



## Selective Copper Deposition on Barrier Layer Ta and TaN in the Presence of a Copper Seed Layer

Chong-yang Liu and Allen J. Bard<sup>\*,\*z</sup>

Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712, USA

Electrochemical deposition of copper on exposed barrier layer (Ta and TaN) was carried out without deposition on an existing Cu seed layer on the same substrate. This was accomplished by immersing the sample in a solution of 1 mM 1-dodecanethiol (RSH) in ethanol, where preferential adsorption of a self-assembled monolayer of RSH deactivated the copper surface. The Cu seed layer could be reactivated again by applying a negative potential pulse. Such an externally controlled reversible change in surface chemistry toward copper deposition is potentially useful for a copper seed layer repair in the fabrication of contacts and interconnects for integrated circuits.

© 2003 The Electrochemical Society. [DOI: 10.1149/1.1543334] All rights reserved.

Manuscript submitted September 2, 2002; revised manuscript received November 1, 2002. Available electronically January 17, 2003.

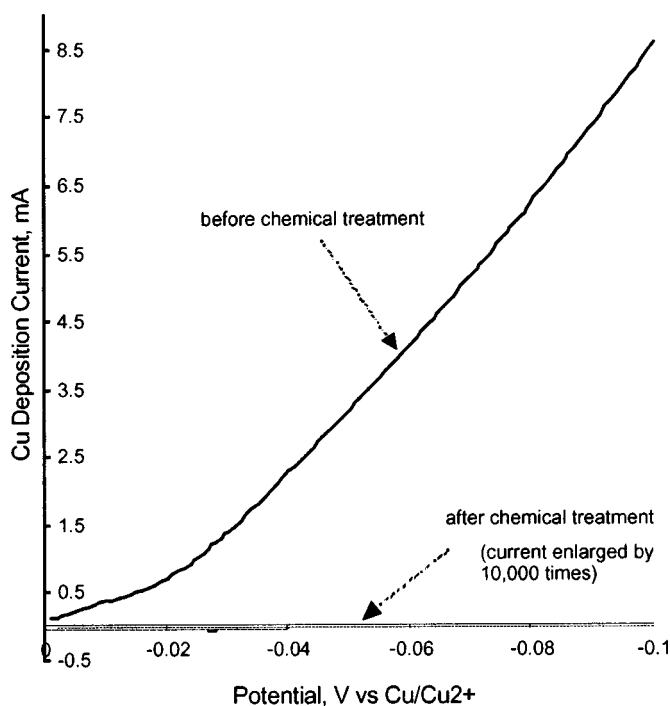
The fabrication of small feature sizes in integrated circuits requires materials with higher electrical conductivity for contacts and interconnects, which has led to the replacement of Al by Cu.<sup>1</sup> To prevent Cu diffusion into the silicon, a barrier layer such as Ta or TaN must first be deposited on the substrate. Because the barrier layer is not very conductive, before Cu electrodeposition, a copper seed layer is formed on top of the barrier layer, *e.g.*, by chemical vapor deposition. As the feature sizes get smaller and aspect ratios get higher, it becomes increasingly difficult to obtain complete coverage by the seed layer, especially on the sidewalls of trenches and vias. Uncovered areas of the barrier layer in such locations can produce voids during the subsequent Cu electroplating step that can deteriorate device performance. Therefore, seed layer repair to remove any gaps in the seed layer is an important step in the ultralarge scale integration metallization. Cu can be electrochemically deposited on a barrier layer such as TiN.<sup>2</sup> However, when Cu and a barrier layer coexist on the same surface, deposition will take place almost exclusively on Cu structures. Ideally, one would like to deposit Cu on any exposed barrier layer (*i.e.*, repair the barrier layer) without deposition of an appreciable amount of Cu on the seed layer already present.

In this paper, we report a method for selective Cu deposition on barrier layer in the presence of Cu structures in a model system to demonstrate the basic principle for Cu seed layer repair. First, alkane thiol was adsorbed on existing Cu structures to deactivate their surface toward electrodeposition, and then Cu was electroplated on exposed barrier layer. Finally, the passivated Cu surface was reactivated for further electrodeposition steps. Note that this method relies completely on the control of the material surface chemistry and does not require use of a mask, mold, stamp, template, or the like used in patterning or printing a desired structure on a substrate.<sup>3</sup> Studies of chemically modified electrodes with self-assembled monolayers (SAMs) of alkanethiols have been mainly focused on Au surfaces,<sup>4</sup> although an STM study of 1-octanethiol on Cu(111) in a ultrahigh vacuum was recently reported.<sup>5</sup>

