doi:10.1246/cl.2012.558

Electroless Deposition of Metal Micropatterns Using Ink-jetted ZnO Thin Films as Templates

Hiroki Kono,[1,2] Munetoshi Sakai,*[1] Xintong Zhang,[1,†] Hajime Yoshiki,[1,3] Kazuya Nakata,[1]
Taketoshi Murakami,[1] Hideki Sakai,[2] Masahiko Abe,[2] and Akira Fujishima*[1,2]
[1]*Kanagawa Academy of Science and Technology, KSP East 412, 3-2-1 Sakado,*
Takatsu-ku, Kawasaki, Kanagawa 213-0012
[2]*Faculty of Science and Technology, Tokyo University of Science,*
2641 Yamazaki, Noda, Chiba 278-8510
[3]*RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198*

(Received February 18, 2012; CL-120137; E-mail: sakai@newkast.or.jp)

Metal (Cu and Ni) micropatterns were electrolessly fabricated on glass substrates using ink-jetted ZnO thin films as templates and without employing photoirradiation. The metal micropatterns conformed to the ZnO templates and had line widths as narrow as 45 µm. The line width depended on the wettability of the glass substrate and on the viscosity of the precursor solution of zinc nitrate and poly(vinylpyrrolidone).

Ink-jet printing is a droplet-based direct writing technique. It has been extensively utilized to dispense organic or bioactive substances that have important applications in electronics and biomedical applications.[1,2] There has been increasing interest in using ink-jet printing to directly prepare inorganic microstructures or films.[3,4] Three-dimensional ceramic structures have been prepared by ink-jet printing from colloidal inks containing ceramic powders.[5,6] Moreover, ink-jet printing has been investigated to form inorganic thin films.[7] Electroless plating of metals such as copper, which act as an adhesive between an electrolessly deposited Cu layer and a smooth glass or ceramic substrate has been used to deposit buffer layers of ZnO thin films on substructure plates.[8,9] Cu layers with excellent adhesion can be achieved using this technique. High adhesion strengths of over 2.5 kg mm^{-2} are generated by strong van der Waals forces[9] and mechanical anchoring[10] at the Cu/ZnO interface. Moreover, we found that ZnO thin films strongly adsorbed palladium cations and could be used to catalyze electroless plating of metals.[11] Electroless Cu micropatterns have even been prepared on glass substrates using ZnO thin film templates patterned by photolithography.[12]

On the other hand, the wettability and motion of a water droplet on a solid surface can be controlled by coating several water-repellent materials.[13–15] The sliding motions of droplets on a hydrophobic surface tilted at an angle of 35° could be categorized into three kinds: constant acceleration motion, constant velocity (i.e., no acceleration) motion, and stasis. For example, droplets on an trimethoxyoctadecylsilane coating with a water contact angle of ca. 100° and (3,3,3-trifluoropropyl)-trimethoxysilane coating with a water contact angle ca. 79° exhibit constant accelerated motion and constant velocity (i.e., no acceleration) motion, respectively.[16] The sliding velocity of a water droplet was greater on the trimethoxyoctadecylsilane coating than on the (3,3,3-trifluoropropyl)trimethoxysilane coating. Moreover, the liquid of nano/micropattern structure on a substance had been formed using photolithography and wettability.[17,18]

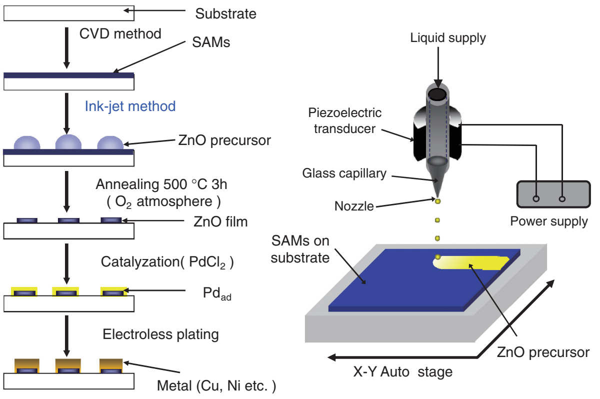

Figure 1. Schematic diagram of novel electroless metal patterning method using ink-jetted ZnO as template.

