconductive plastics, a conductive polypyrrole (PPy) precoat was prepared by in-situ interfacial polymerization of pyrrole on printed circuit boards (PCBs) and the electrodeposition of Cu on PPy precoat was investigated using both voltage-controlled method and current-controlled method. A uniform PPy film was successfully obtained on the PCB surface through modifying the PCB wettability and optimizing the pyrrole solution. Electrochemical measurements showed that sufficient polarization was necessary for the electroreduction and growth of Cu crystals on the PPy precoat due to its high electrical resistance. The presence of through-holes adjacent to copper in PCB boards demonstrates that constant-current electroplating enables effective deposition of uniform, adherent copper layers on polypyrrole (PPy) - pretreated substrates, establishing a viable alternative to conventional electroless copper plating for through-hole metallization in PCB manufacturing.

Keywords: Polypyrrole precoat; Plastic metallization; Printed circuit board

1. Introduction

Metallization of plastics, known for their low density, chemical inertness, and ease of molding, enables synergistic integration of the advantageous properties of metals and polymers. This hybrid manufacturing has gained increasing significance in various industries such as mobile electronics, aerospace, and integrated circuits [1-3]. With the rapid development of the integrated circuit industry, there is a surging demand for high-frequency, high-density interconnected printed circuit boards (PCBs) [4,5]. Electroless plating, the traditional method for metallic layer deposition on insulating polymer surfaces, commonly involves noble metals like silver (Ag) or palladium (Pd) as catalysts [6,7] and a variety of chemicals, some of which pose environmental risks (e.g. reductant formaldehyde [7,8] and complexing agent EDTA [9]). The properties of the resulting metal layer, prone to nanovoid formation and delamination, are greatly influenced by the variability in electroless plating parameters, impacting ductility and adhesion [10]. Furthermore, bath instability can affect the consistency of deposition quality. As a result, there is an increased demand for cleaner, more effective and environmentally friendly metallization methods.

In recent years, several eco-friendly approaches for conductive precoats formation on polymers have been proposed for direct copper (Cu) electroplating. These include laser-assisted selective electrical conductivity fabrication [11] and the development of conductive carbon materials [12-15], as well as polymers like polyacetylene (PA), polyaniline (PANi), polypyrrole (PPy) and polythiophene (PT) [3,16]. PT, in particular, has been studied for its suitability in direct Cu electroplating on insulating substrates due to its high conductivity and chemical-stability [8,17-19]. PPy, renowned for its biocompatibility, non-toxicity, ease of synthesis, high thermal-chemical stability and modifiable properties, has found applications in biosensors, piezoresistive sensors capacitors, secondary batteries, and more [20-26]. Early research in 1990s demonstrated the feasibility of electroplating metal layers onto PPy [23], and its chemical deposition of PPy onto PCBs as a metallization precoat has been realized [27-32]. Uribe et al. [30] developed a method of PPy preparation on PCBs by immersing the substrate in an aqueous bath containing the monomer (e.g., pyrrole) and an oxidizing agent. However, this method may result in significant chemical waste and bath instability due to polymerization occurring throughout the bath. Otero et al. [32] studied Cu electrodeposition on PPy electrodes at varying cathodic potentials and noted that Cu grain growth on the PPy film was less uniform at higher cathodic potentials. This suggests that the cathodic potential affects Cu grain growth and the overall layer performance. Therefore,

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the Cu electrodeposition method on PPy films is crucial for determining the Cu layer performance. To our knowledge, the deposition behavior of Cu on the PPy precoat has not been carefully studied.

In this work, we developed an in-situ chemical polymerization strategy to economically prepare PPy films as conductive precoats for Cu electrodeposition on PCBs. Subsequently, different electrodeposition techniques were used to study the deposition behavior of Cu on PPy precoats. Our aim was to elucidate the deposition mechanism and evaluate the feasibility of using PPy precoats as an eco-friendly alternative to traditional electroless Cu for metallizing holes in PCBs.

2. Experimental

2.1. Preparation of PPy Precoat on PCBs

The preparation process for PPy precoats and Cu electrodeposition is illustrated in Fig. 1. Essential chemicals like pyrrole, ferric chloride ($FeCl_3$) and potassium permanganate ($KMnO_4$), were acquired in analytical reagent grade from www.tansoole.com. The 2×5 cm PCBs (FR4, from Shanghai Meadville Electronics Co. Ltd) were first cleaned in a Na_2CO_3 and OP-10 solution at 60°C for 10 min. After deionized water rinsing, the FR4 boards were microetched in a 50 g L^{-1} $KMnO_4$ solution at 70°C for 3 min. The boards, cleaned after post-microetching, were then dipped in a pyrrole alcohol solution for 5 min, followed by immersion in a 1 mol L^{-1} $FeCl_3$ solution at 0°C for 10 min to form a black PPy film. They were then rinsed thoroughly and air-dried at room temperature.

