Site-Selective Electroless Nickel Plating on Patterned Thin Films of Macromolecular Metal Complexes

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ABSTRACT We demonstrate a simple route to depositing nickel layer patterns using photocross-linked polymer thin films containing palladium catalysts, which can be used as adhesive interlayers for fabrication of nickel patterns on glass and plastic substrates. Electroless nickel patterns can be obtained in three steps: (i) the pattern formation of partially quaterized poly(vinyl pyridine) by UV irradiation, (ii) the formation of macromolecular metal complex with palladium, and (iii) the nickel metallization using electroless plating bath. Metallization is site-selective and allows for a high resolution. And the resulting nickel layered structure shows good adhesion with glass and plastic substrates. The direct patterning of metallic layers onto insulating substrates indicates a great potential for fabricating micro/nano devices.

KEYWORDS: electroless nickel plating • macromolecular metal complex • palladium • plastic substrate • photocross-link • nickel pattern

INTRODUCTION

Electroless nickel plating is the plating of a nickel−phosphorus alloy deposit onto substrates by a chemical reduction process and this process can produce uniform, hard, and lubricious alloy layers on metallic and nonmetallic substrates without an external electrical current. Electroless nickel plating processes have been widely used in many technological applications, including the fabrication of printed circuit boards and decorative coatings. The fabrication of metallic patterns on insulating substrates is especially important because of the increasing demand for cost-effective electronic devices such as plastic-based optical and electronic devices and integrated microelectro-mechanical systems (1−10). Conventional pattering has been achieved by using lithographic methods based on multistep resist patterning, etching, washing, and deposition of metallic layers. Furthermore, the substrates needed chemical treatments such as a chromic acid etching of plastic substrates in order to increase the surface energy and wettability, and improve the mechanical adhesion with deposited metallic layer (11, 12). Recently, several alternative approaches concerning wet-printing technologies for fabricating metallic patterns onto various kinds of substrates have been reported. Akamatsu et al. demonstrated the direct deposition of metallic patterns by drawing poly(amic acid) patterns containing nickel ion onto glass substrates by using a fine-precision dispenser, followed by chemical reduction of nickel (13, 14). The polymer patterns with a nickel thin film acted as an electrode for the electrodeposition of a copper layer as well as an interfacial adhesion layer between the glass substrate and the copper layer.

Palladium is employed as catalyst to initiate the reduction of metal ions (15). The deposition of palladium seeds on the surface of insulating substrates makes it possible to deposit a metallic layer by immersing into an electroless plating bath containing nickel ions and strong reducers. Garcia et al. reported metallization of plastic substrates having covalent grafted poly(acrlic acid) (16). Their results showed that carboxylate groups in grafted poly(acrylic acid) chelated with catalytic metal ions and metal ions initiated the electroless metal deposition on plastic substrates. Herein, we report a versatile approach to creating patterned metallic layers from a polymer thin film incorporating catalytic metal ions by means of the electroless nickel plating. Partially quaterized poly(vinyl pyridine) (PVMP) can produce polymer patterns through photochemical cross-linking, and the resulting positively charged PVMP patterns have been used for the adsorbing negatively charged gold nanoparticles and carbon nanotubes (17, 18). Rotello and co-workers demonstrated the fabrication of conductive metal patterns through the site-selective deposition of gold nanoparticles on PVMP patterns (18). They also reported electroless deposition of silver on sulfonated polystyrene patterns written by electron-beam lithography of PVMP thin film on a silicon substrate (19). However, they did not study the direct growth of metallic
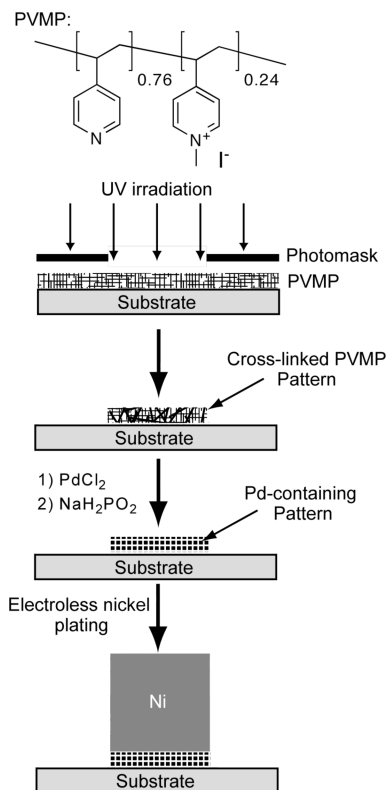
FIGURE 1. Schematic diagram of site-selective electroless nickel plating from the patterned film of macromolecular metal complex on substrates.

layer on PVMP patterns. Accordingly, the present work takes a novel approach for direct electroless patterning of nickel films by using patterned PVMP thin films as the chelating layer for catalytic metal ions (Figure 1). Palladium ions can be directly chemisorbed on a PVMP matrix by the formation of metal complexes with pyridine side chains of PVMP to give a macromolecular metal complex (20). Moreover, highly adhesive metallic layers were formed by using PVMP thin films onto the surface of various substrates such as glass, poly(imide) (PI), and poly(ethylene terephthalate) (PET).

