Formation of Metal Nanoparticle/Acrylic Polymer Hybrid Film by UV-Irradiation

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1. Introduction

Fabrication of metal nanoparticle/polymer hybrid has recently attracted much interest for their application to electronic, optical, magnetic devices. Photochemically generated radicals can reduce metal ions to produce metal nanoparticles in polymer matrix.^{1,2} We have already reported that palladium-nanoparticle/polymer hybrid negative pattern is formed on a flexible film by photolithography and the hybrid pattern is converted to the copper pattern by electroless plating.³⁻⁵ In this paper, we report the formation of palladium-, gold-, and silver-nanoparticle/acrylic polymer hybrid film by UV irradiation process.

2. Experimental

The typical hybrids negative-patterns containing palladium nanoparticle were prepared as follows; palladium (II) acetate, large amount of 2-hydroxy-2-methyl-1-phenyl-propane-1-on (Darocure 1173), trimethylolpropane triacrylate (TMPTA), silica nanoparticles, and small amount of hydroquinone were dissolved in THF. Silica nanoparticles (Fuso Chemical) were added for

increasing the adhesion between the hybrid and copper.³ Hydroquinone is a radical inhibitor and prevents the thermal polymerization, affording higher resolution hybrid negative pattern.⁴ This THF solutions was spin-coated onto a PET film, and then the thin film was irradiated with a high pressure Hg-arc lamp through a photomask. The photo-irradiated film was developed with methyl isobutylketone (MIBK) and the hybrid negative pattern was obtained as shown in Figure 3a. The pattern was annealed at 120 °C for 10 min and then the electroless copper plating was carried out at 40 °C in a copper plating bath (Okuno Chemical). 2-(Methylthio)ethyl methacrylate (MTEM) and triphenyl phosphine were also to the THF solution containing $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ and AgNO_3 , respectively, as a complexing agent.

Transmission electron microscopy (TEM) images were obtained using a JEOL model JEM-2100 microscope at an acceleration voltage of 100 kV. Specimens were prepared by dropping the THF-solution of the mixture onto a carbon-coated copper grid and allowing THF to evaporate, followed by UV-irradiation and the annealing.

3. Results and discussion

The light-yellow film of the mixture containing $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, Darocure 1173, TMPTA, MTEM, silica nanoparticles, and hydroquinone was irradiated with the Hg-lamp, and its color turned deep wine-red. The UV-vis absorption spectrum of the film is shown in Fig. 1a. The absorption band around 560 nm is attributable to the surface

plasmon resonance of gold nanoparticles. This shows the formation gold nanoparticle/acrylic polymer hybrid film. The UV irradiation of the mixture containing AgNO_3 and $\text{Pd}(\text{CH}_3\text{CO}_2)_2$ in a similar way afforded silver- and palladium-nanoparticle/acrylic polymer hybrid films, respectively. The absorption band around 420 nm (Fig. 1b) of silver/acryl hybrid film is attributable to the surface plasmon resonance of silver nanoparticles. The TEM images of the hybrid films also shows the formation of palladium nanoparticles (<ca. 5 nm, black particles in Fig. 2 left) and silver nanoparticles (<ca. 10 – 20 nm, Fig. 2 right) in the films (silica particles appear as gray particles of ca. 50 nm).

Fig. 1. UV-vis spectra of (a) gold-nanoparticle/acrylic polymer hybrid film, (b) silver-nanoparticle/acrylic polymer hybrid film.

Fig. 2. TEM images of the hybrid films: palladium-nanoparticle/acrylic polymer hybrid films (left), silver-nanoparticle/acrylic polymer hybrid film (right).

The corresponding films containing $\text{Pd}(\text{CH}_3\text{CO}_2)_2$, $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, and AgNO_3 were irradiated through a photomask (250 μm L/S pattern) and developed to give the negative patterns of the palladium-, gold-, and silver-nanoparticle/acrylic polymer hybrids, respectively (Fig 3). The electroless plating of the hybrid-patterns was carried out. The copper thin film was formed on the surface of the palladium-nanoparticle/acrylic polymer hybrid, but not on those of gold- and silver-nanoparticle/acrylic polymer hybrids. It seemed that radical species generated from Darocure 1173 by UV-irradiation induce radical polymerization of TMPTA and reduction of the metal ions,⁶ resulting in the formation of metal nanoparticle/acrylic polymer hybrid negative pattern. Only the

palladium nanoparticles on the surface of the hybrid catalyzed the electroless plating.

In summary, UV-irradiation to the film of acrylate monomer, metal salts, photo-radical initiator formed metal nanoparticle/acrylic polymer hybrid pattern. The palladium/acryl hybrid pattern was converted to the copper pattern, which could be applicable for manufacturing flexible printed circuit. The gold and silver/acryl hybrid patterns, which have surface plasmon absorption band, could be applicable for optical devices.

Fig. 3. Optical micrographs of palladium-nanoparticle/acrylic polymer hybrid negative pattern (a) before and (b) after the electroless copper plating, gold/acryl hybrid pattern (c) before and (d) after the plating, silver/acryl hybrid pattern (e) before and (f) after the plating.

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