



Site-selective metallization of polymeric substrates by the hyperbranched polymer templates



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ABSTRACT

We demonstrate a simple, cost-effective and universal technique for the fabrication of copper circuit pattern on flexible polymeric substrate. This method relies on a ternary polyethylenimine-poly(acrylic acid)-substrate film incorporating palladium catalysts, which are used as adhesive interlayers for the copper metallization of flexible polymeric substrates. We demonstrated the fabrication of patterned copper films on a variety of flexible polymers with minimum feature sizes of 200 μm. And the resulting copper circuit showed strong adhesion with underlying flexible polymeric substrates. The films were characterized by ATR FT-IR, contact angle, XPS, XRD, TEM and SEM. The direct patterning of metallic circuit on flexible polymeric substrate indicates great potential for the use in electronics industry.

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1. Introduction

Direct metal patterning onto dielectric substrates such as polymers for use in lightweight plastic electronic devices is of considerable interest due to their potential in electronic, semiconductor, biosensor, and nonlinear optical devices [1–5]. Flexible polymers such as polyimide (PI), poly(ethylene terephthalate) (PET), and poly(ethylene naphthalate) (PEN), have been employed extensively in multichip module (MCM) packaging, printed circuit board (PCB) fabrication, and ultra-large scale integrated circuit (ULSI) technology with high performance [6–8]. The merits of flexible polymeric matrices are their thermal plasticity available for microstructural tuning of the nanocomposite microstructure, and the diversity of chemical bonds and structures that provides additional possibilities for controlling a variety of physical and chemical properties [9]. The conventional patterning has been achieved by using lithographic method based on multistep resist patterning, etching, washing, and deposition of metallic layers [10], however, the application of this method is limited by its disadvantages, *i.e.* high energy consumption and high cost associated primarily with the complicated fabrication procedures. Therefore, there is an obvious need for a facile, faster and less expensive approaches are

currently of research interests for the fabrication of metal patterns on flexible polymers film.

An alternative synthetic route for patterning conductive metal thin films on flexible polymers surfaces is electroless plating. Electroless plating, based on the reduction of metallic ions from solution onto the substrate to be metalized without application of electric current, is especially appealing because of its low cost, inherent simplicity and selectivity, and ability to deposit high-quality films on very thin seed layers [11]. The general process involves three main steps: (i) surface preparation; (ii) surface activation by seeding catalytic metal and (iii) electroless plating bath to generate metal on the surface [12].

To activate the surface, palladium is employed as one of most commonly used catalysts for the electroless plating process. After seeding of palladium catalysts, the deposition of metal layers becomes an autocatalytic redox process due to the catalyst particle lowers the activation energy of metal formation by serving as a temporary electron bridge between the reducing agent and metallic ions [13]. Aldakov et al. reported metallization of gold substrates having self-assembled dithiol monolayers [13]. Their results showed that palladium catalysts incorporated in dithiol layers initiated the electroless metal deposition on gold substrates. Carmichael and co-workers oxidized various polymeric substrates to form surface-bound carboxylic acid groups, patterning of an aluminum porphyrin monolayers to bind a Pd/Sn colloidal catalyst that subsequently initiated the selective deposition of copper in an electroless plating solution, although the toxic Sn compounds were

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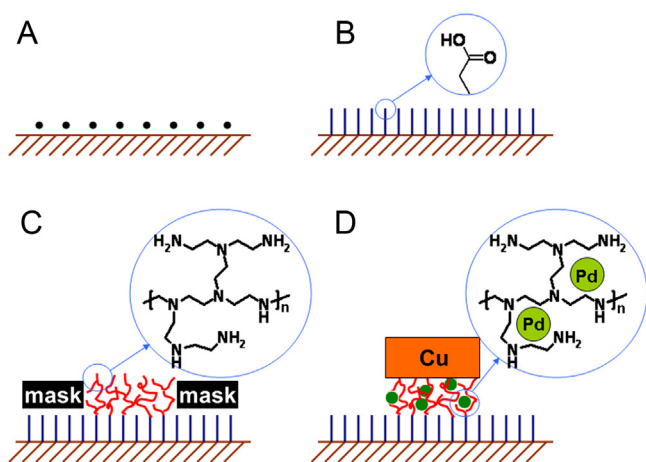


Fig. 1. Experimental scheme: (A) the active radicals on the surface of the pre-irradiated polymeric substrate; (B) the acrylic acid monomer is covalently anchored to the substrate to form surface-bound PAA; (C) PEI molecules were patterned and grafted to the PAA through a screen printed mask; (D) copper selectively deposits onto PEI-modified areas where the Pd catalyst had adsorbed.

employed [14]. Herein, we describe a facile method with potentially broad and perhaps universal scope to fabricate metal patterns onto obvious polymeric substrates *via* radiation technology for the branched polyethylenimine (PEI) molecule grafting and electroless metal deposition. Radiation technology, with applications in a variety of fields such as medical and biomaterials, has attracted substantial attention for it can initiate a radiation-induced graft polymerization to form strong bridges between macromolecules and substrate surface [15–17]. The design of the modification procedure is straightforward, as shown schematically in Fig. 1, monomers containing $-\text{COOH}$ were grafted on a pre-irradiated polymeric substrates and branched polyethylenimine (PEI) were subsequently introduced onto the masked polymeric substrates with surface-bound $-\text{COOH}$ groups as the selective adsorbents for the metal catalysts [18]. The technique shows promise for access to the modification of the most polymeric substrate, and therefore should find broad usage in fields including electronics, optics and information storage.