EXPERIMENTAL SECTION

All of the reagents and solvents were used as received from the chemical supplier without further purification.

Surface Modification. The partially quaterized poly(vinyl pyridine) (PVMP) was synthesized from poly(4-vinyl pyridine) (Sigma-Aldrich, M_w = 60 000 g/mol) and methyl iodide in ethanol as described in detail in ref 17. The PVMP polymer was deposited by spin coating from ethanol solution onto 3×3 cm glass, PI, and PET substrates. The substrates were ultrasonically cleaned with 2-isopropanol for 10 min, were rinsed with deionized water, and finally were dried under nitrogen flow. A photomask (Test-chart-No.1-N type, quartz substrate, 1.524 μm thickness, Toppan Printing Co., Ltd.) was put on top of polymer film, followed by UV-irradiation (254 nm) using a hand-held UV lamp for 15 min. After rinsing with Milli-Q water under ultrasonification at 60 °C, the feature was developed and the micropatterns were formed onto the subtstrates. The resulting polymer patterns were characterized by AFM (JSPM-5400, JEOL Ltd.) and microfigure measuring instruments (Surfcorder ET4000, Kosaka Laboratory Ltd.). The substrates with patterned PVMP films were immersed into the acidic PdCl$_2$ aqueous solution (0.13 mM, pH2.8) at 50 °C for 2 min, followed by washing with

ethanol and deionized water to remove the excess Pd^{2+} in the PVMP film and blowing dry in N$_2$. The complexed Pd^{2+} was activated by the treatment with 48.0 mM NaH$_2$PO$_2$ aqueous solution at 20 °C for 20 s.

Electroless Nickel Plating. The surface-activated substrates were finally placed in the electroless nickel plating bath (100 mL) for 5 min at 60 °C. The plating bath was used that contained NiSO$_4$ 6H$_2$O (100 mM), sodium hypophosphite NaH$_2$PO$_2$ (250 mM), Pb(NO$_3$)$_2$ (1.5 μM), and glycine (300 μM). After the desired nickel thickness was reached, the metal growth was stopped by rinsing the substrate with distilled water. The substrate surface was analyzed by XPS with a Mg Ka X-ray source (KRATOS Axis Ultra DLD, Shimazu Co.) and SEM (VE-8800, Keyence Co.).

RESULTS AND DISCUSSION

Formation of Pd-Containing Polymer Films. Partially quaterized poly(vinyl pyridine) was prepared from poly(vinyl pyridine) and methyl iodide according to the literature method reported by Rotello et al. (17). The degree of quaterization of poly(vinyl pyridine) with methyl iodide, determined by ^{1}H NMR spectra, was 24 %. A substrate was spin-coated at 3000 rpm with an ethanol solution of PVMP (0.5 wt %) followed by irradiation with 254 nm UV light for 15 min. The exposed film was stable in methanol and deionized water, indicating that the irradiation of UV light formed cross-linking points in the PVMP film. The thickness of the resulting PVMP film was ca. 20 nm determined by a cross-sectional analysis. The spin-coated PVMP films were characterized by X-ray photoelectron spectroscopy (XPS). The spin-coated PVMP film before the irradiation of UV light exhibited two distinct chemical states in the nitrogen region at 400.0 and 403.0 eV, which are attributed to pyridine and pyridium ion, respectively (21). The ratio of the integration area of two peaks agreed very closely with that determined by the NMR analysis. The shoulder peak of pyridium ion disappeared in the photocross-linked PVMP film, suggesting that pyridium ions in the PVMP film are converted to cross-linking points by UV irradiation. To produce patterned films, the surface of the spin-coated PVMP film was covered with a photomask containing circular openings with diameter of 2.8 mm. The exposed sample was rinsed with Milli-Q water to develop the features. After the covered regions were rinsed, the patterned PVMP films on various substrates were immersed in acidic PdCl$_2$ aqueous solution to form a macromolecular metal complex of palladium ion with the cross-linked PVMP film. Pd^{2+} species in the PVMP film were reduced to Pd^0 species by treatment with NaH$_2$PO$_2$ aqueous solution as a reducing agent. The presence of palladium ion within the PVMP film can be monitored by the XPS analyses (Figure 2). While no peaks in the palladium region were observed at the noncross-linked region, the PVMP film exhibited two peaks at 342 and 336 eV, respectively, corresponding to the Pd 3d$_{3/2}$ and 3d$_{5/2}$ binding energies for Pd^0. The observed peak positions are almost coincident with the reported values for the Pd^0 species, suggesting that the incorporated Pd^{2+} species were reduced by H$_2$PO$_2^-$ to active Pd^0 species within the PVMP film (22).

