Photomask-Free, Direct Selective Electroless Deposition on Glass by Controlling Surface Hydrophilicity

Kuan-Ting Wang, Wei-Yen Wang, and Tzu-Chien Wei*

Department of Chemical Engineering, National Tsing-Hua University, No. 101, Section 2, Kuang-Fu Road, Hsin-Chu 30013, Taiwan

ABSTRACT: This paper reports a new approach to realize direct selective electroless deposition (ELD) without the requirement of photolithography. This method involves sequential silane-compound modifications in which the first modification creates a hydrophobic surface on the TiO₂-coated glass using a fluorine-rich alkoxysilane compound, followed by a laser ablation to create the pattern. Then, the entire substrate is immersed into an aqueous solution containing amino-silane equipped Pd nanoparticles for the second modification. Because most substrate surface is hydrophobic, the amino-silane-equipped Pd catalysts can only graft on the laser-ablated zone to accomplish selective ELD.

INTRODUCTION

Electroless deposition (ELD) of metal is an important wet process for metallizing nonconductive substrates in circuit board and semiconductor industries.¹⁻⁴ To form metal lines or interconnects of the electronic circuitry, photolithography process involving photoresist coating, photomask aligning, photore sist development, and multiple etchings is widely adopted to create selected sites for ELD. Because photolithography process is tedious and time-consuming, developing alternative methods with shortened steps or even without the need of photomask has become progressively attractive.

The key to realizing direct selective metallization in ELD is to deposit noble-metal catalyst in the desired pattern for the initiation of ELD, either in the form of metal precursors⁵,⁶ or atomic metals.⁷⁻⁹ In attempts to get rid of the use of photomask,¹⁰⁻¹³ microcontact printing,¹⁴⁻¹⁶ inkjet printing,¹⁷⁻²⁰ or direct pen writing²¹,²² of catalyst ink have been studied to realize direct selective ELD on various substrates. It is reported the overall performance of direct selective metallization is highly sensitive to the formula of catalyst ink as well as the property of the substrate.

In this study, we developed a unique approach to realize photomask-free, selective ELD on glass using sequential silane-compound treatments and laser patterning. In particular, the first treatment involves using a fluorine-rich silane compound to form a hydrophobic surface. This hydrophobic surface repels Pd catalyst adsorption from an aqueous solution and thus prevents ELD to serve as an invisible, molecule-level photomask. Then, patterning the substrate by laser ablation to expose selective sites. Those exposed sites are then activated by an amino-silane-equipped Pd nanoparticle for triggering ELD. This approach not only completely eliminates photomask-related processes but also minimizes the usage of expensive Pd catalysts. In this paper, we examine and explain the process using various tools such as water contact angle (WCA) measurement, atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and field emission scanning electron microscope (FESEM). In the meantime, we also provide perspective for practical application of this protocol in the future.

