doi:10.1246/cl.2012.277

A Pd Nanoparticle/Silica Nanoparticle/Acrylic Polymer Hybrid Layer for Direct Electroless Copper Deposition on a Polymer Substrate

Toshiyuki Tamai,* Mitsuru Watanabe, Shingo Ikeda, Yasuyuki Kobayashi,
Yutaka Fujiwara, and Kimihiro Matsukawa
Osaka Municipal Technical Research Institute, 1-6-50 Morinomiya, Joto-ku, Osaka 536-8553

(Received December 13, 2011; CL-111189; E-mail: tositama@omtri.or.jp)

Copper was directly deposited on a polymer substrate whose surface is coated with a palladium nanoparticle/silica nanoparticle/acrylic polymer hybrid layer. On the surface of the hybrid, the palladium nanoparticles function as a catalyst for the electroless copper deposition, and the nanometer-scale roughness, which is due to the silica nanoparticles, increases the adhesion between the polymer and copper.

Hybrid materials composed of polymers and nanoparticles, such as metal nanoparticles and metal oxide nanoparticles, are of great scientific and industrial interest because of their unique properties.[1–7] Efforts have been made to incorporate nanoparticles into polymer matrices, given the fact that a nanoparticle-dispersed polymer material (nanoparticle/polymer hybrid) derives its properties from the nanoparticles, such as catalytic activity[1–3] and high refractive index.[4] Metal nanoparticle/polymer hybrid films can be prepared by means of casting from a solution containing metal nanoparticles and polymers,[5] by the deposition of metal nanoparticles on the surface of a polymer film,[1,2] and by in situ formation of metal nanoparticles[6] via the reduction of metal ions by reducing agents[1–3,5,7] and photochemically generated radicals.[6,8–10] The obtained hybrid films are expected to be metallized by means of electroless plating due to the catalytic activity of the metal nanoparticles. Electroless plating is a simple and cost-effective method not only for metallization of polymer substrates but also for fabrication of metallic patterns on polymer substrates.[11,12] Common electroless processes involve three main steps: i) surface preparation, ii) surface activation or surface seeding with a catalyst, and iii) the electroless plating process itself. While surface preparation, such as etching to increase the surface roughness, is necessary to provide good adhesion, it can affect the physical properties of the deposited metal film and damage the polymer substrate. Conventional patterning on a flexible polymer film, such as the semiadditive process used in the fabrication of microelectronics devices, has been achieved using multistep lithographic methods, which include pretreatment of flexible film, the application of a resist, patterning of the resist by lithography (e.g., UV-exposure and development), the deposition of metal by plating, lifting off the resist, and post-treatment.[1] Recently, to fabricate a micropattern, a simple and cost-effective approach containing direct metallization of photolithographic and printed patterns has attracted much attention.[13–17] Copper is the most important metal in this process, because of its high conductivity and low electromigratory property. Therefore, we have proposed the fabrication of micropatterns by direct electroless copper deposition on a photolithographic pattern.[17] In this paper, we report on such direct electroless copper deposition on a polymer substrate whose surface is coated with a palladium nanoparticle/silica nanoparticle/acrylic polymer hybrid layer (<100 nm), as shown in Figure 1. The copper film was formed in three steps: i) the formation of a layer containing acrylate monomer, palladium salt, silica nanoparticles, and a radical initiator by spin-coating on the flexible polymer film, ii) the formation of a palladium nanoparticle/silica nanoparticle/acrylic polymer hybrid layer by curing the coated layer at 120 °C, and iii) electroless copper deposition on the hybrid layer. The palladium nanoparticles are formed in situ and function as a catalyst for the electroless copper deposition. Silica nanoparticles modified by an acryl group are dispersed uniformly in an acryl polymer matrix,[4] and they endow the hybrid layer surface with a nanometer-scale roughness that increases the adhesion to the copper film. Next, we discuss the nanometer-scale structure of the hybrid surface, which plays an important role in electroless deposition.