2. Experimental

2.1. Materials

Deionized water of 18 M Ω resistivity was used for all experiments. Acrylic acid (AA) and dimethylamine borane (DMAB) were purchased from Sinopharm Chemical Reagent Ltd. (China), PdCl₂ was provided by Beijing Jiuzhoumol Ltd. (China), the electroless Cu bath was purchased from Nanjing Delei Technology Ltd. (China), and polyethylenimine (PEI, $M_w = 25,000$) was purchased from Sigma–Aldrich Co. All of these reagents were used as received unless otherwise noted. Poly(ethylene terephthalate) (PET), poly(ethylene naphthalate) (PEN), and polyimide (PI) films were purchased from Toray–DuPont. The polymeric films were rinsed with ethanol under ultrasonification and dried with nitrogen for 1 min prior to use.

2.2. Preparation of the copper film on flexible substrates

The process of fabricating the copper pattern onto the polymeric films including poly(ethylene terephthalate) (PET), poly(ethylene naphthalate) (PEN), and polyimide (PI) films is schematically presented in Fig. 1. In a typical preparation, flexible films cut into strips of 20 mm \times 40 mm in size were cleaned by acetone, sealed

in a polyethylene bag, and subsequently subjected to γ -ray irradiation for a desired time. Then, the pre-irradiated flexible film along with 10 mL of acrylic acid, 50 mL of Milli-Q water, 1 mL of 0.2 M H₂SO₄, and 2 mL of 2.5×10^{-3} M (NH₄)₂SO₄·FeSO₄·6H₂O was added to a 100 mL three-necked flask, and nitrogen was bubbled into the system during reaction to cut off oxygen. After grafting at 80 °C for 2 h, the PAA-grafted film (PI-g-AA) was removed and washed with methanol thoroughly to remove the residual monomer and homopolymers. The grafting degree of PI-g-AA was calculated using the following equation.

$$G_1 = \frac{W_1 - W_0}{W_0} \times 100\% \quad (1)$$

where W_0 and W_1 are the weights of the original and grafted PP fibers, respectively.

Next, the inert ink was solidified on the substrate surface to form an elaborate invert circuit pattern as a mask *via* a simple screen-printing process [19]. The masked substrate was immersed in a 10 wt% PEI in water for 2 h, then washed with methanol and dried at 100 °C. The grafting degree of PP-g-PEI was calculated according to the following equation

$$G_2 = \frac{W_2 - W_1}{W_1} \times 100\% \quad (2)$$

where W_1 and W_2 are the weights of PP-g-AA and PP-g-PEI, respectively.

Subsequently, the PP-g-PEI was activated at 50 °C for 30 min by immersing in an ethanol solution containing 0.25 g/L of PdCl₂, followed by gentle rinsing with Milli-Q water. Next, this substrate was immersed in a 48 mM DMAB ethanol solution at 20 °C for 3 min to activate the doped Pd catalyst. Then, the activated substrate was immersed in an electroless Cu bath at 50 °C for 30 min. Finally, the substrate was carefully rinsed with Milli-Q water and dried with N₂ gas.

2.3. Characterization

Infrared spectra were obtained in the 4000–750 cm⁻¹ range using a Nicolet 670 Fourier-transform infrared (FT-IR) instrument equipped with an attenuated total reflectance (ATR) attachment. Contact angles were determined using an optical contact-angle meter (Tracker, Teclis-IT Concept, France) in the drop/sessile down mode. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Axis Ultra DLD multi-technique X-ray photoelectron spectroscope with a Mg K α source operated at 14.0 kV and 25 mA. All of the binding energies were referenced to the C 1s peak at 284.6 eV of the surface adventitious carbon. The cross-sectional microstructure of the film was observed using transmission electron microscopy (TEM, H500, HITACHI). For cross-sectional TEM observations, the samples were sectioned into *ca.* 100 nm thick slices with the conventional microtome technique using a diamond knife (Leica, Ultracut R). The adhesion between copper films and the polymeric substrate was tested using the ASTM D3359B-02 tape test. XRD patterns ($10 \leq 2\theta \leq 95$) were recorded on a Rigaku D/Max 2500 PC diffractometer equipped with a Cu K α radiation ($\lambda = 0.154056$ nm) source. The surface morphology of the films was observed by scanning electron microscopy (SEM, S-3400N, HITACHI). For SEM imaging, Au (1–2 nm) was sputtered onto the grids to prevent charging effects and to improve image clarity.

3. Results and discussion

The scheme for preparation of PEI-modified flexible film is presented in Fig. 1. The pre-irradiation method, which has attracted increasing attention for it can be used to introduce a variety of

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