INFLUENCE OF K 4FE (CN) 6 ON ELECTROLESS COPPER PLATED POLYESTER FABRIC USING GLYOXYLIC ACID AS A REDUCING AGENT

GLİOKSİLİK ASİDİN İNDİRGEN OLARAK KULLANILDIĞI ELEKTROSUZ BAKIR KAPLANMIŞ POLİESTER KUMAŞLARDA POTASYUM FERROSİYANATIN ETKİSİ

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ABSTRACT

In this study, electroless copper plating on polyester fabric using glyoxylic acid and potassium ferrocyanide (K4Fe (CN) 6) as reducing agent and brightener agent, respectively. Influence of concentration of potassium ferrocyanide (K4Fe (CN) 6) in the plating solution on the deposited rate, morphology and surface resistance of copper plated polyester fabrics were studied. It was found that the deposition rate significantly decreased with the rise of the concentration of K4 Fe (CN)6 and the copper deposits became more compact and smoother. The copper coating on the fabric exhibited a face centered cubic crystal structure. The surface electrical resistance of the obtained copper plated fabric was 13.8 mΩ/sq when 20 mg/L K4Fe(CN)6 was added in the plating solution. The copper plated fabric possesses excellent electrical conductivity.

Keywords: Glyoxalic acid, electroless, copper, polyester, (K4Fe (CN) 6.

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Introduction

Electroless copper plating has been a hot topic because it is widely applied in many areas such as electromagnetic interference shielding of electronic components, through-hole plating in printed circuit boards, decorative plating of household utensils, conductive traces in electronic interconnection devices and integrated circuit manufacturing (1-3). Copper deposited fabric substrates are important kinds of materials for preventing electromagnetic interference, absorbing radiation of electromagnetic wave, reflecting ultraviolet rays and infrared. Therefore, copper coating on fabrics is particularly interesting because it shows great potentials in the military, commercial and industrial areas.

Formaldehyde or its derivatives are used as a reducing agent in commercial electroless copper plating solutions (4). However, it has been found that this reducing agent may release hazardous gases during the process (5). Therefore, some nonformaldehyde reducing agents in electroless copper solutions such as borohydride (6), Fe(II)(7), Co(II) (8), amine borane (9), glyoxylic alcohol or glyoxylate (11,12), or sodium hypophosphite (13,14) have been investigated. Among them, glyoxylic acid is especially attractive because of its higher deposition rate, less environmental pollution, low cost and more stable solution (15,16). In previous studies, $K_4Fe(CN)_6$ (17-19) have been used as additives in sodium hypophosphite-based of electroless copper plating to improve the physical properties of the copper deposits. Physical properties of the copper deposits also enhanced with $K_4Fe(CN)_6$ (20,21) addition in formaldehyde based electroless copper plating. However The effect of $K_4Fe(CN)_6$ in the bath on electroless copper on polyester fabric using glyoxylic acid as reducing agent has not been reported.

The purpose of this paper is to use more effective additives to improve the microstructure and electrical conductivity of copper deposits. In this study, the effect of $K_4Fe(CN)_6$ in the bath on the microstructure and the electrical resistivity of the copper deposits was investigated.

Experimental

Material

Plain weave 100% polyester fabric (47×40 counts /cm^2, 84 g/m^2) in white color was used as the substrate. Copper sulfate, (>99.0%), EDTA, potassium ferrocyanide, glyoxylic acid and sodium hydroxide were purchased from Aladdin Reagent Co. Ltd. All chemicals were of analytic grade and used without further purification.

Electroless copper plating

Polyester fabrics were washed with deionized water. The fabrics were impregnated into 5g/l copper sulfate solution for 10min, and then they were placed into 5g/l sodium borohydride solution for 10min without being washed. After that, the fabrics were impregnated into copper plating solution. The solution for copper plating was prepared by copper sulfate, EDTA, glyoxylic acid and potassium ferrocyanide and deionized water. The concentrations of copper sulfate, EDTA and glyoxylic acid in the plating solution were 10g/l, 20g/l and 10g/l, respectively. The concentration of potassium ferrocyanide changed from 5 to 30mg/l. Sodium hydroxide was used to adjust the pH of the plating solution. After copper plating, the fabrics were washed by deionized water and dried at 70℃.