In this study, we applied metal microline patterning using ink-jetted ZnO thin films as templates onto glass substrates with various wettabilities. The metal line pattern can be controlled with an accuracy of the order of tens of micrometers. This process consists of the following four steps (Figure 1): (i) wettability modification of the glass surface; (ii) fabrication of ZnO patterns by ink-jet printing; (iii) adsorption of palladium ions onto ZnO patterns in an acidic $PdCl_2$ solution; (iv) development in an electroless plating bath. It is a simpler and less expensive method for forming metal patterns than the conventional methods, which employs photolithography processes.

The wettabilities of soda-lime glass substrate were modified with self-assembled monolayers (SAMs) of several kinds of organosilane molecules, including (3-aminopropyl)triethoxysilane (APS; $H_2N(CH_2)_3Si(OC_2H_5)_3$), [3-(6-aminohexyl)amino-propyl]trimethoxysilane (AHAPS; $H_2N(CH_2)_6NH(CH_2)_3Si(OCH_3)_3$), (5,6-epoxyhexyl)triethoxysilane (EHS; $(C_6H_{11}O)Si(OC_2H_5)_3$), (3,3,3-trifluoropropyl)trimethoxysilane (FAS-3; $CF_3(CH_2)_2Si(OCH_3)_3$), trimethoxyoctadecylsilane (ODS; $CH_3(CH_2)_{17}Si(OCH_3)_3$), and heptadecafluoro-1,1,2,2-tetrahydrodecyltrimehoxysilane (FAS-17; $CF_3(CF_2)_7CH_2CH_2Si(OCH_3)_3$). APS, AHAPS, and EHS were deposited on glass substrates by liquid-phase deposition,[19] whereas FAS-3, FAS-17, and ODS were deposited on glass substrates by chemical vapor deposition.[20,21]

Patterned ZnO films were prepared on the modified glass substrates with several wettabilities by ink-jet printing

(Figure 1). In all the experiments, a microdispenser system with a 50-μm-diameter nozzle (MD-K-130, Microdrop Technologies GmbH, Germany) was used to produce microdroplets of the precursor solution. The substrates were placed on a computer-controlled X–Y stage (ALD-602-HOM, Chuo Seiki Co., Ltd., Japan), and the distance between the nozzle and the substrate was fixed at ca. 10 mm. Aqueous precursor solutions were prepared from zinc nitrate and poly(vinylpyrrolidone) (PVP; MW: 35000, Aldrich) in various concentrations. The polymer was used to form a complex with zinc cations to obtain precursor solutions with the desired viscosity. To prepare patterned ZnO thin films on the glass substrates, the precursor solution was dispensed dropwise on horizontally moving substrates. The substrate speed and the droplet generation rate modulated to obtain a predetermined patterned film of the precursor (i.e., a $Zn(NO_3)_2$/PVP film). The patterned precursor films were then annealed at 500 °C in oxygen for 3 h to obtain patterned ZnO films.

Copper or nickel micropatterns were electrolessly deposited on patterned ZnO films using previously reported procedures.[8] Prior to electroless deposition, the ZnO film was immersed in $PdCl_2$ (1.13 mM, pH 3, Wako Chemicals, Japan) for 1 min to activate the ZnO film, which is important for electroless deposition. After rinsing with deionized water, the ZnO film patterned substrate was immersed in a commercial HCHO-based electroless copper plating bath (PB-503, Ebara-Udylite Co., Ltd., Japan) maintained at room temperature or a commercial electroless NaH_2PO_2-based nickel plating bath (LPX, Uyemura Co., Ltd., Japan) maintained at 90 °C for plating. After plating, the substrates were thoroughly washed with deionized water and dried in air.