RESULTS AND DISCUSSION

Every step in the above-mentioned direct selective ELD process is examined using various tools, and the result is summarized in Figure 1. It can be seen the process contains five main steps including titanium dioxide (TiO₂) coating, hydrophobic surface formation, laser patterning, selective Pd adsorption, and ELD nickel—phosphorous (Ni—P). Before TiO₂ coating, the cleaned substrate surface is very hydrophilic and smooth as the WCA and surface roughness (Sₐ) is 5.0° and 0.2 nm, respectively. After TiO₂ coating, WCA became 16.6° and the AFM topography reveals a rugged surface (Sₐ = 3.9 nm) composed of particles with different sizes from several tens of nanometers, evidencing hydrophilic TiO₂ is compactly coated on the surface. When the TiO₂-coated glass is grafted by 1H,1H,2H,2H-perfluorooctyltriethoxysilane (PFOTES), the AFM topography appeared almost unchanged, but the WCA increased sharply to 113.3°, hinting the CF moieties of PFOTES were situated upwardly. It should be noted when we immersed the substrate of this stage into aqueous 3-2-(2-aminooethylamino) ethylamino propyl trimethoxysilane—poly-(vinyl alcohol)-capped palladium (ETAS-PVA—Pd) catalyst suspension and then ELD Ni-P bath, no ELD occurred due to the hydrophobicity of the surface. When the PFOTES-grafted surface was patterned by laser, WCA of the ablated zone became nearly zero again, indicating not only TiO₂ but also PFOTES has been largely ablated by laser beam and the...
substrate was immersed into the aqueous ETAS which is an evidence of successful ETAS laser-ablated zone after ETAS as few spots were revealed, whereas the area that was not solution, the morphology of laser-ablated zone changed again. The presence of SiO2 signal hints the coverage of TiO2 coating is not perfect but satisfactory due to weak intensity. After PFOTES grafting, two additional peaks were found, in which a major peak at 530.71 eV was assigned to Ti−O−Si and a minor peak at 532.32 eV assigned to Si−O−C were deconvoluted. The finding of Ti−O−Si contribution is a direct evidence that PFOTES grafting occurs on TiO2 via silanol head group and CFx tails were not involved in the grafting. The minor contribution of Si−O−C implies a small portion of PFOTES was horizontally connected, which leaves room for future improvement of the PFOTES grafting process. Figure 3 shows the FESEM images of the sample after ELD, in which Figure 3a–c illustrates the top view of the sample. It can be seen that the line width of the laser pattern is approximately 30 μm, but the ELD Ni−P width grid became 90 μm, indicating that ELD is seriously spilled. The spillover of line width can be explained by the heat effect of laser processing.

The imaginary illustration in Figure 3d shows that when laser beam ablates the PFOTES-grafted TiO2, not only the laser spotting sites but also the nearby area will be affected due to focused laser energy and poor heat conduction of the glass, resulting in the formation of two zones, the laser-irradiated zone (LIZ) and the laser-affecting zone (LAZ), on the workpiece. The LIZ receives laser energy directly and conducts the heat to LAZ. In our experiment, 30 μm wide laser beam was designed to ablate the PFOTES-coated TiO2 film, but it turned out that the overall ablated width reached 90 μm, meaning the LAZ is even wider than LIZ, indicating the PFOTES protection was damaged in the LAZ due to the poor heat conduction of the glass substrate. We believe this drawback can be mitigated by applying heat sink or thermoelectric chip in the bottom of the glass in the future. Consequently, ELD Ni−P occurred on both LIZ and LAZ. As also shown in Figure 3d, the TiO2 coating in LAZ is clearly observed.

## CONCLUSIONS

We demonstrate that the surface modification by fluorine-rich alkoxysilane grafting can be utilized as an invisible photomask with molecular thickness level, which can be applied in direct selective ELD by simple laser patterning and Pd activator adsorption. We also find the ELD Ni−P line is 3 times wider than the laser ablated line due to the poor thermal conductivity of the glass substrate. Future optimization can be realized by minimizing the area of LAZ using either passive cooling or active cooling, both of which are underway in our laboratory.