Site-Selective Electroless Nickel Plating on Pd-Containing Polymer Films. The substrates were
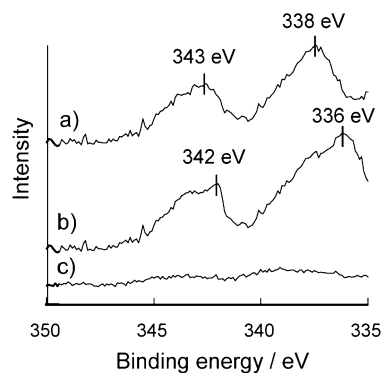
FIGURE 2. Palladium 3d XPS spectra of cross-linked PVMP region on glass substrate; (a) PdCl$_2$-treated sample and (b) NaH$_2$PO$_2$-treated sample. (c) XPS spectrum of non-cross-linked region on glass substrate.
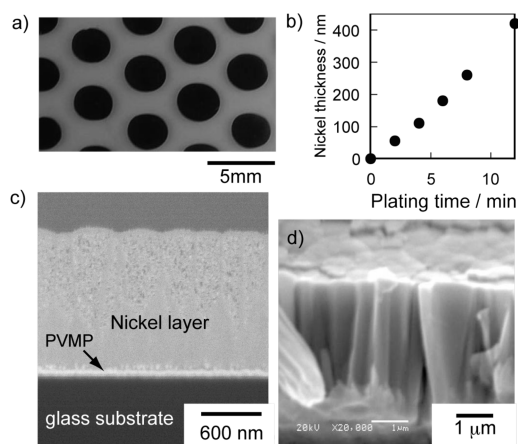

FIGURE 3. (a) Optical image of circular nickel patterns on glass substrate. (b) Variation in the nickel thickness as a function of the plating time for the electroless nickel plating from Pd-containing PVMP film. (c) Cross-sectional FE-SEM image of nickel layer grown from the PVMP thin film. The specimen was milled by FIB after coating the specimen with carbon. (d) Cross-sectional FE-SEM image of nickel pattern. The specimen was cut in liquid nitrogen.

placed in a electroless nickel plating bath containing a mixed aqueous solution of NiSO$_4$ 6H$_2$O, NaH$_2$PO$_2$ as a reducing agent, and Pb(NO$_2$)$_2$ and glycine as stabilizers of the plating solution. Nickel thin films were formed on the PVMP film containing Pd^0 by the continuous reduction of Ni^{2+} ions and the patterned nickel layers were formed through selectively deposited metallization as confirmed by comparing the areas with PVMP film and glass surface. XPS analysis of the nickel layer indicates the presence of phosphorus, and the final composition of nickel layer was estimated as 94 % nickel and 6 % phosphorus ignoring carbon and oxide residues. Figure 3a shows optical microscope images of the patterned nickel layer on glass substrate. The diameter of the circular nickel layer was found to be 2.8 ± 0.2 mm, which is in good agreement with the opening size of the photomask. A plot of the nickel layer thickness versus immersion time into the plating bath indicates a linear relationship (Figure 3b). The metallization rate was found to be ca. 30 nm/min by comparing the nickel thickness on substrates metalized for various time. The cross section image of nickel layer on the glass substrate was examined by field-emission scanning electron microscope (FE-SEM)

after milling by focused ion beam (FIB) (Figure 3c). According to this image, the thickness of nickel layer is around 1.0 μm and a cross-linked PVMP layer is present between the glass substrate and the nickel layer. After the glass substrate with the nickel layer was cut under liquid nitrogen, the FE-SEM image of the cut sample reveals pillar structures in the nickel layer (Figure 3d). This image suggests a perpendicular growth of the nickel layer toward the PVMP surface. The electrical resistivity of as-plated nickel layer was roughly estimated by the two-probe method, and the $I-V$ profile showed ohmic behavior. While almost no current followed through the PVMP pattern, the average resistivity of nickel layers was calculated to be about 6.5 × 10^{-5} Ω cm. The estimated conductivity of nickel layer was relatively higher than the value of bulk nickel (6.84 × 10^{-6} Ω cm), possibly because of the structural defect and the presence of phosphorus.