2.2. Electrodeposition of Cu on PPy Precoats

Before Cu electrodeposition on PPy precoat, the electrodeposition dynamics of Cu on PPy electrodes were studied using cathodic dynamic polarization. Cathodic dynamic polarization was conducted using a Gamry electrochemical workstation (Reference 600+, America) in a three-electrode cell. 1 cm^2 PPy films covered on FR4 boards were used as the working electrodes. A Pt foil and a saturated mercuric sulfate electrode were used as the counter electrode and the reference electrode, respectively. The potential range was from open-circuit potential (OCP) to –3.5 V with a scan rate of 2 mV s^{-1}.

Based on the results of the electrodeposition dynamics, Cu electrodeposition on the PPy precoat was conducted using both voltage-controlled method and current-controlled methods. For the voltage-controlled technique, PPy-precoated PCBs were used as the working electrodes, with electrical contacts set 1 cm above the surface of electroplating bath. The PPy film was sealed with tape to prevent electrolyte climbing (Cathode 1 in Fig. 1). Various bath voltages (1 V, 2 V, 3 V, 4 V, 5 V) were applied for Cu electrodeposition in a stirring solution for 1h. At the critical potential, chronoamperometry was performed to study the Cu film growth. The current-controlled technique involves direct contact of Cu with the plating solution (Cathode 2 in Fig. 1) with a current density of 1.5 A dm^{-2} applied to a 2×4 cm^2 PPy film. The composition of the electroplating solution was 55 g L^{-1} $CuSO_4{\cdot}5H_2O$, 250 g L^{-1} H_2SO_4, 200 mg L^{-1} PEG 10000, 60 mg L^{-1} Cl^- and 1 mg L^{-1} SPS. All experiments were carried out at room temperature.

2.3. Characterization

The morphologies of the samples were examined using Scanning Electron Microscopy (SEM, Hitachi, S3400N). The sheet resistance of the PPy film was assessed by pressing two brass sheets against the sides of a rectangular sample of the FR4 boards covered with PPy film to obtain its electrical properties. The contact angle of a DIW drop on FR4 boards was measured by a goniometer completed with CAM software (Shanghai Zhongchen Digital Technic Apparatus Co. Ltd) to detect the

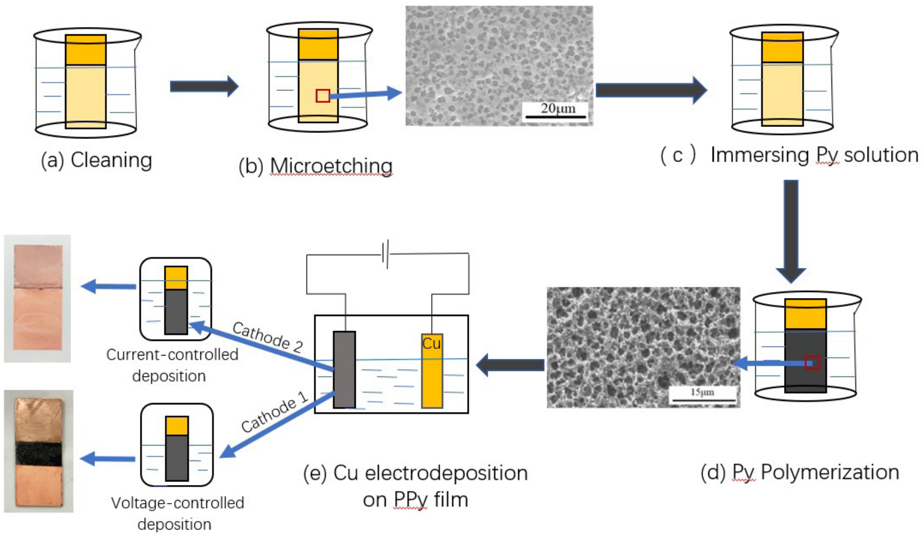

Fig. 1. Flow chart of the preparation of PPy precoat on PCBs and subsequent Cu electrodeposition. (Py = Pyrrole; PPy = Polypyrrole)

surface wettability of the PC board before and after microetching, providing insights into surface wettability.