## EXPERIMENTAL SECTION

A piece of alkali-free glass (Eagle XG, Corning Corporation) is used as the substrate. Before metallization, the substrate was cleaned using standard RCA (NH4OH/H2O2/H2O = 1:1:5) moieties, respectively. In Figure 2c, the Ti spectrum of the TiO2-coated substrate before PFOTES grafting shows two peaks at 465.69 and 458.99 eV, corresponding to Ti 2p1/2 and Ti 2p3/2 respectively. After the PFOTES grafting, both peaks shifted to higher binding energies by approximately 0.4 eV due to the interference of electronegative CFx moieties. On the contrary, the O 1s spectrum of TiO2-coated glass shown in Figure 2d was composed of multiple contributions including a main peak at 530.26 eV from TiO2 and two minor peaks at $\$1.75$ and $33.20$ eV from OH− and SiO2, respectively. The minor contribution of Si−O−C implies a small portion of PFOTES was horizontally connected, which leaves room for future improvement of the PFOTES grafting process.
treatment for 20 min to remove organic species, followed by rinsing with deionized water. After cleaning, the substrate was coated with a thin TiO$_2$ film by spin-coating an isopropyl alcohol solution containing titanium diisopropoxide bis(acetylacetonate) (Aldrich) of concentration 0.15 M, and the spin speed is 6000 rpm for 20 s. After spin-coating, the substrate coated with a thin TiO$_2$ film sintered at 500 °C for 30 min. The purpose of this thin TiO$_2$ coating is because TiO$_2$ can adsorb the energy of laser beams, so it can be ablated by subsequent laser treatment. The TiO$_2$-coated substrate was then immersed in a toluene (99.5%, J.T.Baker) solution containing 1 vol % PFOTES (Gelest) for 30 min, followed by baking at 150 °C for 30 min to form the Si–O–Si covalent bond between PFOTES, form Ti–O–Si covalent bond.

**Figure 2.** XPS (a) survey spectrum, (b) F 1s spectra, (c) Ti 2P spectra, and (d) O 1s spectra of TiO$_2$-coated glass and PFOTES-grafted TiO$_2$-coated glass.

**Figure 3.** (a) Top-view image of the entire ELD area, (b) magnification of zone 2 and zone 3, (c) magnification of zone 1 and zone 2, and (d) imaginary cross-sectional structure of the entire ELD area and three representative FESEM images.
between PFOTES and TiO₂, and remove toluene traces. After PFOTES modification, the surface of the substrate turned hydrophobic due to the presence of CF moieties.29–31 A fiber laser beam with 1062 nm wavelength (LMF-S, EZLaser, Taiwan) was used to pattern the PFOTES-grafted substrate. Laser power is 10 W, with a scan rate of 100 mm/s. After laser patterning, the substrate was immersed into an aqueous solution containing 50 ppm of ETAS-PVA–Pd nanoparticles for 5 min at room temperature. The ETAS–PVA–Pd was synthesized according to our previous reports.23,32 Amino moieties on ETAS–PVA–Pd can graft on the glass surface, which is opened by laser. Finally, the substrate was selectively ELD in a commercial Ni–P bath (NDF-1, YUEMURA, Japan) at 85 °C for 1 min.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: tcwei@mx.nthu.edu.tw. Tel: 886-35715131. Fax: 886-35715408.

ORCID
Kuan-Ting Wang: 0000-0002-4184-2357
Tzu-Chien Wei: 0000-0002-9608-8275

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Ministry of Science and Technology, Taiwan (MOST105-2628-E-007-021-MY2 and 107-2119-M-007-001).