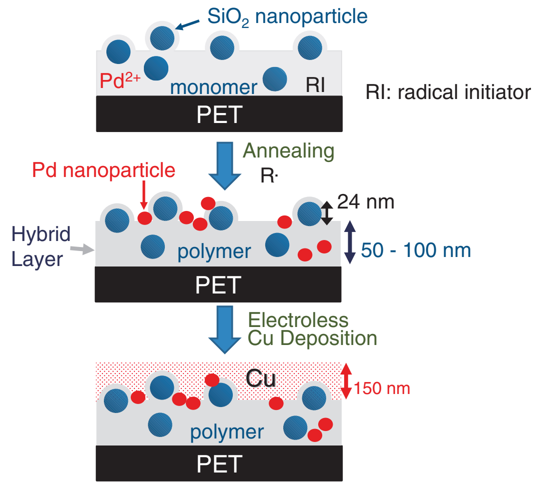

Figure 1. Schematic representation of the formation of a palladium nanoparticle/silica nanoparticle/acrylic polymer hybrid layer on a PET substrate, followed by the electroless copper deposition.

A typical hybrid layer was prepared as follows: tris(acryloyloxymethyl)propane (TMPTA, monomer, 55 mg), palladium(II) acetate (5 mg), 2,2-azobisisobutylonitrile (AIBN, radical initiator, 5 mg), and silica nanoparticles (a primary particle size 24 nm, modified by an acrylic group, toluene dispersion, Fuso Chemical, 10 mg) were dissolved in propylene glycol 1-monomethyl ether 2-acetate (PGMEA, 4 mL). From the PGMEA solution, a poly(ethylene terephthalate) (PET) film (thickness 250 µm) was spin-coated with a layer composed of TMPTA/palladium acetate/AIBN/silica nanoparticle. The coated PET film was annealed at 120 °C for 30 min and then washed with methyl isobutyl ketone (MIBK) to remove the low-

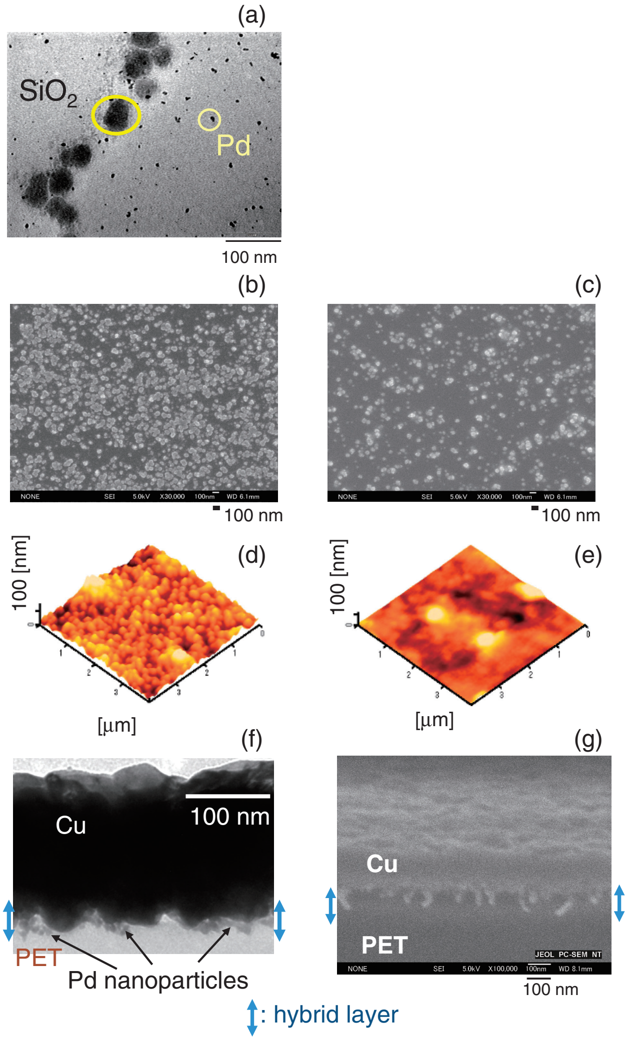

Figure 2. Microscopic images of the palladium nanoparticle/silica nanoparticle/acrylic polymer hybrids. (a) TEM image of the hybrid. FE-SEM images of the surface of the hybrid layers (b) containing silica nanoparticles and (c) containing no silica nanoparticles. AFM surface plots of the hybrids (d) containing silica nanoparticles and (e) containing no silica nanoparticles. Cross-sectional TEM (f) and FE-SEM (g) images of the copper film deposited on the hybrid-coated PET substrate.

