

Patterned Self-Assembled Monolayers Formed by Microcontact Printing Direct Selective Metalization by Chemical Vapor Deposition on Planar and Nonplanar Substrates

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Self-assembled monolayers (SAMs) of alkylsiloxanes were patterned by microcontact printing (μ CP) on a number of substrates: Al/Al₂O₃, Si/SiO₂, TiN/TiO₂, glasses, indium tin oxide (ITO), and plasma-modified polyimide. The patterned SAMs on these surfaces define and direct the selective chemical vapor deposition (CVD) of copper using (hexafluoroacetylacetonato)(vinyltrimethylsilane)copper(I) (Cu^I(hfac)(vtms)) as the source gas. This paper presents several examples of microstructures of copper fabricated by selective, SAM-directed CVD, including fabrication of thin-film interconnects (with feature sizes of 0.5–100 μ m), and selective filling of trenches and vias (models of microstructures having high aspect ratios) with feature sizes below 1 μ m.

This paper describes the use of microcontact printing (μ CP)¹⁻³ to define and direct the selective chemical vapor deposition (CVD) of copper on a variety of surfaces. This procedure uses μ CP to pattern self-assembled monolayers (SAMs) of alkylsiloxanes on substrates having polar surfaces;⁴ these surfaces control the nucleation and subsequent growth of copper. It can be used both to form patterns of copper on planar surfaces and to direct the copper to recessed features (for example, trenches and vias).

The ability of μ CP to form patterned SAMs on metal and nonmetal (SiO₂, Al₂O₃) surfaces is well established; these surfaces can be planar or topographically complex.¹⁻⁴ This ability to pattern surfaces with SAMs suggests a new approach to patterning metalization by CVD. In the simplest rationale for this approach, the patterned SAMs would define the reactive sticking probability of a reagent used for CVD in a system whose growth chemistries are autocatalytic.

One of the most useful classes of SAMs is that formed by alkylsiloxanes on hydroxyl-terminated surfaces, such as Al/Al₂O₃ and Si/SiO₂.⁵ This study demonstrates the formation of patterned structures of copper, using CVD from a source gas of (hexafluoroacetylacetonato)(vinyltrimethylsilane)copper(I) (Cu^I(hfac)(vtms))⁶ on substrates whose surfaces have been patterned by a monolayer of octadecylsiloxane. This Cu(I) reagent yields high-

quality thin films of copper in blanket deposition; it also exhibits modest selectivity in rates of deposition on different substrates, but only in a narrow range of temperatures between 150 and 200 °C.⁷⁻⁹ It thus provides a stringent test of the utility of SAMs in modifying the barriers to initial nucleation and subsequent growth of thin films of copper by CVD.¹⁰ We have employed SAMs both to passivate and activate the surface toward CVD, although for most substrates it appears sufficient only to deactivate specific regions in order to obtain patterned deposition of copper.

Figure 1 outlines the procedures used to prepare patterned SAMs of octadecylsiloxane on the surfaces of substrates used for selective CVD of copper.^{2,4,11} Stamps of poly(dimethylsiloxane) (PDMS) were inked with a solution of octadecyltrichlorosilane (OTS) in hexane or toluene (0.2–25 mM) and brought into contact with the surfaces. Spectroscopic analyses (XPS, FT-IR, ellipsometry) demonstrated the formation of monolayers of octadecylsiloxane with high quality on a range of oxide bearing substrates, including Al, Si, and TiN.¹² SAMs were also formed on glasses (for example, glass microscope slides and indium tin oxide, ITO), and polymers (pyromellitic dianhydride oxydianiline polyimide, PMDA-ODA) whose surfaces had been modified by plasma treatment; these latter structures have been less completely characterized.

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(10) We are exploring an alternative and complementary strategy in which SAMs enhance nucleation in CVD process. Preliminary studies suggest that this technique may allow control over the pattern of the deposition as well as the texture and microstructure of metal films formed by CVD.

(11) The stamps used for making patterns on planar substrates by μ CP were made from poly(dimethylsiloxane) (PDMS) using the procedure described previously.¹⁻³ Large-area planar stamps were prepared by casting PDMS against a polished silicon wafer.

