Patterned Metal Deposition on Si Based on Self-Assembly and Inkjet Printing

Jin-Yi Wang,[1] Sheng-Juan Huo,[1] Wen-Bin Cai,*[1,2] and Qun-Jie Xu[2]
[1]*Shanghai Key Laboratory for Molecular Catalysis and Innovative Materials and Department of Chemistry, Fudan University, Shanghai 200433, P. R. China*
[2]*Department of Environmental Engineering, Shanghai University of Electric Power, Shanghai 200090, P. R. China*

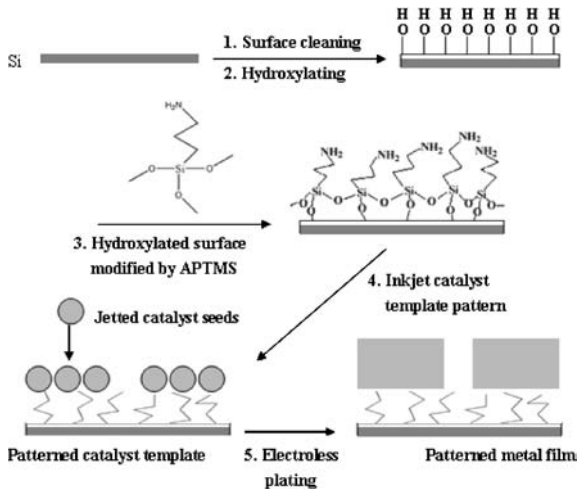
(Received February 28, 2006; CL-060239; E-mail: wbcai@fudan.edu.cn)

A novel maskless and wet process for patterned metallization on a Si wafer was proposed, which incorporates an initial self-assembly of aminosilane as the organic glue layer followed by patterned inkjet printing of Au colloids or Pd(II) species as the catalyst template and finalized by selective chemical plating to form desired patterns of metals.

The ability of fabricating patterned metal structures on the surface of semiconductors and insulators is essential to the microelectronic industry.[1–3] Currently, photolithography is the predominant strategy for patterned molding with masks in the microfabrication. However, this strategy requires high-cost facilities and operations, and may not be suitable for prototype and small patch of board production. Moreover, it is not compatible with newly developed microelectronic materials, for example the organic semiconductors, for the laser used in photolithography may lead to decomposition of the materials. To address these issues, a non-photolithographic strategy is required as a complement.

A widely used "soft lithographic" method[4] is the "microcontact printing" process.[5,6] An elastic PDMS mold is micropatterned by photolithographic method: It is made to adsorb catalyst ink on the surface and is used as a stamp to form patterned catalyst template for selective electroless deposition. This method can provide high resolution, yet it depends on photolithography for molding, and the swelling effect on the stamp must be further considered. Groups in Waseda have developed a very encouraging maskless and wet process for fabricating patterned metallic nanostructures on Si wafers based on nanoindentation technique with a scanning probe microscope (SPM).[7] Nevertheless, for micrometer to millimetter-scaled patterned fabrication, the inkjet printing (IJP) combined with wet process is a promising approch,[8–11] with which desired metallic patterns are obtained by the program-controlled jetting of a catalytic template followed by selective electroless plating without molding, masking and etching steps, thus it is fully independent of traditional photolithographic technology. Unfortunately, so far, success of the IJP approach has been limited only to plastics or organic polyelectrolyte $(PAA/PAH)_n$ multi-layer substrates.

In consideration of the central role of Si in microelectronics, it is highly demanding to extend the IJP approach to patterned metallization on Si wafers. Unlike the previous substrates, natural Si surfaces do not bind strongly the catalyst species. In current preliminary report, 3-aminopropyltrimethoxysilane (APTMS) was self-assembled on a Si substrate to serve as an "organic glue" to bind the catalyst nuclei,[12] either Au colloids or Pd(II) catalytic species formed a desired pattern with IJP as designed and controlled by a PC. The catalyst monolayer was embedded onto the Si substrate through electrostatic force between the positively charged amino group and the negatively charged catalyst species. Selective electroless plating occurs on the patterned catalyst sites. The whole process is demonstrated in Scheme 1. An *n*-(110) Si wafer (5–8 $\Omega\,cm^{-1}$) was cut and ultrasonically cleaned in acetone and water, then treated with the RCA method to remove possible contaminants: soaking it in a piranha solution (H_2SO_4:H_2O_2, 7:3 in volume), and afterward in a solution of $NH_3 \cdot H_2O$, H_2O_2, and H_2O (1:1:5 in volume), then in a solution of HCl, H_2O_2, and H_2O (1:1:5 in volume) at 90 °C for 10 min. The wafer surface was hydroxylated by immersing it in a piranha solution (H_2SO_4:H_2O_2, 7:3 in volume) at 90 °C for 30 min or coated with SiO_2 layer by heating it in an oven at 800 °C for 30 min. The cooled Si wafer was then rinsed with Milli-Q ultrapure water and dried by a Ar stream. The self-assembly was achieved by immersing the Si wafer into an aqueous solution of APTMS (APTMS:H_2O, 1:20 in volume) at room temperature for 4–6 h. Upon removal, the Si was thoroughly rinsed with copious amount of Milli-Q water.



