Applied Surface Science 271 (2013) 303–310

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Adhesion improvement of electroless copper plating on phenolic resin matrix composite through a tin-free sensitization process

Yong Wang, Cheng Bian, Xinli Jing*

Department of Applied Chemistry, School of Science, Xi'an Jiaotong University, Xi'an 710049, People's Republic of China

ARTICLE INFO

Article history:
Received 11 October 2012
Received in revised form 23 January 2013
Accepted 26 January 2013
Available online 4 February 2013

Keywords:
Phenolic resin matrix composite
Electroless copper plating
Sensitization
Adhesion

ABSTRACT

In order to improve the adhesion of electroless copper plating on phenolic resin matrix composite (PRMC), a new and efficient tin-free sensitization process has been developed. Electroless copper plating could be achieved in three steps, namely: (i) chemical etching with potassium permanganate solution; (ii) sensitization and activation with glucose and silver nitrate solution respectively; and (iii) electroless copper plating. Compared with the sample sensitized with stannous chloride ($SnCl_2$), the copper plating obtained in the tin-free process showed excellent adhesion with the PRMC substrate, but had lower plating rate and conductivity. Additionally, the morphology of the copper plating was affected by the sensitization process, and the tin-free process was conducive to the formation of the large spherical copper polycrystal. Although the process is slightly complicated, the new sensitization process is so low-cost and environment-friendly that it is of great significance and could be applied into large-scale commercial manufacturing.

1. Introduction

The deposition of metal coatings on polymers encompasses a broad range of technologically important processes, with applications ranging from communication devices to automotive and electrical industries. Recent years have witnessed a surge of research activities in the metallization processes on polymer substrates, and numerous metallization methods have appeared, such as chemical vapor deposition, electroless plating, vacuum deposition and metal sputtering [1]. Among those methods, electroless plating appears to be one of the most frequently adopted methods to deposit metal coatings on various insulating substrates because of low cost, simplicity of processing and applicability to complicated-shaped substrates. Electroplating is usually required for the electroless plated substrates to obtain excellent metal coatings, and it is a key to improve the adhesion between the metal plating and substrate in such a combination method.

The adhesion between metal plating and substrate depends largely on the chemical composition and physical state of the substrate surface, which could be improved significantly by surface modification. High energy-irradiation method [2–4] and coating reactive intermediate layer [5–7] have been considered as efficient ways of surface modification for electroless plating on polymers, but, these methods are costly and complex. Unlike the methods mentioned above, wet etching treatment by solvent or solution is simple and effective, which could increase the roughness and hydrophilicity of the substrate surface.

The activation process, which could introduce the catalytic sites onto the surface of substrate, usually precedes the electroless plating process, and is the key step for electroless plating. According to the number of steps during the process, the activation process could be classified into "sensitization and activation two-step" method [8] and "sensitization and activation one-step" method [9]. The acid solutions of stannous chloride ($SnCl_2$) and palladium chloride ($PdCl_2$) are successively employed in the conventional "two-step" activation process, while a colloidal mixture of $SnCl_2$ and $PdCl_2$ is used during the "one-step" process. Despite the extensive applications of traditional Sn-Pd catalysts for electroless metal deposition, several shortcomings such as instability and lack of selectivity are still existed.

$SnCl_2$ is frequently used in the sensitization process, and it could be hydrolyzed to form hydrogel easily in water and adsorbed on the surface of substrate, and thus is applicable to almost all of the polymer substrates [10,11]. However, the residual tin ions on the surface of substrate have a negative effect on the uniformity and adhesion of the metal plating, resulting in the poor quality of electroless plating. Some researchers have attempted to avoid the negative effect of the tin ions by ion palladium activation process [12,13], and the method has been applied in some cases. In addition, ultrasonic wave has been used to remove the residual tin ions on the substrate surface [14]. Due to the technical and cost issues, these methods mentioned above are still not used widely in industry. In the present work, glucose is used to completely replace $SnCl_2$ in order to avoid the negative effect of the tin ions.

* Corresponding author. Tel.: +86 29 68640809; fax: +86 29 83237910.
E-mail addresses: rgfp-jing@mail.xjtu.edu.cn, xljing@mail.xjtu.edu.cn (X. Jing).

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http://dx.doi.org/10.1016/j.apsusc.2013.01.188

Despite the emergence of a variety of high-performance thermoset resins, phenolic resin (PR) is still one of the most commonly used polymers in areas such as aerospace and building industries [15]. The deposition of metal coatings on PR and phenolic resin matrix composite (PRMC) broadens the range of applications and creates considerable added values [16]. Although much research has been performed on the metallization processes of polyethylene terephthalate [17,18] and acrylonitrile-butadiene-styrene [7,19], little attention now has been paid to the metallization process of PRMC. Liu plated nickel on phenolic plastic etched with sulfuric acid-hydrogen peroxide and obtained good-performance nickel plating [20].

