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Synthesis of vinyl acetate/Pd nanocomposites as activator ink for ink-jet printing technology and electroless copper plating

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ABSTRACT

A novel method for the preparation of palladium (Pd) nanoparticles reduced by vinyl acetate (VAc) oligomers is presented in this study. VAc was synthesized by free radical polymerization method which was based on vinyl acetate/potassium persulfate (KPS)/water system. The noble metal nanoparticles reduced and stabilized by vinyl acetate oligomer showed their well dispersion in the aqueous solution without surfactant and reductant in the mixture. These Pd nanoparticles can be used as activator to replace the traditional Pd/Sn colloid for electroless metal deposition. Based on our results, the coverage of Cu layer completely on substrate was achieved after 30 min deposition at 75 °C. The ink based on VAc/Pd colloids was successfully inkjet printed onto a FR-4 plate. The formed metallic palladium patterns were subjected to electroless copper plating, yielding well-defined copper lines. This process provides a clean, easy and low-cost method for preparation of high resolution Cu patterning.

1. Introduction

In recent years, the development of plastics to function as radio frequency identification (RFID) tag, sensor, transistor, and material circuits on the plastic substrate by ink-jet printing process has aroused attention in academia [1–6]. However, plastic needs to decorate metals onto polymer surfaces that it is generally lack of electrical conductivity before their applications in electrical industry. Therefore, it is important to increase electrical conductivity of circuits on the plastic substrate. Ink-jet printing because it is a noncontact technique, nonvacuum deposition processing and the image can be easily formed on substrate by computer has become as important as the other deposition techniques such as physical and chemical vapor deposition (PVD and CVD). On the other hand, fabrication of circuits by ink-jet printing of noble material nanoparticles or organic metal precursors on the plastic substrate has been widely investigated [7–10]. Generally, silver and gold nanoparticle-based inks are frequently used due to bulk silver and gold having a low resistivity [11–14]. However, to prevent agglomeration and precipitation of nanoparticles and to obtain stable nanoparticles dispersion, a large amount of surfactant must be added into the ink. It leads to lowering of the electrical conductivity of printing patterns. In addition, the process needs a high temperature sintering to form the metal thin film for a good electric property because sintering can make critical changes in morphology with formation of continuous interconnections [15,16]. However, sintering process will destroy the flexible structure because the glass transition temperature (T_g) of the flexible substrate is usually much lower than temperature for sintering. Therefore, electroless plating of metal film on plastic substrate is used instead of sintering to improve this process due to the plating temperature is less than 100 °C that can prevent substrate from damage. Generally, an activation step in which the activator will adsorb onto the insulating substrate is necessary to initiate the subsequent electroless plating. The most widely used activator is palladium/stannum (Pd/Sn) colloid. However, the Sn/Pd colloid is not suitable for using in ink-jet printing process because it is easy to deteriorate and block nozzles.

Recently, some researchers reported the use of nanosilver colloid, aqueous palladium(II) solution or platinum colloid as inks in an ink-jet printer [17–20]. After it was printed onto the substrate, it served as the activator for subsequent electroless plating. A modification of the surface is generally required to increase the surface adhesion to the catalyst. In our previous work, an organic solvent based-ink containing Pd nanoparticles reduced by styrene oligomers was ink-jet printed onto PET substrate, then, a Ni pattern was fabricated successfully by electroless Ni deposition [21]. From the economic and environmental point of view, as well as the simplicity in process operation, it is desirable to have a water-borne catalytic ink for the electroless copper process.

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In this study, vinyl acetate (VAc) oligomers with sulfate group on chain end were synthesized by a free-radical polymerization method. These VAc oligomers were further applied in reduction and stabilization of Pd nanoparticles without any surfactant. It is well known that polyvinyl acetate has a good adhesive property and hence it will improve adhesion between Pd nanoparticles and a wide range of substrates including surface unmodified one. We also demonstrated that the water-based ink containing these Pd nanoparticles can be ink-jet printed onto the FR-4 substrate, then, a Cu pattern is fabricated successfully by the electroless Cu plating.

2. Experimental

2.1. Synthesis of PVAc/Pd nanoparticles ink

All chemical reagents in this work were of analytic grade purity. The VAc/Pd nanoparticles were fabricated by a two step procedure: (1) the synthesis of VAc oligomers and (2) adsorption of the Pd nanoparticles onto the VAc. The vinyl acetate oligomer was synthesized by free-radical polymerization method. The potassium persulfate was used as the initiator to initiate the polymerization. The recipe used in this study was 95% of H_2O, 5% of vinyl acetate and 3×10^{-3} M of $K_2S_2O_8$ initiator. The polymerization was carried out at 70 ± 1 °C for 3 h in glass ampoules. The number-average molecular weight (Mn) of VAc oligomer measured by GPC was 5675 g/mol. VAc oligomer was used after purification.

After synthesis of the VAc oligomer, 20 mL of 800 ppm aqueous $PdCl_2$ solution was poured into a 50 mL VAc solution and mixed well. The Pd nanoparticles could be obtained at temperature of 100 °C for 20 min.

