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Polymer grafting surface as templates for the site-selective metallization

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ABSTRACT

We report a simple, low-cost and universal method for the fabrication of copper circuit patterns on a wide range of flexible polymeric substrates. This method relies on procedures to modify the polymeric substrates with grafted polymer template to form surface-bound N-containing groups, which can bind palladium catalysts that subsequently initiate the site-selective deposition of copper granular layer patterns. The fabrications of patterned copper films were demonstrated on three kinds of flexible polymeric films including poly(imide) (PI), poly(ethylene naphthalate) (PEN) and poly(ethylene terephthalate) (PET) with minimum feature sizes of 200 μm. The films were characterized by ATR FT-IR, contact angle, XPS, XRD, TEM, SEM. Furthermore, the copper layered structure shows good adhesion with polymeric film. This method, which provides a promising strategy for the fabrication of copper circuit patterns on flexible polymeric substrates, has the potential in manufacturing conductive features adopted in various fields including modern electronics, opto-electronics and photovoltaic applications.

1. Introduction

The fabrication of metallic patterns on functional materials is extremely important for manufacturing processes of microelectronic devices [1–4]. Especially for optical device, biomedical and microelectronics applications, the surface metallization of flexible polymeric substrates has attracted increasing attention because of the polymers' thermal plasticity that enables tuning of the nanocomposite microstructure, and the diversity of chemical bonds and structures available that provides additional possibilities for controlling physical and chemical properties [5–8]. The conventional patterning has been achieved by laser-induced deposition or chemical vapor deposition with a lithographic technique [9,10]. However, the adhesion of the metal pattern onto polymeric substrate is generally poor because the surface energy of polymer is low. Besides, these conventional patterning techniques do not modify polymer surfaces, and adhesion of the metal pattern onto polymeric substrate is due mainly to the physical anchoring effect, which is based on the roughness of the polymeric substrate [8,10,11]. Therefore, the development of a process for the fabrication metallic patterns with higher adhesion still remains a great challenge for chemists and material scientists.

Recently, Akamatsu et al. [12] reported site-selective surface modification for the generation of copper micropatterns on a polyimide surface. Masuda and co-workers [13] fabricated a micropattern of copper thin film on a poly(ethylene terephthalate) substrate by electroless deposition using a self-assembled monolayer patterned with different functional groups (SH and OH terminal groups) as a template. Carmichael and co-workers [14] oxidized the 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. The above fabrication method can tune the polymer surface characteristics and enhance the adhesion between metal and polymeric substrate. However, diverse treatments needed for the fabrication of metal patterns onto different polymeric substrates result in more complicated and expensive manufacturing process. As a result, it is highly desirable to develop a simple, cost-effective and universal metallization method for different kinds of polymer materials.

In this paper, we describe a facile method with potentially broad and perhaps universal scope to fabricate metal patterns onto polymeric substrates by electroless metal deposition, which is initiated by the palladium catalysts chemisorbed onto the modified

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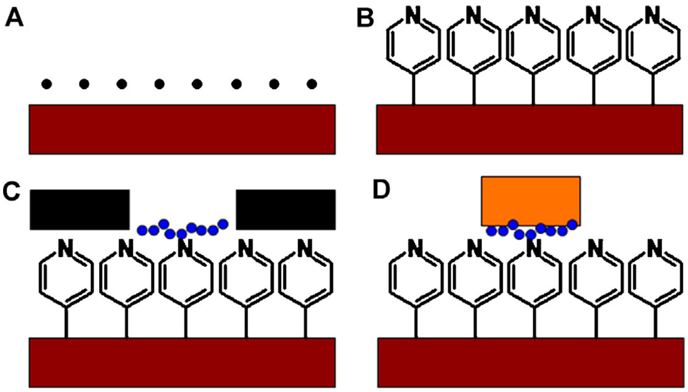

Fig. 1. Experimental scheme: (A) the formation of active radicals on the surface of the pre-irradiated flexible polymeric substrate; (B) the formation of P-4VP polymer-templated surface of the substrate; (C) the formation of patterned Pd catalyst onto the P-4VP polymer-template through a screen printed mask; (D) selectively deposition of copper onto the Pd catalyst-modified areas.