3. Results and discussion

3.1. Performances of PPy precoat on BC boards

In this work, the polymerization of pyrrole on the FR4 surface was based on the chemical oxidation of pyrrole attached to the surface by trivalent iron ions in an aqueous solution. Therefore, before applying the PPy film to the surface of FR4, the FR4 surface was cleaned and microetched with an alkaline $KMnO_4$ solution to increase the surface area of pyrrole adsorption and the wettability of the FR4 surface. SEM analysis (Fig. 2) reveals significant changes in the surface morphology of the FR4 board. An increase in the number of micropores can be observed after the oxidation treatment. The contact angle of the FR4 board before and after microetching is inserted in Fig. 2. Obviously, the contact angle of the FR4 board decreases from 82.7° to 38.4° after $KMnO_4$ oxidation treatment. The increase in micropores and the reduction in contact angle indicate the promotion of the specific surface area and the wettability of the PC board surface [31]. Therefore, the microetching process is beneficial for obtaining a uniform PPy precoat with good adhesion on PCBs.

The concentration of pyrrole in the alcohol solution critically influences the uniformity and conductivity of the PPy film. When the concentration of pyrrole is high (50 vol%), PPy particles are aggregated on the PPy surfaces, which is detrimental to the uniform deposition of copper. Lower concentrations of pyrrole (35 vol%, 20 vol%) are beneficial for the formation of conformal films. Compared to the solutions containing 50 vol% and 20 vol% pyrrole, a 35 vol% pyrrole solution produces a uniform PPy surface with the best electrical conductivity,

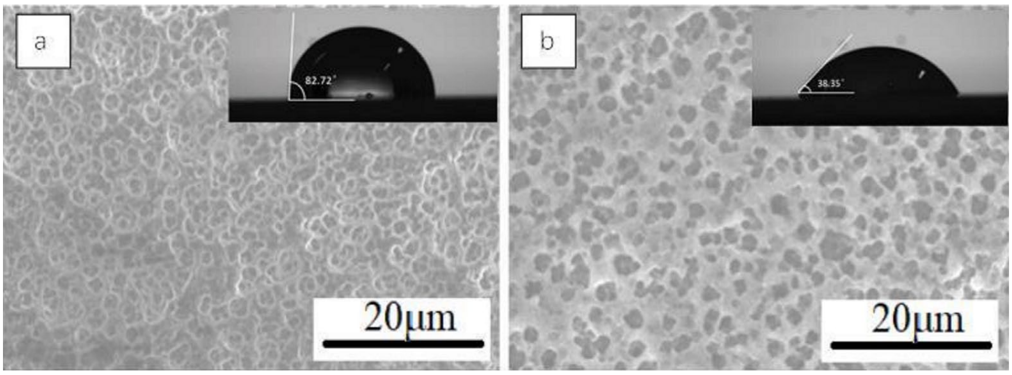

Fig. 2. SEM images of the FR4 board surface before (a) and after (b) microetching (The inserted images are their contact angles)

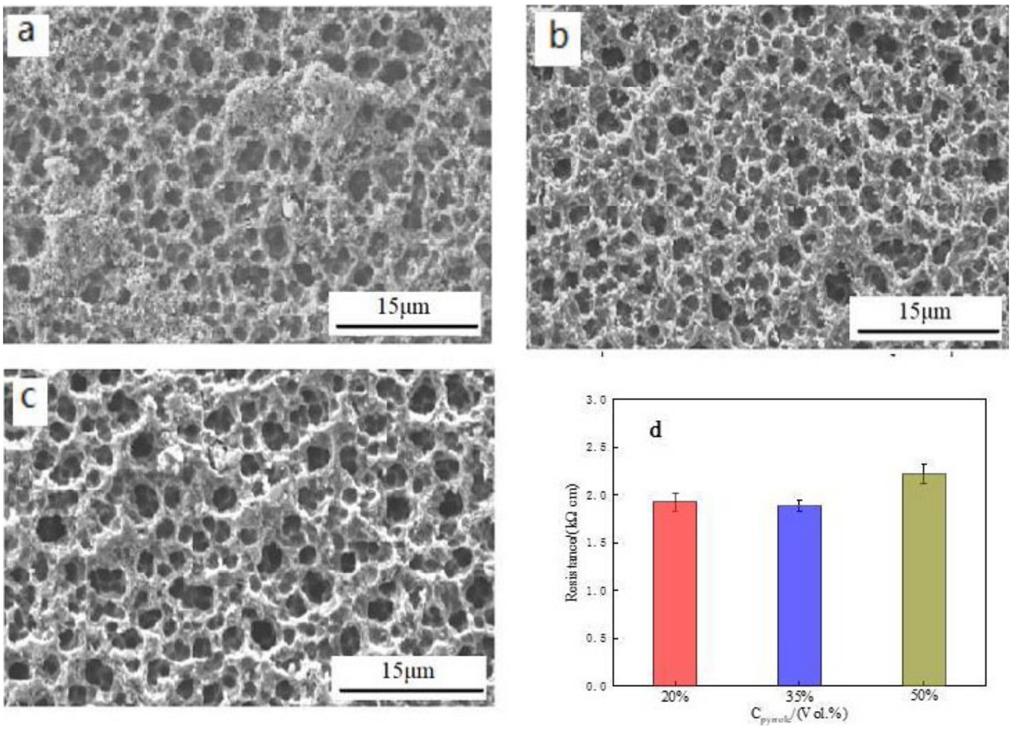

Fig. 3. SEM images of Polypyrrole films obtained in 50 vol% (a), 35 vol% (b) and 20 vol% (c) pyrrole solutions and their specific electrical resistances (d)

