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Electroless plating of Cu–Ni–P alloy on PET fabrics and effect of plating parameters on the properties of conductive fabrics

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Abstract

Electroless plating of Cu–Ni–P alloy on polyethylene terephthalate (PET) fabrics and effect of plating parameters on the properties of alloy-coated fabrics were investigated. The deposition rate increased with the increase of temperature, pH and nickel ion concentration. The addition of $K_4Fe(CN)_6$ to the solution could reduce the deposition rate and make the deposits become more compact. The color of the deposits also had a corresponding improvement, changing from dark-brown to copper-bright with the addition of $K_4Fe(CN)_6$ to the plating solution. The deposits have an intensified copper (1 1 1) plane orientation with the addition of $K_4Fe(CN)_6$ to the plating bath. The surface electrical resistance of alloy-coated fabrics increased with increase of nickel ions concentration in the solution. The addition of $K_4Fe(CN)_6$ to the solution reduced significantly the surface resistance of alloy-coated fabrics. The conductive fabrics with high shielding effectiveness could be prepared at the optimum condition with 0.0038 M nickel ions and 2 ppm $K_4Fe(CN)_6$. As the deposit weight on the fabric was 40 g/m^2, the shielding effectiveness of alloy-coated fabrics was more than 85 dB at frequency ranging from 100 MHz to 20 GHz.

Keywords: Electroless plating; Cu–Ni–P alloy; PET fabric; Deposition rate; Crystal structure; Surface morphology; Surface resistance; Shielding effectiveness

1. Introduction

As the use of electronic products and communication instruments increases, electromagnetic interference (EMI) is a problem for the lifetime and efficiency of the instruments. In addition, the regulation of EMI shielding such as by the Federal Communications Commission (FCC) has become more rigorous [1]. Although EMI-transmitted electromagnetic waves can easily damage electronic components, good conductive materials can act as a shield against electromagnetic penetration [2]. Conductive textiles, which are coated with aluminum, copper, silver and nickel, are an important kind of materials for preventing electromagnetic interference. Conductive fabrics coated with different metals have been used in many electronic instruments in a variety of manufactured forms such as fabric tape or foam gaskets. Current metal coating techniques on fabrics are conductive paints and lacquers, sputter coating, vacuum deposition, flame and arc spraying, and electroless plating [3,4]. Among them, electroless plating is probably the preferred way of producing metal-coated EMI shielding textiles. This technique has advantages, such as coherent metal deposition, excellent conductivity, shielding effectiveness (SE) and applicability to complex-shaped materials or nonconductors. It can be applied to almost all fiber substances. It can be performed at any step of textile production such as yarn, stock, fabric or cloth [5].

Because of the high conductivity of copper, electroless copper plating is currently used to manufacture conductive fabrics. The effect of plating process on the SE of copper-coated fabrics has been studied by some researchers [6–8]. The SE of copper-coated fabrics is all not more than 75 dB and electroless copper plating solutions all use formaldehyde as reducing agents [9]. It is operated at pH values above 11 and this bath may release hazardous gases during operation [10]. Therefore, sodium hypophosphite, as the reducing agent, is especially attractive because of its low pH, low cost, and relative safety features [11,12]. Several papers have studied the electroless copper plating solutions using hypophosphite as reducing agent [13–17]. Those researches focused mainly on the effect of additives on the properties of the deposits and the application of electroless copper plating to fabrication of printed circuit boards.

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However, the hypophosphite-based electroless copper plating process is more complicated than formaldehyde-based bath because copper is not a good catalyst for the oxidation of hypophosphite resulting in little or no plating on a pure copper surface. One approach to catalyze the oxidation of hypophosphite is to add nickel ions to the bath, resulting in a very small amount of co-deposited nickel and phosphorus in the deposit. The nickel serves to catalyze the oxidation of hypophosphite, enabling continuous copper deposition [9]. Therefore, the deposit of electroless copper plating using hypophosphite as the reducing agent is actually Cu–Ni–P alloy.

The objective of this study is to apply the electroless plating of Cu–Ni–P alloy on PET fabrics using hypophosphite as the reducing agent to the preparation of conductive fabrics and investigate effects of operating parameters on the deposition rate, composition and properties of deposits such as the crystal structure, surface morphology and surface resistance.

2. Experimental

Polyethylene terephthalate (PET) fabrics (51 × 38 count/cm^2, 64 g/cm^2, taffeta fabric) were used as substrates. The surface area of each specimen is 100 cm^2.

Electroless plating was carried out by a multistep process, which included: scouring, rinsing, etching, rinsing, sensitization, rinsing, activation, electroless plating, rinsing and drying. The specimens were scoured in 10 g/L NaOH solution (1 L) at 70 °C for 3 min prior to use. The samples were then rinsed in distilled water and etched in a mixture of 15 g/L $KMnO_4$ and 40 mL/L H_2SO_4 solution (1 L) for 3 min. Surface sensitization was conducted by immersion of the samples into an aqueous solution (1 L) containing 10 g/L $SnCl_2$ and 40 mL/L 38% HCl at 30 °C for 3 min. The specimens were then rinsed in distilled water and immersed in an activator solution (1 L) containing 0.50 g/L $PdCl_2$ and 20 mL/L 38% HCl at 40 °C for 5 min. The specimens were then rinsed in a large volume of deionized water for more than 5 min to prevent contamination of the plating bath. The specimens were then immersed in the electroless plating bath for 10 min. The volume of the plating bath was 3 L. The electroless plating bath contained: 0.032 M copper sulfate, 0.0019–0.0076 M nickel sulfate, 0.283 M sodium hypophosphite, 0.071 M sodium citrate, 0.493 M boric acid and 0–6 ppm $K_4Fe(CN)_6$. Deionized water was used to prepare the solutions. The pH was adjusted using NaOH or H_2SO_4 to a final value of 8.5–10.5. The temperature was held at 60–75 °C. Finally, the samples were rinsed with distilled water, ethyl alcohol and dried in an oven at 55 °C.