Characterization

The electronic balance (Hang Ping FA2004N) was used to weigh the fabrics before and after copper plating. The deposition rate was calculated by the following equation.

$$\mathrm{d} = \frac{m_2 - m_1}{S \times t} \quad (1)$$

Where *d* is deposition rate; m_1 and m_2 are the weight of fabrics before and after copper plating, respectively; S is area of the fabrics and t is time of copper plating, respectively.

SEM images were obtained using TM-3000 Tabletop Microscope with various magnifications to study the surface morphology of the polyester fibers and the copper coated polyester fibers. Elemental composition of the copper plated fabrics was obtained by EDX Detector on JEOL JSM6490. Crystal structure of copper deposits on the polyester fabrics was characterized by D8 DISCOVER X-Ray Diffractometer.

Surface resistance of the copper coated polyester fabrics was measured by RTS-9 Dual Electric Logging Four Point Probe Tester, produced by Guangzhou Four-point Probe Technology Company.

RESULT AND DISCUSSION

Effect of $K_4Fe(CN)_6$ on deposition rate of the electroless Cu plating

The effect of $K_4Fe(CN)_6$ concentration on the deposition rate of electroless Cu plating is shown in Fig. 1. The deposition rate sharply decreased between 5 and 15 mg/L $K_4Fe(CN)_6$ concentration and then levelled off. This effect may be due to the higher dielectric constant of $K_4Fe(CN)_6$ adsorbed onto the deposit surface. This increased the thickness of electric double layer and decreased the electron mobility and nucleation rate.

However, the deposition rate was relatively stable when the $K_4Fe(CN)_6$ concentration was between 15 and 30 mg/L. The above-mentioned adsorption achieved equilibrium state. Furthermore, the strong complex ability of the $K_4Fe(CN)_6$ and Cu ion, which reduced the concentration of the Cu ion, improved the stability of the plating solution and decreased the reduction rate of Cu ions.

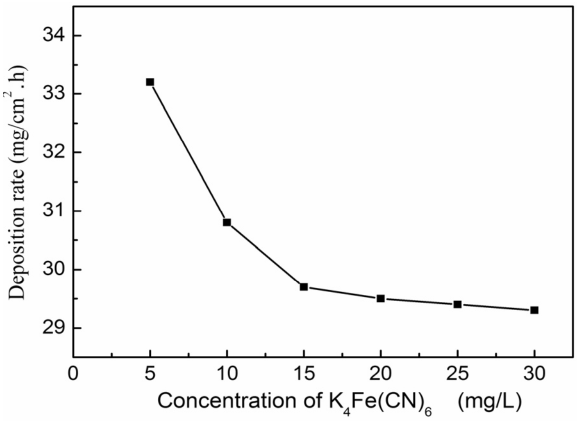

Fig.1. Influence of concentration of $K_4Fe(CN)_6$ on the deposition rate

Surface morphology of copper plated fibers

The SEM morphology of the Cu deposited fabrics obtained at different $K_4Fe(CN)_6$ concentrations are presented in Fig. 2. Figs. 2(a) and (b) show that the Cu grains were plated on the fabric, but the existence of large particles in copper deposits will affect the conductivity of deposits. It can be seen from Figs. 2(c)–(e) that the electroless copper film covered on fabric surface is the more uniform, compact and smoother with the increase of $K_4Fe(CN)_6$ concentration in the plating solution. The color of the deposits also had a corresponding improvement, changing from red-brown to Cu-bright with an increase of $K_4Fe(CN)_6$ concentration. The Cu deposits became bright and even, and the grain gap was not observed in Fig. 2(d) when 20 mg/L $K_4Fe(CN)_6$ was added in the plating solution. The bright appearance of the deposits generally indicates better mechanical and electrical properties.

Chemical composition of copper plated fabrics

The composition of deposits was tested by Energy Dispersive X-ray Detector. Fig.3 shows the EDX spectrum of the copper plated polyester fabrics when 20 mg/L $K_4Fe(CN)_6$ was added in the plating solution. It is obvious that there are three characteristic peaks of copper, and characteristic peaks of oxygen and carbon. From the data of EDX spectrum, there are the elements of copper (81.92%), oxygen (4.5%) and carbon (16.62%) in the deposition. It indicates that the coating is mainly composed of Cu, and other possible ingredient, such as Cu_2O, is invisible. Therefore, after the copper plating, metallic copper is deposited on the fabric.

