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3D porous polysiloxane ion-adsorption films for additive fabrication of conductive patterns with high adhesion

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ABSTRACT

Fabrication of conductive patterns by selective electroless plating is a widely studied process in recent years for its advantages of lower waste, simpler process, less pollution and lower cost compared to the traditional subtractive process. But the poor adhesion of the as-fabricated patterns is the prior problem of this process, which limits the thickness of the conductive patterns in sub micrometer range and thus degrades the electrical properties of the patterns. Many chemical and physical modifications have been used to increase the chemical bonding or physical interaction between substrates and deposited metal, but the effects are limited, especially after thick metal is deposited. However, increasing the interfacial mechanical anchor is an effective alternative to enhance the adhesion but has often been neglected. In our previous work, we have developed a novel patterning-adsorption-plating (PAP) process to additively fabricate copper patterns on flexible polymer substrates. In this paper, polystyrene (PS) microspheres are added into the ion-adsorption ink as templates to fabricate three-dimensional (3D) porous polysiloxane films. Thereafter, the as-fabricated copper patterns show excellent conductivity competitive to that of bulk copper and good adhesion with a distinct increase of mechanical anchor.

1. Introduction

Conductive patterns, as basic elements of electronic devices, are essential parts of printed circuit boards (PCB), flexible printed circuit boards (FPC), radio frequency identification (RFID) tags, touch screens, wearable electronics, *etc.* [1–5]. The traditional method to fabricate conductive patterns of PCB, FPC, RFID, *etc.* is called subtractive process. Metal foil was cladded on substrates with a layer of photoresist on it and the designed patterns were selectively exposed to UV through a photomask. Then the uncured photoresist was removed, followed by etching the metal underneath and removal of the residual photoresist. However, the process appears to be complicated, time-consuming, environmentally unfriendly and limited in line width [6–8].

Additive processes, including printing of conductive paste, conductive ink, selective electroless plating, *etc.* to fabricate conductive patterns show great advantages compared to the subtractive process for their lower cost, less waste, fewer procedures and finer line width, which have been attracting enormous fundamental and technological interests in recent years [9–13]. Herein, inkjet printing of conductive ink, which is etching free with simple procedures and low waste, has been widely studied in the past decade. The conductive ink, mainly containing nanosized metal particles dispersed in solvent, is inkjet printed on substrates and sintered to fabricate conductive patterns [14–16]. Sintering step after printing is essential to remove organic components in the conductive ink and melt the conductive nanoparticles. Thus, the resistivity of the sintered conductive patterns can be comparable to that of bulk metal. However, the sintering procedure with high temperature in atmosphere often leads to the oxidation of non-noble conductive ink and degradation of flexible polymer substrates with low thermal resistance [17–19]. Many sintering technologies have been developed to sinter non-noble conductive ink in ambient condition, such as photonic sintering, microwave sintering, plasma sintering [20–22], but the high cost and low efficiency of the required equipment limit their applications in large scale. Conductive paste, in which conductive pigments are dispersed in

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polymer binder, has been widely used by screen printing in the fabrication of the conductive patterns of RFID, sensors, *etc.* As heat treatment is also needed after printing, this method is confronted with the same oxidation and cost problems with conductive ink.

Electroless plating, which is the chemical reaction between metal ion and reductant to produce pure metal in the present of the catalyst, is widely applied in electronic industry. Selective electroless plating, in which catalyst can be patterned by screen printing, inkjet printing, photolithography, *etc.* is a promising way to fabricate conductive patterns with high conductivity. Non-noble metal patterns with equivalent conductivity of bulk metal can be prepared, making it a low-cost process to prepare conductive patterns with excellent properties.

However, the poor adhesion of patterns after long time electroless plating is the major problem of selective electroless plating process. In order to guarantee the adhesion, the plating time is limited, leading to low line thickness and high line resistance [23–25]. Generally speaking, the strategies to improve the adhesion include enhancing the chemical bonding (ionic bonding, covalent bonding, hydrogen bonding), physical interaction (van der Waals interaction, electrostatic interactions), mechanical anchoring, interfacial diffusion *etc.*, where the first three strategies are the prime ones [26].