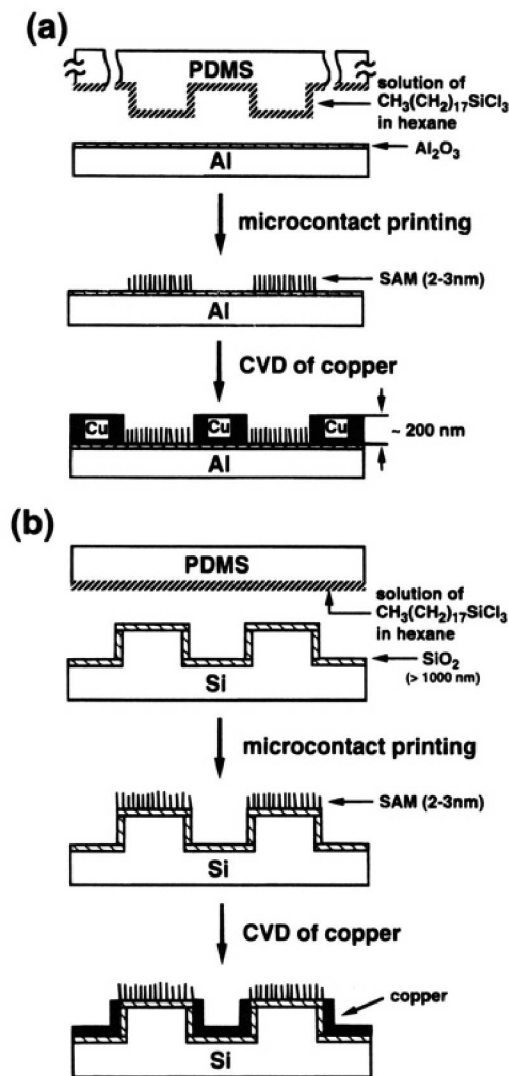


Figure 1. Schematic outline of the procedures for patterning alkylsiloxanes on a planar (a) and a nonplanar (b) substrate. Nucleation and deposition of copper only occur on those regions underivatized by the SAM.

We also used OTS at similar concentrations in anhydrous ethanol; the coverage of the monolayer on the surface obtained with this solvent appears to be lower than that with RSiCl_3 in hydrocarbons.

Figure 2a shows the scanning electron micrograph of a patterned monolayer of octadecylsiloxane generated by μCP on a planar surface of $\text{Al}/\text{Al}_2\text{O}_3$.^{4,13} Figure 2b shows the patterned deposition of copper on these surfaces;¹⁴ copper forms on surfaces *not* covered by the SAM. The selectivity of the deposition is more obvious from the Auger

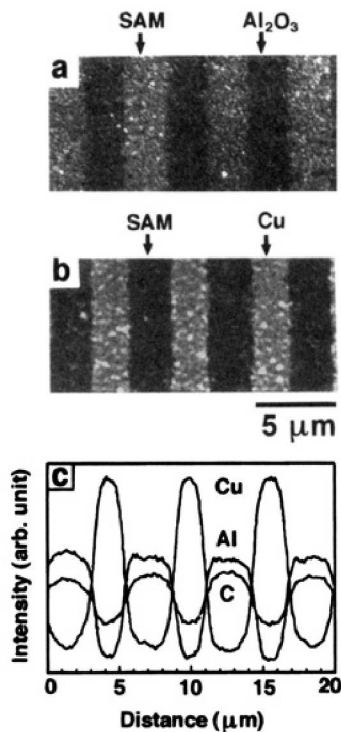


Figure 2. (a) Scanning electron micrograph of patterned SAMs of octadecylsiloxane (parallel lines, $3\ \mu\text{m}$ in width and separated by $2\ \mu\text{m}$) on the surface of $\text{Al}/\text{Al}_2\text{O}_3$. (b) Scanning electron micrograph of lines of copper ($2\ \mu\text{m}$ in width and $\sim 200\ \text{nm}$ in thickness) deposited by selective CVD on the same patterned surface shown in (a). The bright regions correspond to the lines of copper. (c) Auger electron spectroscopy (AES) line scans on the samples of (b) in the direction perpendicular to the lines of copper.

electron spectroscopy (AES) line scan shown in Figure 2c: the regions derivatized with OTS are seen to be largely free of $\text{Cu}(0)$ (although defects are clearly evident).

The micrographs shown in Figure 3 demonstrate the most intriguing application for μCP as a method of controlling CVD—the passivation of highly textured surfaces.¹⁵ Figure 3a shows the results obtained for a blanket deposition of copper on the trench architecture; Figure 3b shows the selective deposition of copper on the same kind of substrates as in Figure 3a, but with the surface of the plateau regions passivated by a monolayer of octadecylsiloxane (following the procedure outlined in Figure 1b). Figure 3c shows selective deposition of copper in via holes by CVD; again, the top surface of the substrate had been passivated by a monolayer of octadecylsiloxane. This last result is most striking: $0.7\ \mu\text{m}$ diameter holes are filled selectively (with the growth initiating at the walls and base of the via), while the more exposed plateaus escape deposition of copper. This method of selective CVD on recessed or hidden surfaces may be useful in micro-

(12) The structural characterization of these SAMs will be reported separately. In general, we found that the structural characteristics of the SAM depended very sensitively on the experimental procedures used. The solvents used must be dry to prevent prepolymerization of the silane. Concentration of "ink" solution and printing time are critical experimental variables. Dilute solutions ($< 10\ \text{mM}$) and short printing times ($< 1\ \text{min}$) usually resulted in low mass coverage while more concentrated solutions ($> 100\ \text{mM}$) and/or longer printing times ($> 1\ \text{min}$) led to multilayer coverages ($> 100\ \text{\AA}$). A $10\ \text{mM}$ solution and a printing time of $\sim 1\ \text{min}$ deposited an overlayer of $\sim 23\ \text{\AA}$ thickness as measured by ellipsometry. Vibrational spectroscopy suggests the assembly of a densely packed structure under these conditions. The structure obtained is very similar to that obtained by immersion of a substrate in a solution of OTS in hexane. The structures of both the submonolayer and multilayer phases are complex; the former yielded very poor selectivity for CVD.