In the present work, wet chemical etching method was employed to modify the surface of PRMC composed of PR, glass fibers, silica and calcium carbonate particles. The electroless copper plating was preceded by sensitization and activation steps, during which glucose and silver nitrate were used respectively. The chemical composition of the substrate surface was characterized by energy dispersive X-ray (EDX) analysis and X-ray photoelectron spectroscopy (XPS), and the reaction mechanisms were also discussed. The appearances of the sample surface before and after each step were characterized by scanning electron microscopy (SEM).

2. Experimental

2.1. Materials

PR (henna liquid with an average molecular weight of 980 g/mol, Beijing glass fiber reinforced plastics Co., Ltd.), short-cut glass fiber (6 mm, Zibo Sanyu Composite Material Co., Ltd.), silica powder (1250 mesh, Shaanxi Jinying Super Fine Materials Co., Ltd.) and calcium carbonate powder (800 mesh, Shaanxi Gaoguan Nonmetal Mine Products Appliance and Development Co., Ltd.) were industrial grade, while other reagents were analytical grade. All of the materials were used without further purification unless otherwise mentioned. Deionized water was used for all experiments.

2.2. Preparation and molding of PRMC

Zinc stearate, magnesia, hexamethylenetetramine, mixed fillers (mass ratio of calcium carbonate and silica powder is 1) and glass fibers were added into the liquid PR orderly and intensively stirred to uniform at room temperature. The obtained mixture was placed in the air at least for 24 h to remove the solvent (ethanol) and then heated for 30 min at 100 °C. The heated PRMC was molded under the condition of 160 °C and 20 MPa, and the molding time was calculated according to the thickness of products (2 min/mm thickness). The cured PRMC was cut into specific sizes in accordance with the requirements of the tests.

2.3. Pre-treatment and electroless plating of PRMC

Pre-treatment was required before electroless copper plating of PRMC. The compositions and conditions for each step were shown in Table 1. Firstly, the PRMC was cleaned with alkaline degreaser and then rinsed by water. Secondly, the substrate was etched with etching solution and rinsed by water for three times. Afterwards, neutralization was used to reduce the residual oxidants on the surface of PRMC. Then the prior etched substrate was sensitized by glucose solution. Served as control group, acidic $SnCl_2$ solution was also used to sensitize the PRMC. The sensitized substrate was reductive, on which catalyst could be produced during the following activation process. Finally, the substrate was plated in an acid copper sulfate solution.

2.4. Characterization

2.4.1. XPS

The XPS measurements of PRMC (3 mm × 3 mm × 1 mm) were carried out by ESCA LAB 220-XL XPS, monochromatized Al Kα radiation (1486.6 eV) was used as the excitation. Elemental binding energies were corrected with the C1s binding energy at 284.6 eV.

2.4.2. SEM

SEM images were obtained using field emission scanning electron microscope JSM-6700F manufactured by JEOL. The samples (3 mm × 3 mm × 1 mm) were deposited on a sample holder with a piece of adhesive carbon tap.

2.4.3. EDX

Oxford instruments INCAX-SIGHT 7547 energy dispersive X-ray spectroscopy was applied to analyze the contents of elements on the treated surface of PRMC. The samples (3 mm × 3 mm × 1 mm) were deposited on a sample holder with a piece of adhesive carbon tap.

2.4.4. Contact angle measurement

The hydrophilicity of the surface was observed by contact angle measured with JY-82 contact angle tester (Chengde Dahua Testing Machine Co., Ltd.) at 25 °C. 10 μl of deionized water were employed to form a three-phase system on the surface of samples (20 mm × 50 mm × 2 mm).

2.4.5. Conductivity measurement

The conductivity of the copper plating was measured by SZ85-digital four-probe conductivity measurement (Suzhou Diangong Instrument Factory). The distance between two tips was 1 mm.

2.4.6. Adhesion strength measurement

The adhesion strength of copper plating was tested by adhesionmaster QFD (Tianjin Material Testing Machine Factory) according to GB1720-79 (Paint and film adhesion strength measurement, our results showed the method was also applicable to metal plating). The adhesion strength is divided into 7 grades ranging from grade 1 to 7 according to the completeness of copper plating (as

Table 1
The compositions and conditions of each step during the electroless plating process.

Steps	Compositions	Conditions
Degreasing	NaOH 1 M, Na_2CO_3 0.5 M, OP 3–5 mL/L	60 °C, ultrasonic, 15 min
Etching	$KMnO_4$ 0.2 M, H_2SO_4 0.5 M	60 °C, 30 min
Neutralization	$H_2C_2O_4$ 0.5 M	40 °C, 10 min
Sensitization	(a) $C_6H_{12}O_6$ 0.2 M	(a) 25 °C, 30 min
	(b) $SnCl_2{\cdot}2H_2O$ 0.2 M, HCl 0.5 M	(b) 25 °C, 10 min
Activation	$AgNO_3$ 0.03 M, $NH_3{\cdot}H_2O$ 0.1 M	25 °C, 10 min
Electroless copper plating	$CuSO_4$ 0.07 M, $C_4O_6H_4KNa$ 0.2 M, NaOH 0.4 M, $NiSO_4$ 5 mM, $C_{10}H_8N_2$ (α,α′-Dipyridyl) 0.2 mM, HCHO 0.2 M	25 °C, 60 min