which is sufficient for direct electroplating (Fig. 3). This study identifies that conformal PPy deposition with good adhesion and low resistance can be achieved by adsorbing an appropriate concentration of pyrrole solution followed by interfacial polymerization in a solution containing an oxidant. This preparation process can reduce chemical consumption and is an attractive method for practical application.

3.2. Cu Electrodeposition Dynamics on PPy Precoat

Cathodic dynamic polarization curves of Cu electrodeposition on PPy and Cu electrodes are shown in Fig. 4. Obviously, Cu electrodeposition on the Cu electrode occurs at a very small overpotential, and the current density dramatically increases with the increase of the overpotential, indicating a low polarization of Cu^{2+} electroreduction on Cu. Unlike the Cu electrode, the current density on PPy electrode is low and gradually increases with the increase of the polarization potential. The small value in current density indicates the low rate of Cu electroreduction on the PPy film due to its high electrical resistance. Considering that the conductivity of PPy mainly results from the trapping of counterions when the structure shrinks and closes during the cathodic polarization [32], the magnitude of polarization will greatly affect the electrical conductivity of the PPy film, thereby affecting the cathodic reaction rate. No obvious Cu layer and hydrogen bubbles appear on the PPy electrode until the overpotential reaches 3 V, exhibiting a significant resistance to both hydrogen evolution and Cu electroreduction. The polarization studies highlight the necessity of sufficient polarization for initiating Cu^{2+} electroreduction on PPy film. In fact, direct electrodeposit Cu on the PPy film was attempted at 1.5A dm^{-2}. As expected, the overpotential on the PPy electrode was very high and a uniform Cu layer could not be obtained except for many Cu nodules appearing at the PPy-electrolyte interface. Interestingly, uniform Cu electrodeposition was actually achieved by the processes shown in Fig. 1. One method involves electrodepositing copper by controlling the polarization potential of the PPy electrodes (see cathode 1 in Fig. 1). Another method is to use copper as a contact with the plating solution and perform copper electrodeposition on a PPy electrode under controlled current density conditions (see cathode 2 in Fig. 1)

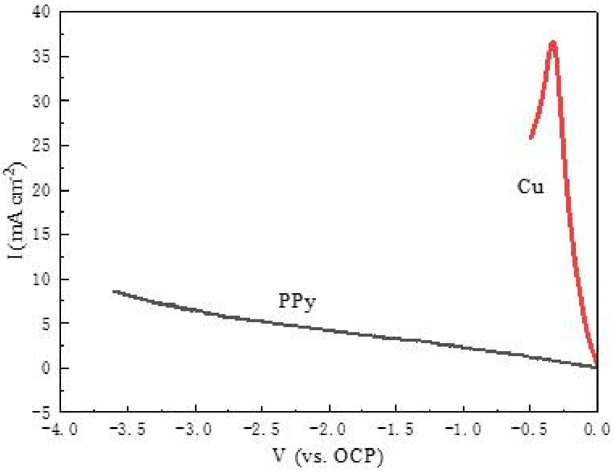

Fig. 4. Cathodic polarization curves of a polypyrrole (PPy) electrode and a Cu electrode in Cu plating solution

3.3. Cu Electrodeposition on PPy Precoats

3.3.1. Potential-controlled Cu Deposition

The potential-controlled technique involves varying bath voltages to induce Cu deposition on the PPy film. It is clearly found that the black PPy film electrodeposited at 1 V for 1 h is still black, and no visible Cu layer is observed. When the bath voltage is increased to 2 V, the color of the black PPy electrode turns gray, and still, no obvious Cu layer covers the entire PPy film except for some solid Cu grains appearing at some interface sites of the PPy electrode. Continuing to increase the bath voltage to 3 V and above, the Cu deposit firstly grows from the PPy-solution interface (Fig. 5a), and finally, at a certain moment, the PPy film is completely covered by a uniform shiny Cu layer (Fig. 5b).