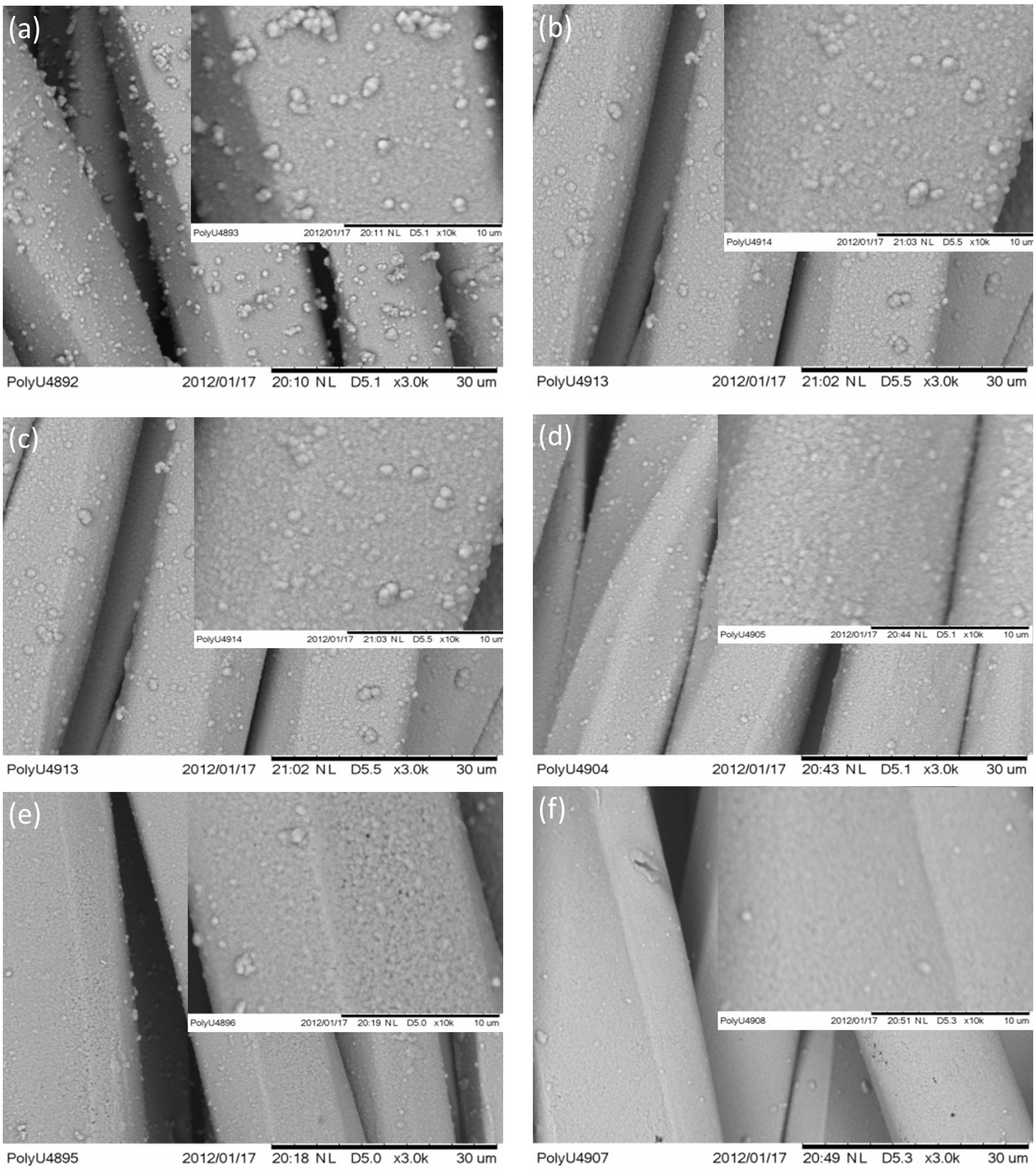

Fig.2. The SEM of copper plated polyester fibers with different concentrations of $K_4Fe(CN)_6$ (a)5mg/L, (b)10mg/L, (c)15mg/L, (d)20mg/L, (e)25mg/L and (f)30mg/L.