Many chemical and physical modifications have been applied to the substrates and ink to increase chemical bonding and physical interaction between substrates and deposited metal. Hsu et al. modified polyvinyl alcohol-capped palladium nanoclusters (PVA-Pd) catalyzed silicon wafers using 3-2-(2-aminoethylamino) ethylamino propyl trimethoxysilane (ETAS). The pull-off strength of as-prepared 200 nm-thick electroless plated nickel-phosphorus films on the silicon wafers after 700 °C annealing can increase to 7.86 MPa [27]. Jeong et al. and Jang et al. strengthened the binding between conductive patterns and substrates by coating an adhesive layer of 3-aminopropyltriethoxysilane (APTES) on substrates and adding glass frit additives into conductive ink, respectively. The adhesion of as-fabricated conductive patterns can all be categorized as 5 B following the standard of ASTM D3359 [28,29]. Hou *et al.* used a blue pulse to scribe and modify the surface of flexible sandpaper substrates. Gold nanoparticles were then absorbed to the surface laser scribing zone to catalyze the electroless copper plating. The adhesion strength of fabricated conductive patterns can reach 39.68 N m^{-1} [30]. In order to reduce the electrical and signal attenuation in circuitry and thus fulfill the requirement of practical application, the thickness of the conductive patterns for PCB, FPC, RFID, *etc.* should be higher than 10 μm. However, the thickness of the conductive patterns fabricated by these methods cannot fulfill the requirement because the adhesion of the patterns decreases significantly with the thickness increases. Besides, some of these methods can only be used on certain substrates or under extreme treatments, which are not applicable for common conductive patterns on flexible polymer substrates such as poly(-ethylene terephthalate) (PET) and polyimide (PI) substrates.

Except generating chemical bonding, increasing mechanical anchor at interfaces is a facile and efficient method to increase interfacial adhesion. In general, the surface energy term G_0 from the standard definition of surface energy, i.e. the fracture energy per unit area, is often used to evaluate the energy necessary to break the interfacial interaction and produce new surfaces. A rough or microporous surface leads to an effective increase of surface area per area of the substrate, leading to an increase of mechanical anchor as well as chemical bonding (e.g. Cu-S, Cu-N bonds) and physical interaction (e.g. van der Waals interaction) between the conductive patterns and the coarse ion-adsorption film beneath (Fig. 1c). Hence, the interfacial adhesion is improved with a higher value of G_0 [26].

In previous study, we have developed a novel patterning-adsorption-plating (PAP) process to additively fabricate conductive patterns on flexible polymer substrates [31,32]. Polysiloxane functional ink prepared by hydrolyzing APTES with 3-mercaptopropyltriethoxy silane (MPTES) was directly coated on a substrate to form an ion-adsorption film. Silver ion, which was reduced to catalytic silver nanopaticles during electroless plating, was then adsorbed to designed parts through photoresist [32]. Afterwards, the patterns were metalized by electroless plating (Fig. 1a). When adding the solvent with low polarity into the ink, the mechanical anchor between the ion-adsorption coating and deposited metal was increased with an increase of the surface roughness of the cured ion-adsorption coating, leading to an improvement of adhesion compared with the conductive patterns prepared using the functional ink with high-polarity solvent. However, the roughness repeatability of the ion-adsorption coating by changing solvent is susceptible to many environment parameters, for instance, curing temperature, curing humidity, heating rate and storage temperature. In this paper, a more stable and efficient method is developed to increase the surface roughness of polysiloxane ion-adsorption coating. A 3D porous ion-adsorption film is fabricated (Fig. 1b) by coating PS microspheres-contained ion-adsorption ink on a polymer substrate, followed by drying, curing and dissolving the PS microspheres. Thereafter, the silver ion adsorption and electroless plating steps were applied. Finally, the metal patterns with high adhesion can be prepared (Fig. 1d). Compared to the film without PS microspheres (Fig. 1e), the 3D polysiloxane film with a distinctly rougher surface (Fig. 1f) has a higher value of fracture energy per unit area and thus increases the interfacial interaction between the deposited copper and the ion-adsorption film. Consequently, the adhesion of the patterns can be improved. Quantitative lead pull test was done to measure the adhesion strength of the conductive patterns about 11 μm in thickness fabricated by 15 min electroless plating and 5 min electroplating. Profilometer and scanning electron microscope (SEM) were respectively used to inspect the surface roughness and morphology of the 3D polysiloxane films. Finally, the relationship between the size and concentration of PS microspheres in the ink and the adhesion of conductive patterns was also conducted.

2. Experimental section

2.1. Materials

APTES (98%), MPTES (98%), ammonia (25%–28%), styrene, polyvinyl pyrrolidone (PVP), ethanol, sodium hydroxide, sodium carbonate, calcium chloride, ethyl acetate, silver nitrate, copper sulfate, EDTA disodium, potassium ferrocyanide, potassium sodium tartrate, formaldehyde, polyethylene glycol-1500 (PEG-1500), potassium pyrophosphate, ammonium citrate, PET film (125 μm in thickness) were all AR grade purchased from Sinopharm chemical reagent Co. Ltd. 2,2′-bipyridyl was AR grade obtained from Shanghai Aladdin reagent company. 2,2′-Azobisiso-butyronitrile (AIBN) was AR grade obtained from Tianjin Guangfu fine chemical research institute. Copper pyrophosphate hydrate (99%) was purchased from Shanghai Macklin Biochemical Co. Ltd. Photosensitive dry films (PH-2325) were obtained from Hitachi Chemical Co. Ltd. PI (200-H) films were purchased from DuPont Co. Ltd.

2.2. Synthesis of polystyrene microspheres

Styrene monomer was washed by 5% sodium hydroxide aqueous solution and deionized water, successively, to remove the inhibitor. The inhibitor-free styrene was collected by pumping