■ REFERENCES

(1) Schlesinger, M. Electroless Deposition of Nickel. Mod. Electroplat. 2000, 667–684.
(2) Zabetakis, D.; Dressick, W. J. Selective Electroless Metallization of Patterned Polymeric Films for Lithography Applications. ACS Appl. Mater. Interfaces 2009, 1, 4–25.
(3) Michel, B.; Bernard, A.; Bietsch, A.; Delamarche, E.; Geissler, M.; Juncker, D.; Kind, H.; Renault, J.; Rothuizen, H.; Schmid, H.; Schmidt-Winkel, P.; Stutz, R.; Wolf, H. Printing Meets Lithography: Soft Approaches to High-resolution Patterning. IBM J. Res. Dev. 2001, 45, 697–719.
(4) Shacham-Diamand, Y.; Dubin, V.; Angyal, M. Electroless Copper Deposition for ULSI. Thin Solid Films 1995, 262, 93–103.
(5) Liu, W. L.; Hsieh, S. H.; Tsai, T. K.; Chen, W. J.; Wu, S. S. Temperature and pH Dependence of the Electroless Ni–P Deposition on Silicon. Thin Solid Films 2006, 510, 102–106.
(6) Yin, X.; Hong, L.; Chen, B. H.; Ko, T. M. Modeling the Stability of Electroless Plating Bath—Diffusion of Nickel Colloidal Particles from the Plating Frontier. J. Colloid Interface Sci. 2003, 262, 89–96.
(7) Wu, L.; Li, B. L.; Huang, Y. Y.; Zhou, H. F.; He, Y. M.; Fan, Q. H. Phosphine Dendrimer-Stabilized Palladium Nanoparticles, a Highly Active and Recyclable Catalyst for the Suzuki–Miyaura Reaction and Hydrogenation. Org. Lett. 2006, 8, 3605–3608.
(8) Strimbu, L.; Liu, J.; Kaifer, A. E. Cyclodextrin-Capped Palladium Nanoparticles as Catalysts for the Suzuki Reaction. Langmuir 2003, 19, 483–485.
(9) Hu, H. H.; Teng, C. W.; Lin, S. J.; Yeh, J. W. Sn/Pd Catalyzed and Electroless Cu deposition on TaN Diffusion Barrier Layers. J. Electrochem. Soc. 2002, 149, C143–C149.
(10) Sugimura, H.; Hanji, T.; Takai, O.; Masuda, T.; Misawa, H. Photolithography Based on Organosilane Self-assembled Monolayer resist. Electrochem. Acta 2001, 47, 103–107.
(11) Nishimoto, S.; Kubo, A.; Zhang, X.; Liu, Z.; Taneichi, N.; Okui, T.; Murakami, T.; Komine, T.; Fukushima, A. Novel Hydrophobic/Hydrophilic Patterning Process by Photocatalytic Ag Nucleation on TiO₂ Thin Film and Electroless Cu Deposition. Appl. Surf. Sci. 2008, 254, 5891–5894.
(12) Cao, J.; Wu, Z.; Yang, J.; Li, S.; Tang, H.; Xie, G. Site-selective Electroless Plating of Copper on a Poly(ethylene terephthalate) Surface Modified with a Self-assembled Monolayer. Colloids Surf., A 2012, 415, 374–379.
(13) Sawada, S.; Masuda, Y.; Zhu, P.; Koumoto, K. Micropatterning of Copper on a Poly(ethylene terephthalate) Substrate Modified with a Self-Assembled Monolayer. Langmuir 2006, 22, 332–337.
(14) Xia, Y.; Whitesides, G. M. Soft Lithography. Angew. Chem., Int. Ed. 1998, 37, 550–575.
(15) Hübner, P. C.; Helbig, W.; Kim, E.; Whitesides, G. M. Microcontact Printing of Palladium Colloids: Micron-Scale Patterning by Electroless Deposition of Copper. Langmuir 1996, 12, 1375–1380.
(16) Carmichael, T. B.; Vella, S. J.; Afzali, A. Selective Electroless Metal Deposition Using Microcontact Printing of Phosphine–Phosphonic Acid Inks. Langmuir 2004, 20, 5593–5598.
(17) Geissler, M.; Xia, Y. Patterning: Principles and Some New Developments. Adv. Mater. 2004, 16, 1249–1269.
(18) Huang, L.; Huang, Y.; Lian, J.; Wan, X.; Chen, Y. Graphene-based Conductive Inks for Direct Inkjet Printing of Flexible Conductive Patterns and Their Applications in Electric Circuits and Chemical Sensors. Nano Res. 2011, 4, 675–684.