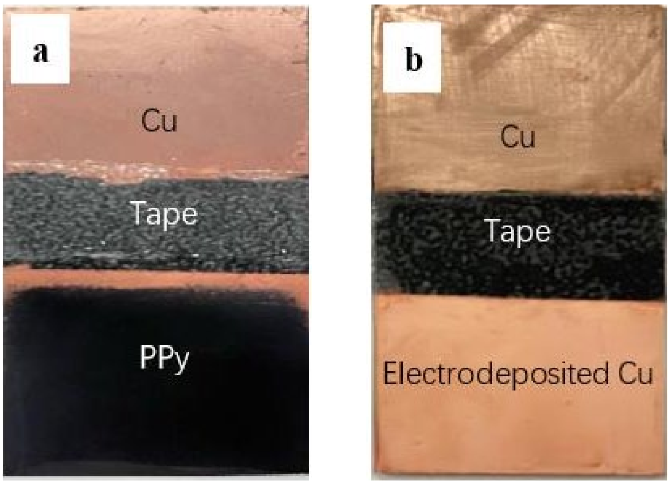

Fig. 5. Typical optic photos of the polypyrrole (PPy) samples deposited at 3 V and above at the growing stage (a) and the finishing stage (b) of Cu electrodeposition process

Fig. 6 gives the SEM images of the obtained PPy electrodes under different bath voltages for 1 h. Evidently, at a bath voltage of 1 V, although there is no significant copper layer, many small copper grains can be observed (Fig. 6a), indicating that the growth rate of copper crystals is relatively slow at low overpotentials. A bath voltage of 2 V makes the color of the PPy electrode change from black to gray because there are more Cu particles (Fig. 6b). Visible solid Cu grains aggregate at interface sites of the PPy film where the polarization is larger than that of the other parts immersed in plating bath, resulting in faster Cu electrodeposition at the interface between the electrode and the plating solution. However, the failure propagation of the Cu layer along the PPy film indicates the low electronic transfer in

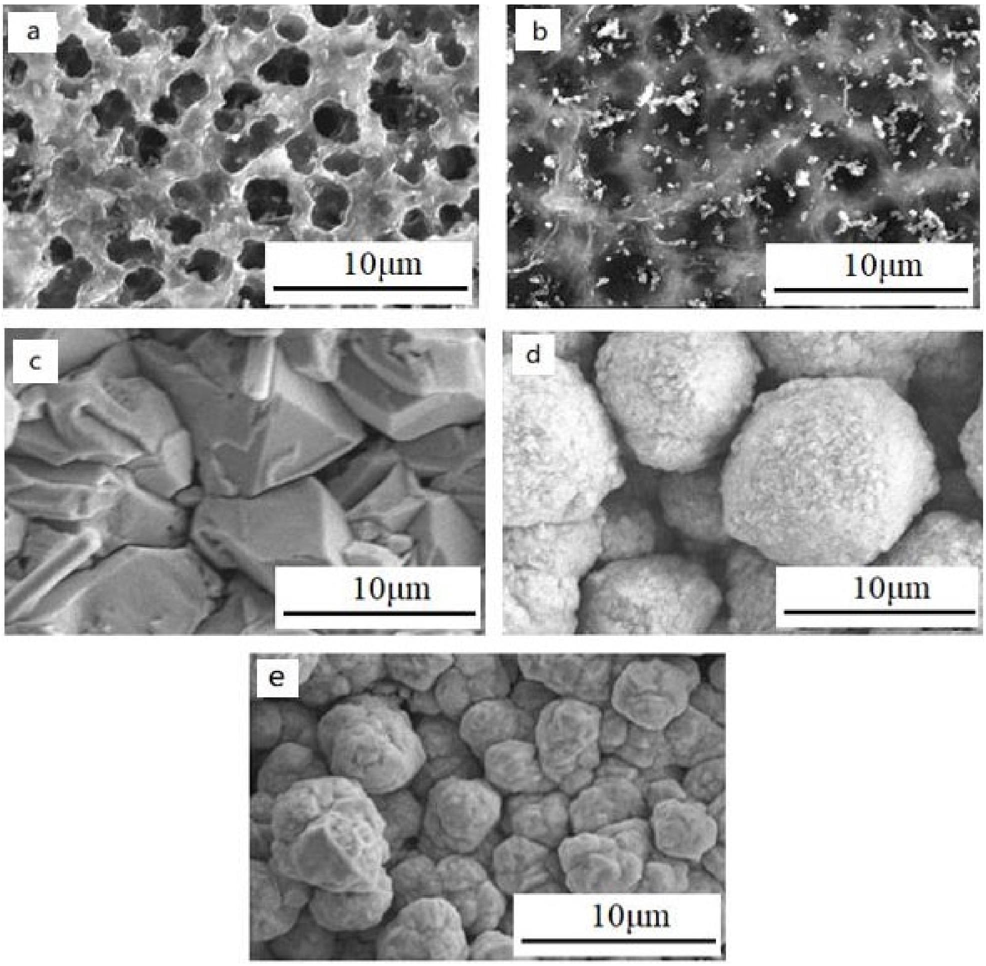

Fig.6 SEM images of the obtained polypyrrole electrodes at different bath voltages (a 1 V; b 2 V; c 3 V; d 4 V; e 5 V) for 1 h