The line widths of the ZnO patterns were found to depend on the substrate wettability and the viscosity of the precursor solution. The wettability of glass substrates can be controlled by using SAMs of various silane coupling reagents. The SAM-modified substrates had water contact angles between 43.9 and 107.5° (Table 1). The sessile drop method using a contact angle meter (Dropmaster 500; Kyowa Interface Science Co., Ltd., Japan) was used to measure the contact angles. Atomic force microscopy (AFM; Nanoscope IV; Veeco Instruments, U.S.) measurements revealed that all the SAM-modified glass substrates had homogeneous and smooth surfaces with root-mean-square roughnesses of less than 1 nm.[23] The viscosity of the aqueous solution can be controlled by the PVP concentration. Patterned ZnO films suitable for electroless metal plating were obtained from a precursor solution with a $Zn(NO_3)_2 \cdot 6H_2O$:PVP molar ratio of 6:10 (viscosity: 13.6 mPa s).[23] The viscosity of the precursor solution was optimized to stabilize the droplet shape on the substrate by using the microdispenser system. The effect of wetting spread is suppressed for a high viscosity precursor solution. Additionally, although smaller droplets can be formed from higher viscosity solutions, aqueous solutions with high PVP concentrations were not used to prevent the nozzle being clogged with the solution.

Figure 2 shows the relationship between the surface free energies (γ_s) of the surface-modified glass substrates and the line width of the $Zn(NO_3)_2$/PVP patterned precursor film formed on the substrates. The surface free energies were calculated from the static contact angles (θ_s) of water and methylene iodide (Table 1) using the Owens–Wendt equation.[22] This equation consists of two components: dispersive interactions γ_{sd} and polar interactions γ_{sp}. The precursor films were prepared at a droplet dispensing rate of 8.3 mm s^{-1} and a substrate speed of 6.2 mm s^{-1}. Under these conditions, continuous $Zn(NO_3)_2$/PVP lines were obtained on the substrates modified with APS, AHAPS, EHS, and FAS-3. The line widths of the precursor films decreased with decreasing surface free energies of the substrates (Figure 2). No continuous precursor film was observed on ODS- and FAS-17-modified substrates, due to their excessively high water contact angles (Figure 3). Consequently, the minimum line width for a precursor film was obtained on the surface modified with FAS-3.

Table 1. Static contact angles for two probe liquids (3 μL) and surface free energy

Surface	Contact angle θ_s/degree		Surface free energy γ_s/mJ m^{-2}		
	CH_2I_2	H_2O	γ_{sd}	γ_{sp}	γ_s
Glass	29.7	<3.0	28.4	44.9	73.3
APS	47.9	43.9	29.2	27.4	56.6
AHAPS	35.2	58.7	35.2	14.9	50.1
EHS	39.5	68.7	34.7	9.6	44.3
FAS-3	73.4	88.2	18.0	6.2	24.2
ODS	72.7	99.9	20.0	1.7	21.7
FAS-17	91.2	107.5	10.9	2.0	12.9

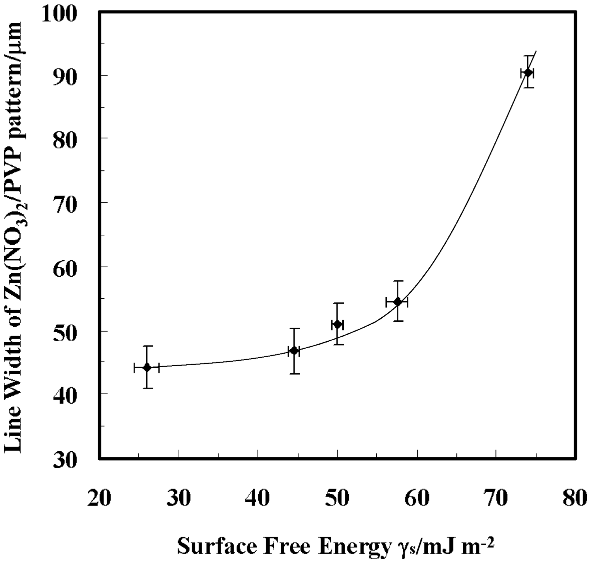

Figure 2. Line width of ink-jetted $Zn(NO_3)_2$/PVP patterns as a function of the surface free energy of the substrate.