Deposition rate was calculated from the weight gain of the specimen before and after plating, the surface area and plating time. The units are expressed as g/(m^2 min).

A PARSTAT model 2273 potentiostat was used for electrochemical measurements. The linear sweep voltammetry (LSV) experiments were carried out at 70 °C and at a scan rate of 10 mV/s. The working electrode was pure copper with 1.0 cm^2 surface area; the counter electrode was a platinum foil, and the reference electrode was a commercial Ag/AgCl electrode saturated with KCl. Prior to each test, the electrodes were immersed in the electrolyte until a steady open circuit potential (OCP) was reached.

The crystal structure of the deposits was investigated using X-ray diffraction (XRD, Cu Kα radiation and graphite filter at 40 kV and 100 mA). Scanning electron microscope (SEM, JEOL JSM-6460) was used to characterize the surface morphology of the deposits. The chemical composition of the deposits was determined using energy dispersive X-ray (EDX) analysis attached to the SEM.

The surface resistance R_s was measured by the four-probe method as described in ASTM F 390. R_s is considered to be the resistance of a square sample, the units of R_s are commonly expressed as ohms-per-square or Ω/sq.

The coaxial transmission line method as described in ASTM D 4935-99 was used to test the EMI shielding effectiveness of the conductive fabrics. A number of researchers have described the detailed set-up and test procedure using a plane-wave electromagnetic field [18–20].

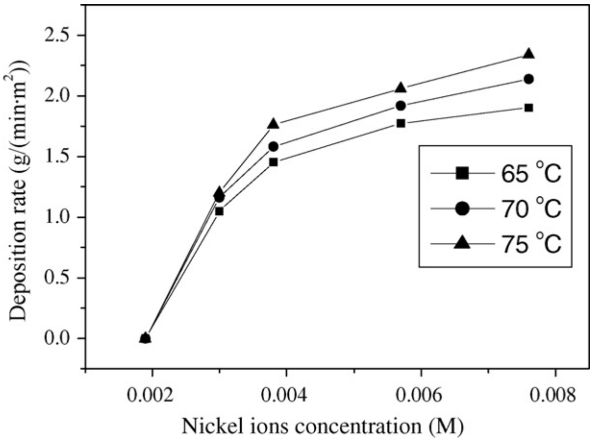

Fig. 1. The effect of nickel ions concentration on the deposition rate at different temperature (pH 10.0; $K_4Fe(CN)_6$: 0 ppm).

3. Results and discussion

3.1. Deposition rate

The effects of bath composition, pH and temperature on the deposition rate were studied.

As mentioned above, nickel ions were added to the bath to catalyze the oxidation of hypophosphite. When the nickel ions concentration in the bath is low, the deposition rate of the plating decreased with time, and finally stopped because the surface catalytic activity was not replenished. Thus, it was necessary to maintain the nickel ions concentration above a critical value in the bath to sustain the deposition rate. The effect of nickel ions concentration on the deposition rate at different temperature is shown in Fig. 1. It shows that the deposition rate increased when the nickel ions increased from 0.0030 to 0.0076 M at 65–75 °C. However, when nickel ions concentration was lower than 0.0030 M, a thin layer of deposits was obtained, and then electroless plating stopped. Therefore, 0.0030 M is the critical point of nickel ions concentration in the solution.

The dependence of deposition rate on pH for different temperature is shown in Fig. 2. At 60 °C, pH had little influence

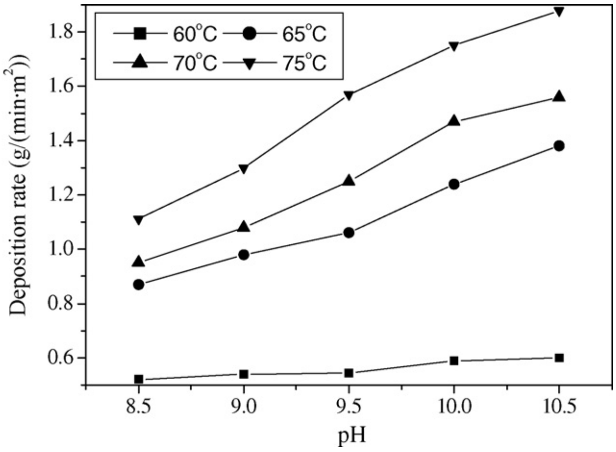

Fig. 2. The effect of pH on the deposition rate at different temperature (Ni ions: 0.0038 M; $K_4Fe(CN)_6$: 0 ppm).