surface of the polymeric substrate (Fig. 1). To strongly immobilize the catalyst onto the substrate, surface modification with nitrogen (N)-containing molecules has attracted substantial investigative interest [15,16]. Kimura et al. demonstrated a route to deposite nickel layer patterns using photocross-linked partially quaterized poly(vinyl pyridine) thin films on insulate substrates [16]. However, adhesion of the modified polymer template onto polymeric substrate is mainly relied on the physical anchoring effect, which may affect the adhesion between the metal layer and polymer substrate. The addition of chemical bonding may help to enhance the metal/polymer adhesion. Here, we introduced the pyridine centers onto the polymeric surface by the graft copolymerization of pyridine-containing monomers via gamma irradiation. The main advantage of the application of irradiation applied to polymeric substrate is the formation of strong bridges between macromolecules [17], which contributes to the highly adhesive metallic layers formed onto the modified surface of various flexible polymeric substrates such as poly(imide) (PI), poly(ethylene naphthalate) (PEN) and poly(ethylene terephthalate) (PET).

2. Experimental

2.1. Materials

Deionized water of 18 MΩ resistivity was used for all experiments. Dimethylamine borane (DMAB) was purchased from Shenyu Chemical Ltd. (China), 4-vinylpyridine (4-VP) was purchased from J&K Scientific Ltd. (China), $PdCl_2$ was provided by Beijing Jiuzhoumol Ltd. (China), the electroless Cu bath was purchased from Nanjing Delei Technology Ltd. (China). All of these reagents were used as received unless otherwise noted. Poly(ethylene terephthalate) (PET), polyimide (PI) and poly(ethylene naphthalate) (PEN) 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 copper film on flexible substrates

The process of fabricating the copper pattern onto the polymeric films is schematically presented in Fig. 1. The polymeric films cleaned with ethanol were sealed in a polyethylene bag and subjected to γ-ray irradiation at a dose rate of 30 kGy. After irradiation, the pre-irradiated films were sealed and placed in a refrigerator at 4 °C for future use. In a typical preparation process, a mixed solution containing 10 mL of 4-vinylpyridine monomer, 88.6 mL of H_2O, and 1.4 g $(NH_4)_2{\cdot}Fe(SO_4)_2{\cdot}6H_2O$ was added to a 500 mL three-necked flask. The reactor was purged with nitrogen for 10 min to eliminate oxygen. Then the pre-irradiated film was added to the solution. The grafting reaction was carried out at 80 °C for 3 h with constant stirring under argon gas. After the grafting reaction was complete, the grafted modified films were cleaned with ultrasonic vibration with methanol for 10 min to remove the residual monomer and homopolymer. The obtained product was dried in vacuum at 60 °C. Next, the inert ink was solidified on the polymeric surface to form a fine-precision invert circuit pattern as a mask via a simple screen-printing process [18]. The modified sample substrate was subsequently activated at 50 °C for 30 min by immersion in a hydrochloric acid solution containing 0.5 g/L of $PdCl_2$, followed by gentle rinsing with Milli-Q water. Next, this substrate was immediately immersed in a 0.1 M DMAB aqueous solution at 50 °C for 30 min to activate the doped Pd catalyst. Finally, 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 Nitrogen 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 (JC2000C1, Shanghai Powereach Digital Technology Equipment Co., Ltd., China) 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 Kα 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 ($10^\circ \leq 2\theta \leq 95^\circ$) were recorded on a Rigaku D/Max 2500 PC diffractometer equipped with a Cu Kα radiation ($\lambda = 0.154056$ nm) source. The surface morphology of the films was observed by scanning electron microscopy (SEM, S-3400N, HITACHI) and atomic force microscopy (AFM, Veeco Co.). 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

3.1. Mechanism of the interaction between polymer template and substrate

The interaction between the modified polymer template and the polymeric film surface is important for it can affect the adhesion of copper layer onto the polymer substrate. In this study, the pre-irradiation method, which has attracted increasing attention for it can be used to introduce a variety of functional groups and does not require chemical initiators or catalysts, was employed [19]. In the pre-irradiation method, polymeric matrix is first irradiated to generate free radical stable at ambient temperature in order to initiate covalent bonds with monomers after irradiation [20]. Then free radicals initiate grafting polymerization as shown in reactions (reaction (1–4)).

$$P \rightarrow P^{\bullet} \qquad (1)$$