2.2. Ink-jet patterning and electroless Cu metallic line

These Pd nanoparticle-based ink with concentration of 1 wt.% was ink-jet printed onto a FR-4 substrate at room temperature by a commercially available piezoelectric Drop-on-Demand ink-jet Dimatix DMP-2811 printer. Two line widths (60 and 120 μm) for wiring patterns of Pd on the FR-4 substrate were printed. The printed Pd was utilized as the catalyst for subsequent electroless plating to obtain the desired Cu film. The electroless bath contains 14.9 g/L copper sulfate ($CuSO_4 \cdot 2H_2O$), 35.1 g/L ethylenediaminetetraacetic acid (Na_2EDTA), and 10 mL/L formaldehyde (HCOH). The electroless plating was carried out at the conditions of pH 12.5, T = 75 °C, stirring rate of 300 rpm and deposition time of 10, 20, and 30 min, respectively.

2.3. Analytical studies

The FTIR analysis was carried out using a BRUKER TENSOR 27 FTIR spectrometer. The FTIR spectra were recorded in a wave number range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1}. X-ray diffraction studies were performed by depositing the colloidal particles on a glass slide (after solvent evaporation) followed by drying in a vacuum. A Philips powder X-ray diffractometer PW 1710 with Cu Kα source (wavelength 1.542 Å) was used for recording the data at room temperature. The transmission electron microscopic studies of the samples were performed by depositing the colloidal particles on a copper grid and then air drying. A JEOL electron microscope JEM-1230 operated at 80 kV accelerating voltage was used for these measurements. A field emission scanning electron microscopy (FE-SEM, S-4700, HITACHI, 15 kV) and optical microscope (OM, MIRAGE L-2020A) was employed to examine the surface morphology and line width of Cu. Finally, the electrical resistivity of deposited Cu films was measured by a four-point probe (RT70/RG7S) at 25 °C.

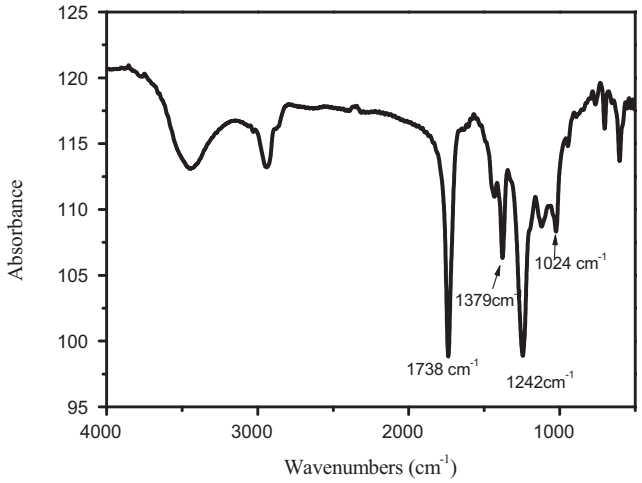

Fig. 1. IR spectrum of pristine VAc oligomer.

3. Result and discussion

3.1. Characterization of Pd nanoparticle

Fig. 1 displays the IR spectra of pristine vinyl acetate oligomer. As shown in the figure, the vibrational bands typical for polyvinyl acetate, such as C=O stretching at 1741 cm^{-1}, C–O–C symmetrical stretching at 1238 and 1024 cm^{-1} and CH_3 deformation at 1379 cm^{-1} are clearly observed. It indicates the successful polymerization of vinyl acetate oligomer.

Our previous result showed that the sulfate group could reduce Pd^{2+} to form Pd nanoparticles on the surface of the styrene oligomer [22]. In this study, potassium persulfate was used as the initiator so that the oligomer chains were capped with sulfate groups, thus, the formation of VAc/Pd nanocomposite according to expectation is confirmed by TEM image (Fig. 2). It shows from fig. 2 that the diameter of Pd nanoparticles reduced by VAc is 6 ± 2 nm. The reported diameter value for commercial Pd/Sn colloid is in the range of 10–80 nm [23,24] reported that the interfacial adhesion strength between polymer and metal was significantly enhanced through complex formation between metal and oxygen in an oxygen-containing polymer and showed the carbonyl functional group in PMMA interacted specifically with copper. Therefore, a strong

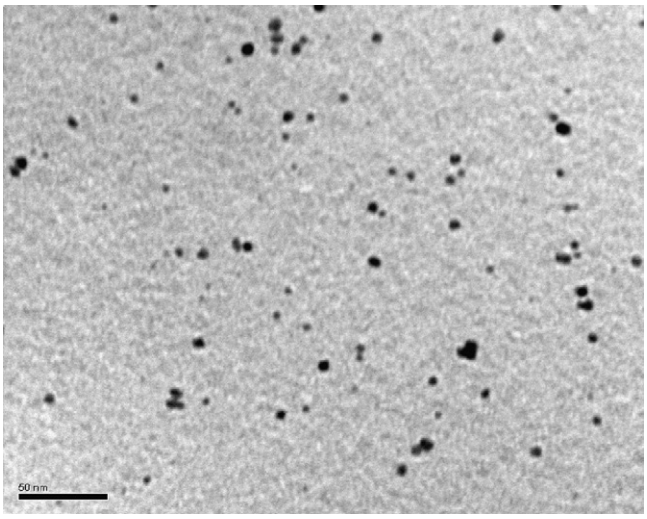

Fig. 2. TEM image of VAc/Pd nanoparticles.