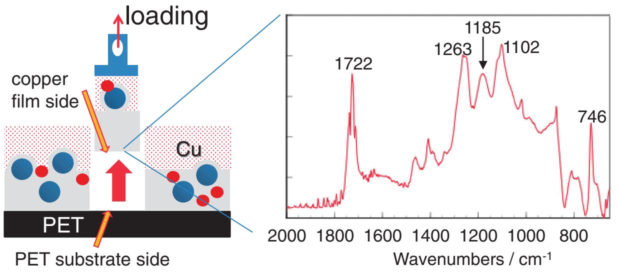

Figure 3. ATR-IR spectrum obtained from the copper film side after the pull test on the copper-deposited PET substrate.

molecular-weight components, which resulted in the formation of a palladium nanoparticle/silica nanoparticle/acrylic polymer hybrid layer (thickness 50–100 nm) on its surface. Electroless copper deposition was then carried out at 40 °C in a copper deposition bath (Okuno Chemical Industries).

The layer containing acrylate monomer, palladium salt, silica nanoparticles, and radical initiator on a PET substrate was converted to a palladium nanoparticle/silica nanoparticle/acrylic polymer hybrid layer by annealing at 120 °C.[18] The radicals would induce the radical polymerization of the acrylate monomer and also would reduce the palladium ion to form the palladium nanoparticles. A transmission electron microscopy (TEM) image (Figure 2a) of the hybrid shows the palladium nanoparticles (black particles, diameter: <ca. 5 nm) and silica nanoparticles (gray particles, diameter: 30–50 nm), although most of the palladium nanoparticles seem to be aggregated. Using electroless copper deposition, a copper film (thickness 150 nm) was deposited on the surface of the hybrid-coated PET substrate. The copper film was free of cracks and defects. A field emission scanning electron microscope (FE-SEM) image and an atomic force microscope (AFM) image of the copper film show granular copper deposits (Figures S1–S3[23]). The adhesion between the copper film and the PET substrate was evaluated through a peel adhesion test using 3M tape. In the test, copper film (20 mm × 10 mm) was scored into 1 mm × 1 mm squares, after which tape was applied to the cut surface and then peeled off. When the test was performed, the copper film on the PET substrate coated with the hybrid containing silica nanoparticles was completely undamaged, whereas most of the copper film on the substrate coated with the hybrid containing no silica nanoparticles was damaged (Figure S4[23]). This shows that silica nanoparticles increase the adhesion between the copper film and the hybrid (copper/hybrid interface). The adhesive strength between the copper and the PET substrate as obtained by the pull adhesive test was 4.1 N mm^{-2}. After the pull test, the copper film side and the PET substrate side of the sample were analyzed by ATR-FT-IR (Figure 3). Some peaks that are attributable to the acrylic polymer (Figure S5[23]), which is a major component of the hybrid, were observed for the copper film side[19] but not for the PET substrate side (Figure S6[23]). The pull-off occurred at the interface between the hybrid layer and the PET substrate side (hybrid/PET interface), because the copper/hybrid has a greater adhesive strength than the hybrid/PET. This result also shows that there is a high degree of adhesion between the copper film and the hybrid.

The surfaces of the hybrid layer containing silica nanoparticles (Figure 2b) and that containing no silica nanoparticles (Figure 2c) were observed by FE-SEM. The roughness of the hybrid surface was evaluated in further detail by AFM (Figures 2d and 2e). A comparison of all the images shows that palladium nanoparticles and silica nanoparticles are present on the hybrid surface as shown below. The FE-SEM image of the surface of the hybrid containing silica nanoparticles (Figure 2b) shows particles with diameters of 10–100 and 30–50 nm, which are thought to be aggregated palladium nanoparticles and silica nanoparticles, respectively (see Supporting Information[23]). The AFM image (Figure 2d) shows the roughness of the hybrid surface (<ca. 50 nm), which is due to the silica nanoparticles. In contrast, the FE-SEM (Figure 2c) and AFM (Figure 2e) images of the surface of the hybrid containing no silica nanoparticles show aggregated palladium nanoparticles and a flat surface (roughness: <ca. 10 nm), respectively. It