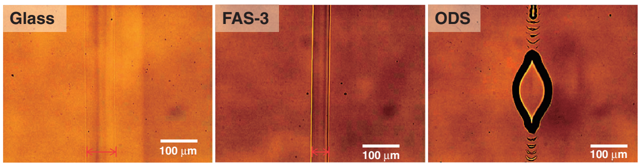

Figure 3. Optical micrographs of (a) precursor film on glass, (b) precursor film on FAS-3 coating, and (c) precursor film on ODS coating.

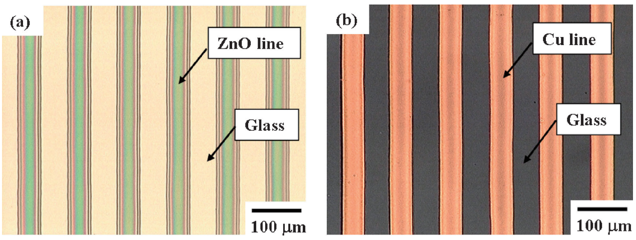

Figure 4. Optical micrographs of (a) ZnO lines formed by ink-jet printing and (b) copper lines formed by electroless plating using ZnO lines as a template.

Patterned ZnO films were obtained from the $Zn(NO_3)_2$/PVP precursor lines after annealing in oxygen. The X-ray diffraction (XRD; RINT1500, Rigaku, Japan) pattern of the annealed sample clearly shows characteristic diffraction peaks of ZnO corresponding to the (100), (002), and (101) faces. The patterned ZnO films were transparent in the visible region and were strongly adhered to the glass substrates. The strong adhesion at the ZnO pattern/glass substrate interface is probably due to zinc ions thermally diffusing into the glass substrate during annealing. The line widths of the obtained ZnO patterns were almost the same as those before annealing. Figure 4a shows an optical micrograph (VH-5000, Keyence, Japan) of 45-µm-wide ZnO lines formed on the FAS-3 surface. These lines were found to be ca. 0.6 µm thick by scanning electron microscopy (JSM-5400, JOEL, Japan); this satisfies the requirement for the adhesive layer for electroless metal plating.[8] Both the line widths and the thicknesses of ZnO lines can be controlled by varying the substrate wettability and/or the viscosity of the precursor solution. Various ZnO patterns can be conveniently fabricated by programming the movement of the X–Y stage.

Aftertreatment with the $PdCl_2$ solution, the ZnO lines changed from being colorless to yellow, which is consistent with previous reports.[8,11] No significant change in the ZnO line widths was observed after treatment. Cu or Ni lines were deposited on the activated ZnO lines (Figure 4a) by plating for 10 min in an electroless copper or nickel plating bath. Figure 4b shows an optical micrograph of Cu lines formed by electroless plating on the ZnO lines. The activated ZnO lines were selectively metalized without abnormal Cu deposition on the untreated glass surface. Electroless Ni lines were also obtained by electroless plating onto ZnO lines. When the metal ion in the electroless plating solution was reduced by using palladium as a catalyst, the metal was deposited on the ZnO line pattern surface. The Cu and Ni lines had line widths of 45 µm and passed a standard peel test using Scotch tape, which suggests they have excellent adhesion to the ink-jetted ZnO lines. Therefore, Cu and Ni micropatterns with excellent adhesive properties were conveniently prepared on glass substrates using a novel electroless plating method that employs ink-jetted ZnO patterns as templates and that does not use photolithography processes. Moreover, the technique can be applied to other metals by employing appropriate palladium-catalyzed electroless plating solutions (e.g., Au and Ag).