(19) Zhang, T.; Wang, X.; Li, T.; Guo, Q.; Yang, J. Fabrication of Flexible Copper-based Electronics with High-resolution and High-conductivity on Paper via Inkjet Printing. J. Mater. Chem. C 2014, 2, 286–294.
(20) Petukhov, D. I.; Kiri kova, M. N.; Bessonov, A. A.; Bailey, M. J. A. Nickel and Copper Conductive Patterns Fabricated by Reactive Inkjet Printing Combined with Electroless Plating. Mater. Lett. 2014, 132, 302–306.
(21) Liao, Y. C.; Kao, Z. K. Direct Writing Patterns for Electroless Plated Copper Thin Film on Plastic Substrates. ACS Appl. Mater. Interfaces 2012, 4, 5109–5113.
(22) Hu, M.; Cai, X.; Guo, Q.; Bian, B.; Zhang, T.; Yang, J. Direct Pen Writing of Adhesive Particle-Free Ultrahigh Silver Salt-Loaded Composite Ink for Stretchable Circuits. ACS Nano 2016, 10, 396–404.
(23) Kao, Y. H.; Wei, T. C. In Novel Active Nano-Palladium Catalyst for Adsive Electroless Plating of Ni–P Layer on Glass Interposer, 2017 12th International Microsystems, Packaging, Assembly and Circuits Technology Conference (IMPACT), 2017; pp 130–133.
(24) Lu, Y.; Sathasivam, S.; Song, J.; Crick, C. R.; Carmalt, C. J.; Parkin, I. P. Robust Self-cleaning Surfaces That Function When Exposed to Either Air or Oil. Science 2015, 347, 1132.
(25) Erdem, B.; Hansicker, R. A.; Simmons, G. W.; Sudol, E. D.; Dimonie, V. L.; El-Aasser, M. S. XPS and FTIR Surface Characterization of TiO₂ Particles Used in Polymer Encapsulation. Langmuir 2001, 17, 2664–2669.
(26) Xu, Q. F.; Liu, Y.; Lin, F. J.; Mondal, B.; Lyons, A. M. Superhydrophobic TiO₂–Polymer Nanocomposite Surface with UV-Induced Reversible Wettability and Self-Cleaning Properties. ACS Appl. Mater. Interfaces 2013, 5, 8915–8924.
(27) Kim, J. G.; Jung, E. J.; Kim, Y.; Makarov, Y.; Choi, D. J. Quality Improvement of Single Crystal 4H SiC Grown with a Purified β-SiC Powder Source. Ceram. Int. 2014, 40, 3953–3959.
(28) Lv, M.; Liu, J.; Wang, S.; Ai, J.; Zeng, X. Higher-resolution Selective Metallization on Alumina Substrate by Laser Direct Writing and Electroless Plating. Appl. Surf. Sci. 2016, 366, 227–232.
(29) Ishizaki, T.; Masuda, Y.; Sakamoto, M. Corrosion Resistance and Durability of Superhydrophobic Surface Formed on Magnesium Alloy Coated with Nanostructured Cerium Oxide Film and Fluorooalkylsilane Molecules in Corrosive NaCl Aqueous Solution. Langmuir 2011, 27, 4780–4788.
(30) Wang, H.; Xue, Y.; Ding, J.; Feng, L.; Wang, X.; Lin, T. Durable, Self-Healing Superhydrophobic and Superoleophobic Surfaces from Fluorinated-Decyl Polyhedral Oligomeric Silsesquioxane and Hydrolyzed Fluorinated Alkyl Silane. Angew. Chem., Int. Ed. 2011, 50, 11433–11436.

DOI: 10.1021/acsomega.9b00259
ACS Omega 2019, 4, 7706–7710
(31) Wang, J.; Ober, C. K. Self-Organizing Materials with Low Surface Energy: The Synthesis and Solid-State Properties of Semifluorinated Side-Chain Ionenenes. *Macromolecules* **1997**, *30*, 7560−7567.

(32) Hsu, C. W.; Wang, W. Y.; Wang, S. H.; Kao, Y. H.; Wei, T. C. In *Adhesive Nickel−Phosphorous Electroless Plating on Silanized Silicon Wafer Catalyzed by Reactive Palladium Nanoparticles*, 2015 10th International Microsystems, Packaging, Assembly and Circuits Technology Conference (IMPACT), 2015; pp 245−249.