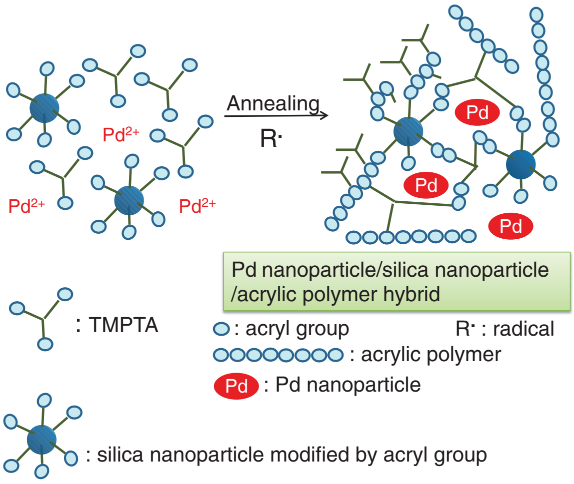

Figure 4. Proposed mechanism for the formation of the palladium nanoparticle/silica nanoparticle/acrylic polymer hybrid.

appears that the roughness due to the aggregated palladium nanoparticles is smaller than ca. 10 nm. Cross-sectional TEM and FE-SEM images of the copper film deposited on the hybrid-coated PET substrate are shown in Figures 2f and 2g. In Figure 2f, palladium particles (gray particles, diameter: <ca. 5 nm) and a rough interface derived from silica nanoparticles (diameter: 20–30 nm) were observed in the layer between the copper film (upper layer) and the PET substrate (lower layer),[20] which is considered to be the hybrid layer. Figure 2g shows that copper is penetrated into the lower layer, which is considered to be the hybrid layer. Copper seems to be deposited between the silica nanoparticles, which are present on the surface of the hybrid layer. All these images clearly indicate that the palladium nanoparticles on the surface of the hybrid catalyze the electroless deposition and that the interface between the deposited copper and the hybrid is rough for the silica nanoparticles. The nanometer-scale roughness (<ca. 50 nm) due to the silica nanoparticles would promote the adhesion through nanoscale mechanical interlocking effects.[21]

The hybrid layer would be formed as shown in Figure 4. The radical from AIBN induces the reduction of the palladium ion[6,8–10,22] as well as the radical polymerization of the acrylate monomer (TMPTA). The acryl group at the surface of the silica nanoparticles copolymerizes with the acrylate monomer, forming the crosslinking network composed of acrylic polymer chain and the silica nanoparticles. During the polymerization process, palladium nanoparticles are formed in situ, and they do not grow into larger size particles because they cannot diffuse in the crosslinking network. The proposed mechanism for the copper deposition is shown in Figure 1. The hybrid layer (thickness 50–100 nm) composed of the palladium nanoparticles, the silica nanoparticles (average diameter 24 nm), and the acrylic polymer is formed by annealing, and its surface is characterized by roughness (<ca. 50 nm) that is due to the presence of silica nanoparticles, as described above. Electroless copper deposition catalyzed by palladium nanoparticles on the hybrid layer forms a copper film,[18] whose strong adhesion results from the nanometer-scale roughness of the hybrid surface. This process enables direct electroless copper deposition on a smooth polymer film. In common electroless processes, metals are deposited onto a polymer surface that has a micrometer-scale roughness formed by chemical etching,[11,12] which can affect the physical properties of the metal film and damage the polymer substrate.

In summary, copper was deposited directly on a polymer substrate coated with a hybrid layer. On the surface of the hybrid, the palladium nanoparticles function as a catalyst for the electroless deposition, and the silica nanoparticles interlock the copper and the hybrid to increase their adhesion. This process is expected to be applicable to the fabrication of micropatterns by means of printing techniques that use an ink composed of monomer, palladium salt, and so forth, followed by curing and electroless plating.