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(14) Depositions of copper using $\text{Cu}^{\text{I}}(\text{hfac})(\text{vtms})$ as the organometallic precursor were carried out at $150\ ^\circ\text{C}$ in a cold-wall reactor. The reagent was carried into the integral high vacuum reactor using a $10\ \text{sccm}$ Ar carrier gas flow and delivered to the susceptor region at a total system pressure of $100\ \text{mTorr}$. The source reservoir and gas carrying lines were maintained at $40\ ^\circ\text{C}$. By use of these conditions, deposition rates of $\sim 200\ \text{\AA}/\text{min}$ were achieved. The resulting copper films were found to be nearly elementally pure ($< 2\%$ C, O, and F) by Auger electron spectroscopy. The films shown here ($0.2\text{--}0.3\ \mu\text{m}$ in thickness) have resistivities of $\sim 2.3\ \mu\Omega\ \text{cm}$ (measured by the four point probe technique); this value compares well with the resistivities of thick, elementally pure films of copper, $\sim 1.72\ \mu\Omega\ \text{cm}$.

(15) The substrates used in these experiments were Si(100) wafers that were patterned with an array of trenches ($0.7\ \mu\text{m}$ trenches with $0.35\ \mu\text{m}$ plateaus) or via holes ($0.7\ \mu\text{m}$ in diameter) using standard fabrication methods. The surfaces of these substrates were covered by a layer of SiO_2 ($> 1000\ \text{nm}$ in thickness) grown by plasma-assisted CVD.

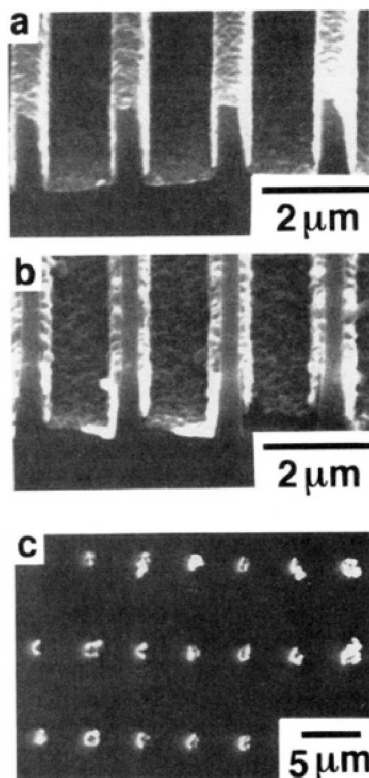


Figure 3. Scanning electron micrographs of microstructures of copper fabricated by CVD on substrates whose surfaces were (a) underivatized and (b, c) derivatized by a monolayer of OTS. Specimens (a) and (b) were fractured in cross section to reveal the thickness of copper—here ~ 200 nm. Copper deposited only in the recessed regions not covered by OTS (the tops of the ridges in b and the surface into which the holes were drilled in c).

electronics processing: the topology of the substrate in this demonstration is related to that of vias in high-density DRAMs and other devices.^{16,17}

Although others have used SAMs to pattern the chemical vapor deposition of metals, the approach taken here is different from these other processes.^{18–21} Jain et al.¹⁹ and Gelatos²⁰ enhanced the selectivity of copper in

filling tungsten lined trenches by adding silating agents (methylchlorosilanes or hexamethyldisilazane) to the mixture of gases (predominantly $\text{Cu}^{\text{I}}(\text{hfac})(\text{vtms})$ and H_2) fed to the CVD reactor. Schoer et al. passivated a gold surface with SAMs of octadecyl mercaptan and, after patterning them by micromachining with a scanning probe device, selectively deposited copper.²¹ Potochnik and co-workers recently reported the use of a lithographically patterned, metal-promoted SAM to effect patterned Cu CVD.²² In an early application of μCP , Kumar et al.² used patterns of SAMs of alkanethiolates on planar surfaces of gold to deposit nickel selectively in an electroless plating solution. The process described in this report could be used, in principle, to deposit Cu selectively on many substrates without photolithography. This procedure should also provide a wide process window due to its insensitivity to the surface defects that typically act as heterogeneous nucleation centers.²³

This study suggests that patterned SAMs direct the selective CVD of metals by inhibiting nucleation. The method is not yet optimized to a level where realistic evaluation of utility in demanding technological applications is possible;²⁴ the principles demonstrated by this study are, however, general.

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