the PPy film at 2 V bath voltage. Interestingly, when the bath voltage exceeds 3 V, the copper layer grows and spreads from the junction of PPy electrode and the plating solution, and finally forms a uniform copper layer (Fig. 6c-e). Based on the above results, it can be concluded that sufficient polarization is required to produce a glossy copper layer on the PPy film within a reasonable operating time. Otherwise, the shapes of copper grains at different bath voltages indicate the influence of polarization on grain nucleation and growth. Larger polarization tends to grow spherical particles. Clearly, the overpotential on PPy electrode is the key factor to fulfil the Cu electroreduction and the growth of Cu layer on PPy film.

To further investigate the growth of Cu layer on the PPy film, the chronoamperometry at 3V is provided in Fig. 7. It is found that the current passing through the PPy electrode significantly decreases in the first 300s, at a point, gradually increases to a constant value. The high current in the initial stage should be attributed to the impact of high voltage on the surface of the PPy electrode where a large amount of charge initially accumulates at the junction of the PPy electrode and the solution due to the high electrical resistance of the PPy film, generating a high current. As time prolongs, the charge density gradually decreases, and the current begins to decrease. At the same time, the copper electroreduction reaction also occurs. Therefore, the resistance of the PPy electrode begins to decrease, causing the current under a constant voltage condition to increase as the resistance decreases. The SEM images of the PPy electrodes corresponding to particular points marked on the chronoampero-

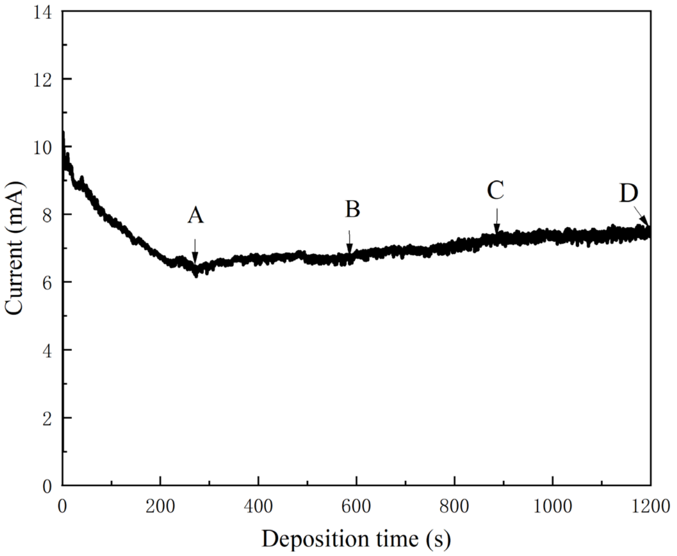

Fig. 7. Chronoamperogram recorded during copper electrodeposition at 3.0 V (A, B, C, D are the sites of observing microscopy of deposited Cu layer)