The adhesions of the nickel layer on glass, PI, and PET substrates were evaluated by a standard peel adhesion test of 3 M tape (ASTM D3330) (23). The nickel layers on glass substrate were completely undamaged after scoring the nickel layer (25 × 20 mm) into 1 mm × 1 mm squares, applying tape to the cut surface, and peeling it off. Without the use of the cross-linked PVMP film the plastic and glass substrates, the nickel layer on the substrates was easily removed by the tape test. When a strain was induced in the circular nickel patterns with 300 ± 20 μm thickness on the flexible PI substrate (30 × 30 mm) by bending the substrate around cylinders with radii decreasing from 10 mm to 500 μm, there was no removal of nickel at bending, suggesting that the nickel pattern withstood substantial deformation without damage (23). Nickel patterns on the PVMP film exhibit remarkable adhesion to various substrates. The PVMP film stick with the surface of substrates and the film was stabilized by UV irradiation. The Pd^0 species incorporated within the cross-linked PVMP film initiate a catalytic reaction for the reduction of Ni^{2+} and the nickel layer was deposited as a pillar structure on the PVMP film. Each pillar is directly attached to the PVMP film, and chemical adhesion is caused by strong bonds at the interfaces. Hence, the PVMP film produces strong adhesion between the substrates and the nickel layer. The strong adhesion and pillar structures on flexible substrates result in a distribution of the strain over the entire area of the nickel patterns, thereby allowing the patterns and flexible substrate to deform together.

Creation of Micropatterning. Micropatterning of the nickel layer with high resolution was successfully achieved on UV-patterned PVMP films by using specially designed photomasks (Figure 4) (24). Figure 4a shows an optical micrograph of a nickel micropattern, which was formed by the electroless nickel plating process from the patterned PVMP films on glass substrate. The photomask contains various line widths and pitches to evaluate the resolution of plating processes. Nickel structures corresponding to the highest resolution features available (>1 μm) on the mask were successfully fabricated. Nonspecific deposition of a nickel layer was observed at the line patterns with width of
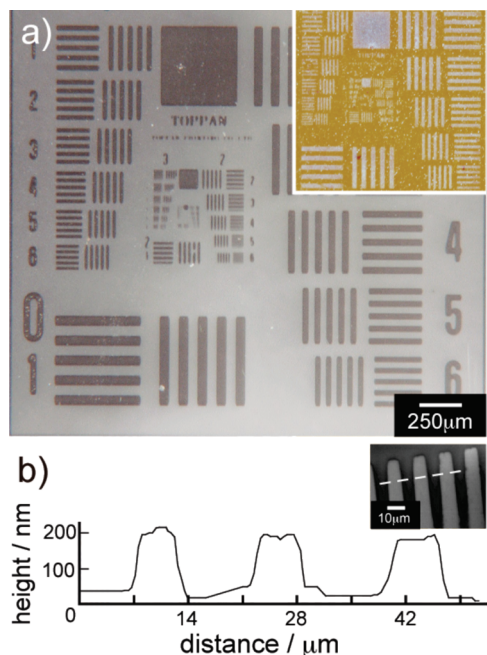
FIGURE 4. (a) Optical image of nickel micropattern on glass substrate through site-selective electroless nickel plating process. The inset shows the nickel patterns on PI substrate (size: 2 × 2 mm). (b) Cross-sectional height profile along the dotted line shown in the SEM image.

less than 1 μm. The heights of the nickel lines are almost uniform evaluated by the height profile analyses of nickel patterns (Figure 4b). Micropatterns of the nickel layers can be also generated on the flexible PI substrate in the same way as shown in the inset of Figure 4a.

In summary, a simple and versatile method for direct site-selective plating of durable nickel layers on a polymer film, which was prepared by photocross-linking films of the polymer through a photomask, was developed. Growth of the nickel layer from a PVMP pattern containing catalytic Pd^0 makes it possible to create of precise nickel patterns with widths as small as 1 μm onto glass, PI, and PET substrates. Moreover, the use of a PVMP film produced strong adhesion between the final metallic layer and the substrates. Since the nickel pattern can initiate subsequent electrodeposition of highly conductive metallic layers such as gold, silver and copper, a multilayer structure on insulating substrates can be fabricated. The direct patterning of metallic layers onto insulating substrates indicates a great potential for fabricating micro/nano devices such as microfluidic devices, microelectronics, biochips, and biosensors (1, 25). The developed fabrication method is suited for low-cost and flexible plastic electronic devices. Moreover, it is adaptable to use in the fabrication of electronic devices by utilizing the printing technology like inkjet and screen printing of PVMP ink on the inert glass and polymeric substrates without the use of photomasks.

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