Scheme 1. Protocol for the process of self-assembled monolayer, the ink-jetted patterned catalyst template (Au colloids or Pd(II) ions here), and selective electroless plating to form a patterned metal film (Au or Ni–B alloy).

A Au colloidal solution with an average particle size of 2.5 nm was prepared according to the reported procedure,[12] serving as the source of the catalyst ink for the patterned deposition of Au layer. The catalyst ink was fed into the modified cartridge of a Canon IP1000 color inkjet printer. Catalyst template patterns were designed on a PC using a standard image-editing program. The catalyst ink was printed at 1200 dpi onto the APTMS modified Si surface. After drying, the surface was rinsed thoroughly with ultrapure water. The Au plating bath was a mixed solution containing 5 g/L $HAuCl_4$ and 0.5 g/L hy-

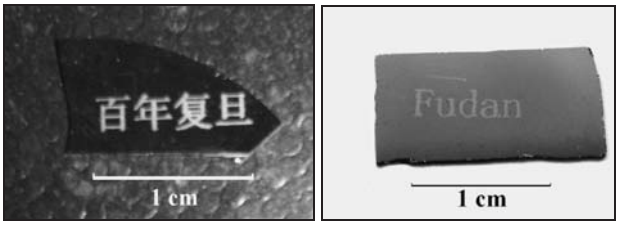


Figure 1. (a) Photograph of the patterned deposition of Au on a Si wafer (Left). (b) Photograph of the patterned Ni–B deposit with a "Fudan" logo on a Si wafer (Right).

droxylamine hydrochloride. The substrate was dipped into the bath solution at room temperature for 5 min to conclude the selective electroless plating on patterned catalyst template sites. The image of as-plated pattern with four Chinese characters (meaning Centenary Fudan) is shown in Figure 1a.

Ni alloy films are very good candidates for barrier layers and corrosion-resistant coatings in microelectronics applications.[2,13] Patterned deposition of a Ni–B film can be realized by the same approach except that the catalyst ink was replaced with a Na_2PdCl_4-containing solution. The recipes for plating the Ni–B alloy layer are the same as those reported in Ref. 9, consisting of 40 g/L nickel sulfate, 20 g/L sodium citrate, 10 g/L lactic acid, and 1 g/L DMAB in water with pH adjusted to 6.5. The electroless plating was carried out at room temperature for 2 min. Shown in Figure 1b is the digital photo of as-formed Ni–B pattern of "Fudan" on Si.

As a result of a drop-on-demand printing, this approach is very cost-effective regarding the catalyst layer. The patterned Au or Ni–B layer was rather continuous, uniform, conductive and in accordance with the designed characters. Adhesion of thus-formed Au film on Si is much better than that of vacuum-evaporated Au film on Si,[12] whereas the adhesion of Ni–B on Si passes the peeling test following the testing standard of IPC 6013 No. 2.4.1 (www.ipc.org). The improved adhesion can be ascribed to the presence of self-assembled organic glue interlayer. Direct jetting of Au colloid or Pd(II) catalyst templates on Si without the use of the aminosilane layer will not lead to formation of desired metallic patterns on Si in the subsequent chemical plating. This is totally different from the previous reports on plastics and polyelectrolyte $(PAA/PAH)_n$ multi-layer.[8–11] For a regular drop-on-demand inkjet printer as we used here, the ink jetted from the printer nozzles onto the substrate was not continuous but initially composed of numerous ink spots with a minimum volume of ca. 10 pL for each drop. The ink was absorbed by APTMS and the spots diffused and coalesced before drying on the monolayer surface to obtain a rather continuous pattern as designed. Therefore, the resolution and the quality of the printing depend on the spot volume of the printer and the surface properties. Although the minimum line width achieved in current work is around 100 μm, it can be expected that with advancement of inkjet printing technology[14] (for example, using a high-precision custom-made printer with a function of a plotter) and optimization of catalyst ink recipes (for example, adjusting the viscosity) the line-width limit down to ca. 10 μm can be hopefully reached with our current approach. In term of the line resolution, the IJP is slightly better than the electrochemical printing (EcP) method in which a microelectrode (anode) was controlled to move over a conductive substrate (cathode) according to a designed pattern.[15] It should be mentioned that the above IJP approach can be extended to many other metals such as Cu, Ag, and Co, and substrates such as glass, quartz, ITO, Ti/TiO_2, ceramics, and some organic semiconductors onto which siloxane molecules can be self-assembled as the binding glue. Such work is in progress and will be reported in due course.

In conclusion, we presented a non-photolithographic approach to fabricate patterned metallic layers on a Si wafer with the unique combination of self assembly for surface modification, inkjet printing of catalyst ink, and selective electroless plating on the catalyst template.

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