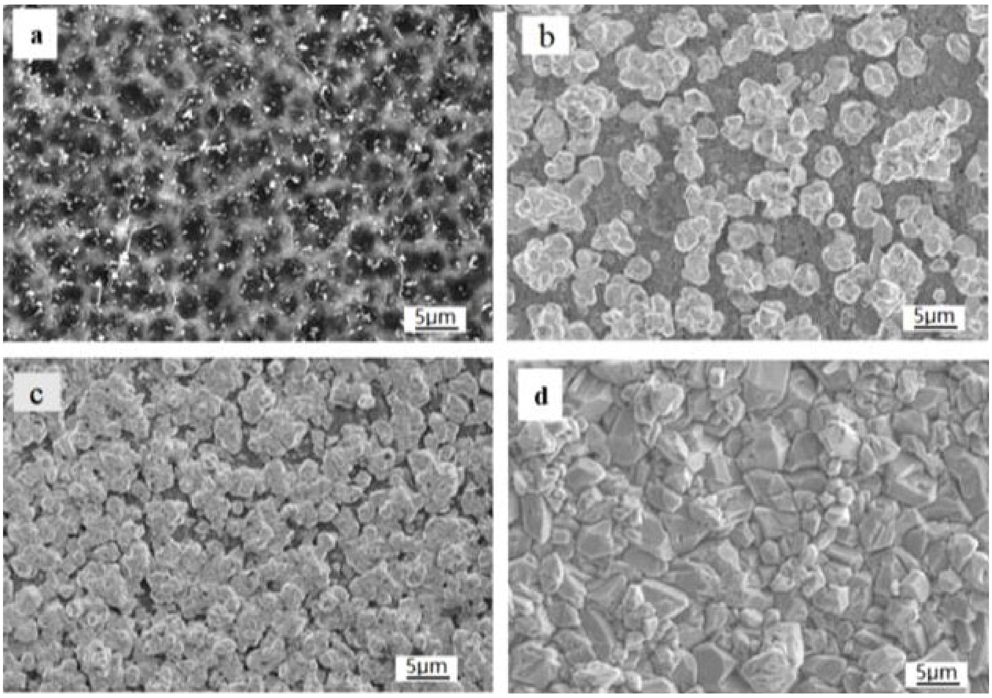

Fig. 8. SEM images of the samples deposited at 3 V for 300 s (a), 600s (b), 900s (c), 1200s (d)

gram curve are shown in Fig. 8. Evidently, at the inflection point of the reduction current (point A), many dispersed Cu nanograins emerged on the PPy film (Fig. 8a), indicating that Cu crystals reduce the resistance of the PPy electrode [33]. As the polarization time prolongs, the Cu crystals gradually grow up (Fig. 8b and c). Finally, at a certain moment, a Cu layer can be immediately formed through the mutual contact of Cu crystals and covers the whole PPy electrode (Fig. 8d). The study of chronoamperometry shows that, in voltage-controlled technology, the nucleation of Cu crystals occurs throughout the PPy electrode and gradually grows up to form a visible Cu layer. Therefore, due to the much higher electrical resistance of PPy film compared to copper metal, sufficient overpotential is required to achieve the electroreduction and growth of Cu on the PPy film. Reducing the electrical resistance of PPy films is a good method to achieve direct copper plating on it.

3.3.3. Current-controlled Cu Electrodeposition

When Cu electrodeposition is conducted by the current-controlled method, the electronic contact Cu is in contact with the plating solution (Cathode 2 in Fig. 1). The chronopotentiogram at a current density of 1.5 A dm^{-2} is recorded and shown in Fig. 9. Obviously, a very large bath voltage of 1300 mV appears at the initial stage of Cu electrodeposition. With the increase of the electrodeposition time, the bath voltage gradually decreases and stabilizes at around 500 mV. The large voltage bath at the initial stage is mainly due to the high electrical resistance of the PPy electrodes. The reduction in bath voltage can be attributed to the electrodeposition of Cu on the PPy film. The stabilization of bath voltage in the later stage indicates that the conductivity of the electrode gradually stabilizes due to the coverage of deposited Cu on the PPy electrode. The optical photos observed at different growth stages of Cu electrodeposition clearly show that the Cu layer first grows and propagates from the junction of the copper electric contact and the electrolyte. The preferred Cu electrodeposition on the Cu electric contact results from the low electroreduction polarization on Cu metal. Then, the propagation of Cu electrodeposition along the surface of the PPy film takes place and finally covers the entire PPy film uniformly. The driving force for the propagation of the Cu layer comes from the overpotential caused by the accumulation of charges at the edge of formed copper film due to the tip effect. This overpotential

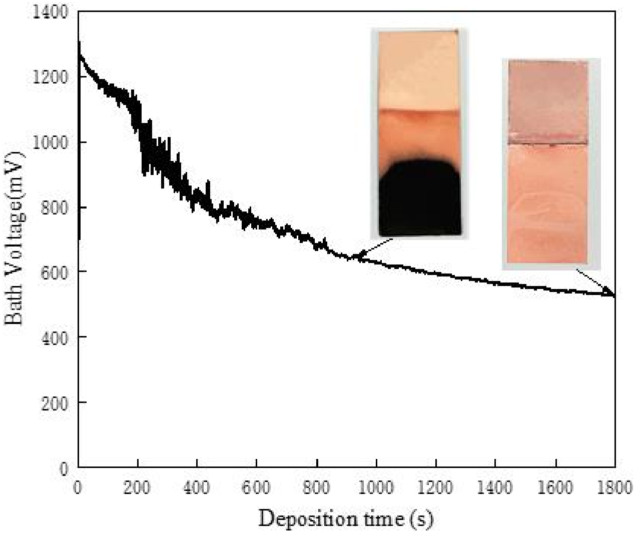

Fig. 9. Chronopotentiogram recorded during copper electrodeposition at 1.5A dm^{-2} for 1800s (the optical photos of the sample obtained at 900s and 1800s are inserted)

will continuously move forward with the growth of the copper layer and eventually cover the entire PPy electrode.