This study was partly supported by a Grant-in-Aid for Scientific Research (C) (No. 22550138) from the Ministry of Education, Culture, Sports, Science and Technology of Japan. Financial support from the City of Osaka is also gratefully acknowledged. We would also like to thank Okuno Chemical Industries Co., Ltd. and Fuso Chemical Co., Ltd. for gift of copper deposition bath and silica nanoparticles (organo silica sol), respectively.

References and Notes

1 D. Zabetakis, W. J. Dressick, *ACS Appl. Mater. Interfaces* **2009**, *1*, 4.
2 M. Kimura, H. Yamagiwa, D. Asakawa, M. Noguchi, T. Kurashina, T. Fukawa, H. Shirai, *ACS Appl. Mater. Interfaces* **2010**, *2*, 3714.
3 S. Fujii, S. Matsuzawa, Y. Nakamura, A. Ohtaka, T. Teratani, K. Akamatsu, T. Tsuruoka, H. Nawafune, *Langmuir* **2010**, *26*, 6230.
4 M. Inkyo, Y. Tokunaga, T. Tahara, T. Iwaki, F. Iskandar, C. J. Hogan, Jr., K. Okuyama, *Ind. Eng. Chem. Res.* **2008**, *47*, 2597.
5 L. Qi, B. I. Lee, S. Chen, W. D. Samuels, G. J. Exarhos, *Adv. Mater.* **2005**, *17*, 1777.
6 W. D. Cook, Q. D. Nghiem, Q. Chen, F. Chen, M. Sangermano, *Macromolecules* **2011**, *44*, 4065.
7 T. Taniguchi, T. Inada, T. Kashiwakura, F. Murakami, M. Kohri, T. Nakahira, *Colloids Surf., A* **2011**, *377*, 63.
8 M. Sakamoto, T. Majima, *Bull. Chem. Soc. Jpn.* **2010**, *83*, 1133.
9 T. Itakura, K. Torigoe, K. Esumi, *Langmuir* **1995**, *11*, 4129.
10 J. C. Scaiano, P. Billone, C. M. Gonzalez, L. Marett, M. L. Marin, K. L. McGilvray, N. Yuan, *Pure Appl. Chem.* **2009**, *81*, 635.
11 C. A. Deckert, *Electroless Copper Plating* in *ASM Handbook: Surface Engineering*, ASM International, Ohio, **1994**, Vol. 5, p. 311.
12 S. Siau, A. Vervaet, S. Nalines, E. Schacht, A. Van Calster, *J. Electrochem. Soc.* **2004**, *151*, C831.
13 J. R. Lancaster, J. Jehani, G. T. Carroll, Y. Chen, N. J. Turro, J. T. Koberstein, *Chem. Mater.* **2008**, *20*, 6583.
14 K. Akamatsu, S. Ikeda, H. Nawafune, H. Yanagimoto, *J. Am. Chem. Soc.* **2004**, *126*, 10822.
15 S. Ikeda, H. Yanagimoto, K. Akamatsu, H. Nawafune, *Adv. Funct. Mater.* **2007**, *17*, 889.
16 T. Kano, K. Kawamura, *PMSE Prepr.* **2006**, *94*, 495.
17 T. Tamai, M. Watanabe, S. Watase, N. Nishioka, K. Matsukawa, *Trans. Jpn. Inst. Electron. Packag.*, in press.
18 Copper was not deposited on the hybrid film formed at 80 °C. The film formation temperature (annealing temperature) of 120 °C is indispensable for the electroless plating.
19 Minor peak observed at 746 cm^{-1} is attributable to $-C_6H_4-$ group of PET.
20 The interface between the hybrid (acrylic polymer) and the PET substrate could not be observed.
21 It was reported that metal nanoparticles at the interface between the metal film and polymer layer promote the adhesion by increasing the contact area between the metal and the polymer (refs. 15 and 16).
22 T. Tamai, M. Watanabe, Y. Hatanaka, H. Tsujiwaki, N. Nishioka, K. Matsukawa, *Langmuir* **2008**, *24*, 14203.
23 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.