In summary, ZnO patterns (minimum line width: 45 µm) with strong adhesion were successfully prepared on glass substrates by ink-jet printing with a precursor solution of $Zn(NO_3)_2$ and PVP. The ZnO patterns function as templates for electroless plating of copper and nickel, and the as-plated metal exhibits sufficiently strong adhesion to the smooth glass substrates for practical applications. This technique combines ink-jet printing and electroless plating, making it simple, low cost, and photolithography free. It is thus expected to have various applications in areas that require metal micropatterns.

This research was partially supported by the Japan Society for the Promotion of Science (JSPS) through the "Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST Program)," initiated by the Council for Science and Technology Policy (CSTP).

References and Notes

† Present address: College of Physics, Northeast Normal University, 5268 Renmin Street, Changchun, Jilin Province, P. R. China

1 H. Sirringhaus, T. Kawase, R. H. Friend, T. Shimoda, M. Inbasekaran, W. Wu, E. P. Woo, *Science* **2000**, *290*, 2123.

2 Z. Wang, H. Shang, G. U. Lee, *Langmuir* **2006**, *22*, 6723.

3 P. F. Blazdell, J. R. G. Evans, M. J. Edirisinghe, P. Shaw, M. J. Binstead, *J. Mater. Sci. Lett.* **1995**, *14*, 1562.

4 W. D. Teng, M. J. Edirisinghe, *J. Am. Ceram. Soc.* **1998**, *81*, 1033.

5 J. H. Song, M. J. Edirisinghe, J. R. G. Evans, *J. Am. Ceram. Soc.* **1999**, *82*, 3374.

6 X. Zhao, J. R. G. Evans, M. J. Edirisinghe, J.-H. Song, *J. Am. Ceram. Soc.* **2002**, *85*, 2113.

7 D.-H. Lee, Y.-J. Chang, G. S. Herman, C.-H. Chang, *Adv. Mater.* **2007**, *19*, 843.

8 H. Yoshiki, V. Alexandruk, K. Hashimoto, A. Fujishima, *J. Electrochem. Soc.* **1994**, *141*, L56.

9 H. Yoshiki, K. Hashimoto, A. Fujishima, *J. Electrochem. Soc.* **1998**, *145*, 1430.

10 R.-D. Sun, D. A. Tryk, K. Hashimoto, A. Fujishima, *J. Electrochem. Soc.* **1999**, *146*, 2117.

11 H. Yoshiki, K. Hashimoto, A. Fujishima, *J. Electrochem. Soc.* **1995**, *142*, 428.

12 H. Yoshiki, K. Hashimoto, A. Fujishima, *Met. Finish.* **1996**, *94*, 28.

13 H. Irie, T. S. Ping, T. Shibata, K. Hashimoto, *Electrochem. Solid-State Lett.* **2005**, *8*, D23.

14 M. Sakai, J.-H. Song, N. Yoshida, S. Suzuki, Y. Kameshima, A. Nakajima, *Langmuir* **2006**, *22*, 4906.

15 M. Sakai, H. Kono, A. Nakajima, X. Zhang, H. Sakai, M. Abe, A. Fujishima, *Langmuir* **2009**, *25*, 14182.

16 A. Nakajima, *NPG Asia Mater.* **2011**, *3*, 49.

17 A. Hozumi, P. Bien, T. J. McCarthy, *J. Am. Chem. Soc.* **2010**, *132*, 5602.

18 D. F. Cheng, T. J. McCarthy, *Langmuir* **2011**, *27*, 3693.

19 S. R. Wasserman, Y.-T. Tao, G. M. Whitesides, *Langmuir* **1989**, *5*, 1074.

20 A. Hozumi, K. Ushiyama, H. Sugimura, O. Takai, *Langmuir* **1999**, *15*, 7600.

21 H. Sugimura, A. Hozumi, T. Kameyama, O. Takai, *Surf. Interface Anal.* **2002**, *34*, 550.

22 D. K. Owens, R. C. Wendt, *J. Appl. Polym. Sci.* **1969**, *13*, 1741.

23 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.