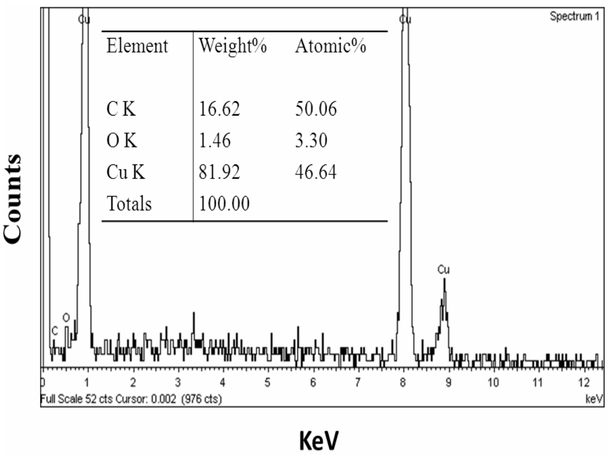

Fig.3. EDX image of copper plated polyester fabric

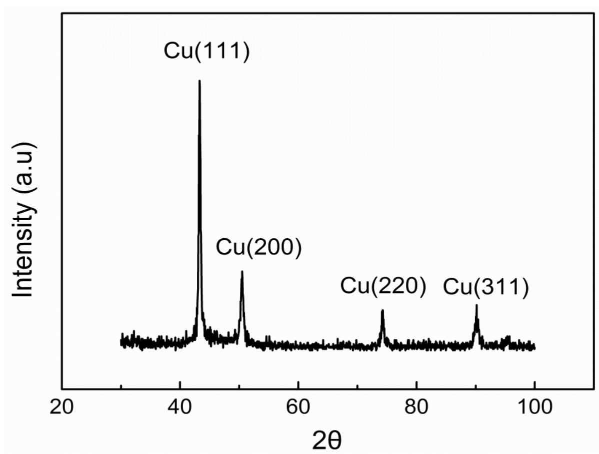

Fig.4. XRD pattern of copper plated polyester fabric

Crystal Structure

Fig.4 shows the X-ray diffraction (XRD) pattern of the electroless plating copper on polyester fabric when 20 mg/L $K_4Fe(CN)_6$ was added in the plating solution. From the pattern, the sharp peaks that appear at 2θ = 43°, 50°, 74°, and 90° represent crystals planes of cubic metallic copper (111), (200), (220) and (311), respectively, confirming the existence of copper in the form of Cu crystals, which is in a very good agreement with the standard of copper peaks (JCPDS Card No.85-1326).The diffraction peaks of copper oxide are not detected in the XRD pattern. The result shows that the plated copper is pure and there is no impurity Cu_2O under this process conditions. The peak (111) is sharp and the full width at half maximum (FWHM) is small. This leads to good crystallization.

Surface Resistances

The effect of $K_4Fe(CN)_6$ concentration on the electrical resistance of the Cu deposited polyester fabric in the condition of the same weight of copper is illustrated in Fig. 5. Initially, electrical resistance decreased sharply. At the same Cu weight gain, it was observed that higher $K_4Fe(CN)_6$ concentration resulted in lower electrical resistance. Conductivity of the deposits improved with the increase in $K_4Fe(CN)_6$ concentration in the plating solution. The surface resistance is 13.8 mΩ/sq when 20 mg/L $K_4Fe(CN)_6$ was added in the plating solution. The improved morphology of the Cu deposits accounted for this effect because the deposit structure was compacted and the deposit surface was smoothened with the addition of $K_4Fe(CN)_6$ to the plating solution.

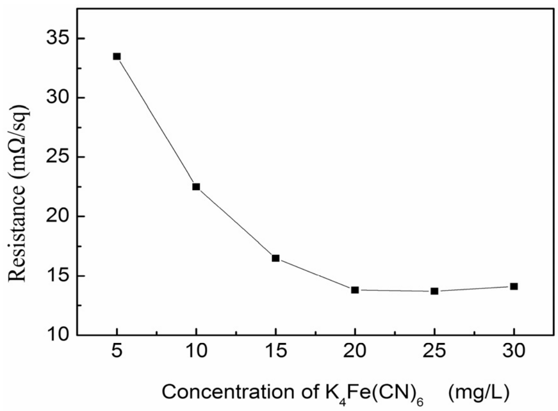

Fig.5. Surface resistance of copper coating on polyester fibers with different concentrations of $K_4Fe(CN)_6$

4. CONCLUSION

Copper was deposited on polyester fabric using glyoxylic acid as reducing agent with different concentrations of $K_4Fe(CN)_6$ in the plating solution by electroless plating. The deposition rate obviously decreased with the rise of the concentration of $K_4Fe(CN)_6$ in the bath. Copper coating on plated polyester fabrics mainly contained metallic copper with good crystallinity when 20 mg/L $K_4Fe(CN)_6$ was added in the plating solution. The surface resistance is 13.8 mΩ/sq when 20 mg/L $K_4Fe(CN)_6$ was added in the plating solution.

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