The SEM images of the PPy film at the initial Cu crystal growth and the final Cu electrodeposition are shown in Fig. 10. Clearly, the number of copper grains near the copper contact is dense, and the number of copper grains gradually decreases with increasing the distance from the Cu contact, illustrating the effect of polarization potential gradient. This Cu layer formation mechanism is different from the potential-controlled method. As the continuity of the copper film on the PPy film increases, the high polarization gradually advances along the edge of the copper film, and finally the copper completely covers the entire PPy film.

3.4. Line Pattern Creation on PPy Precoat

Based on the successful Cu layer formation on insulating PC boards by precoating a conductive PPy film, a line pattern (line width was 500 um) was designed on FR4 boards (see Fig. 11a). Before Cu electrodeposition, the line is covered by a PPy layer through the process shown in Fig. 1. Copper electrodeposition is carried out using the current-controlled method, with an applied current density of 1.5 A dm^{-2}. After 20 minutes of electrodeposition, a Cu layer is deposited on the surface of PPy and a conductive line is formed. Fig. 11b give a usage of the obtained conductive Cu line. When a battery is connected with this line, the LED lights up, demonstrating that the electrical conductivity of the line is excellent and can be used as a conductive layer, underscoring the potential of employing PPy precoats as an effective alternative to traditional electroless Cu in PCB hole metallization.

The results of Cu electrodeposition on the PPy precoat, either by potential or current control, demonstrate that sufficient polarization is essential for effective Cu electroreduction and growth on PPy films. Meanwhile, the technique of Cu electrodeposition significantly influences the quality of the resultant Cu layer. These results have significant implications for the design of metallization processes in PCB manufacturing.

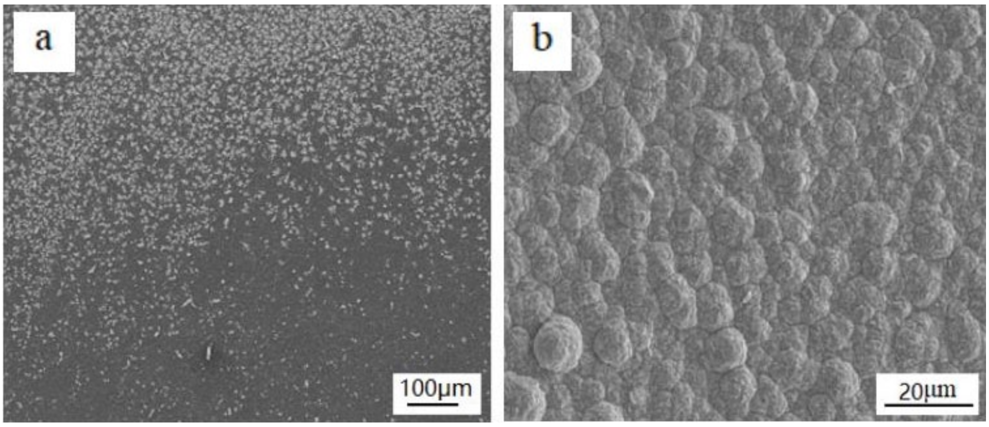

Fig. 10. SEM images of the electrodeposited Cu layer at the initial electroplating stage (a) and the finished stage (b)

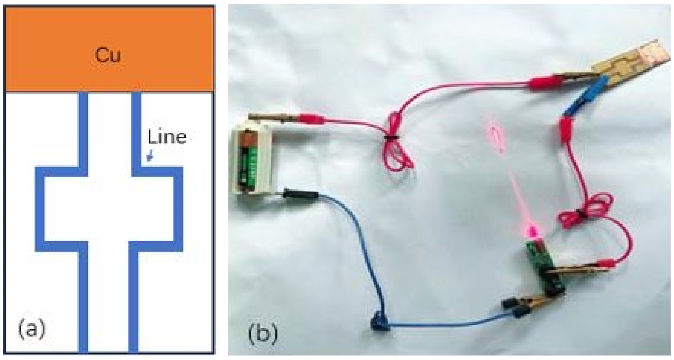

Fig. 11. (a) Line pattern formed on FR-4 board. (b) The Cu line pattern and the lighted LED

4. Conclusions

PPy film was successfully prepared by in-situ interfacial chemical polymerization on the surface of PCBs and used as a feasible precoat for Cu electrodeposition. Cathodic polarization indicates a substantial hindrance in Cu electroreduction on the PPy surface, elucidating the necessity of sufficient polarization for successful Cu electroreduction and growth on PPy films. The applied polarization plays a significant role in determining the crystal growth and uniformity of the Cu layer. In the potential-controlled technique, sufficient polarization is the driving force for the generation and growth of copper grains into thin films while the tip effect of charges at conductive terminals is the driving force for the grain generation and film growth of Cu in the current-controlled method. This research contributes valuable insights into the potential of using PPy precoats as environmentally friendly alternatives to conventional electroless Cu in the metallization of PCB holes.

Acknowledgements

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