The effect of surface modification for electrochemical deposition of Cu on a Cu rod (3.1 mm in diameter, 99.999%, Aldrich, area 2.2 cm<sup>2</sup>) is shown in Fig. 1. The experiments were carried out in a solution of 1 M CuSO<sub>4</sub> in water with a three-electrode system. Cu rods were also used as both counter and reference electrodes. The scan rate was 20 mV/s and current densities were 1 to 10 mA/cm<sup>2</sup>. The deposition current was at the mA level for bare Cu surface before chemical treatment and uniform deposition of Cu was observed. However, after the sample was immersed into a solution of ethanol containing 1 mM 1-dodecanethiol (98 + %, Aldrich) overnight, the electrochemical deposition current diminished to negligible (baseline) levels (less than the  $\mu$  A level). Note that the current

shown in Fig. 1 after treatment was amplified 10,000 times compared to the unmodified surface under the same experimental conditions. No trace of Cu deposition was seen under an optical microscope, indicating successful suppression of Cu deposition on the Cu surface by this chemical treatment. In contrast, when barrier layers of Ta and TaN were subjected to the same chemical treatment, their behavior in Cu plating was essentially unchanged, strongly suggesting that no SAM was formed on these materials. This suggested that Cu would preferentially deposit just on barrier layers coexisting with Cu structures on the same substrate by using this treatment. Moreover, the adhesion between deposited Cu and TaN was 15.7 J/m<sup>2</sup> significantly stronger than that between Scotch tape and the same barrier layer ( $\sim$ 5 J/m<sup>2</sup>).

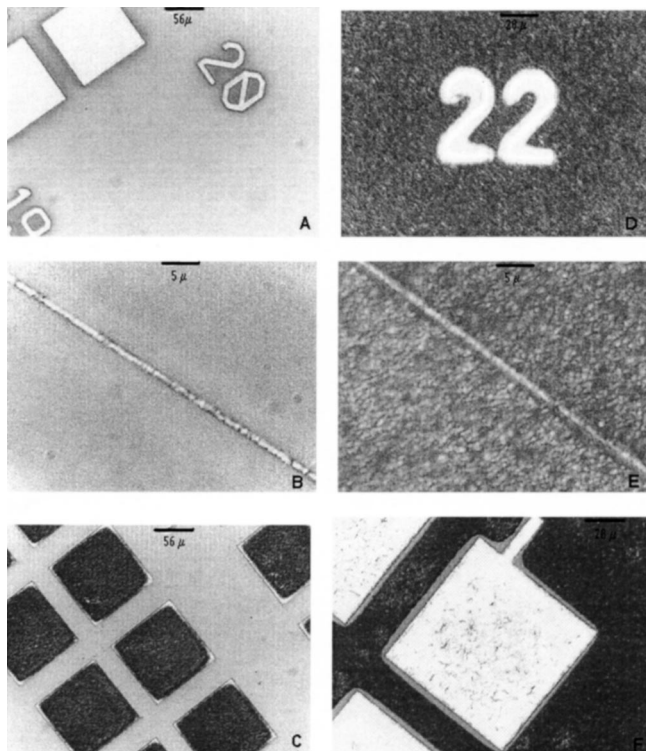
Samples for the selective Cu deposition were provided by Sematech (Austin, TX). These were silicon wafers coated with a barrier layer of Ta or TaN. A deposited Cu film over the barrier layer was subjected to chemical mechanical polishing down to the barrier layer, to leave small ( $\sim$  $\mu$ m) Cu structures on the trench, vias and other features on the same surface. Figure 2A and B show images of



**Figure 1.** Cu deposition current as a function of bias voltage in water containing 1 M CuSO<sub>4</sub> on Cu electrode (2.2 cm<sup>2</sup>). Cu rods were used as both counter and reference electrodes. The scan rate was 20 mV/s.

\* Electrochemical Society Active Member.

<sup>z</sup> E-mail: ajbard@mail.utexas.edu



**Figure 2.** Micrographs showing selective Cu deposition on Ta barrier layer coexisting with Cu structures on the same Si substrate. Images A and B were taken from a sample showing Cu structures surrounded by a barrier layer of Ta at two different locations before Cu deposition; image C, without chemical treatment Cu deposited only on Cu surfaces; images D, E, and F, with chemical treatment (SAM formation) Cu deposited only on barrier layer at three different locations. The Cu deposition conditions were the same as those used in Fig. 1.

samples with Cu structures surrounded by the Ta barrier layer. Without chemical pretreatment to form the SAM, electrodeposition of Cu occurred only on Cu surfaces as shown in Fig. 2C. However, after the sample was immersed in a solution of 1 mM 1-dodecanethiol/ethanol for 4 h, electrodeposition of Cu occurred only on the barrier layer, as shown in Fig. 2D, E, and F. In this case, the SAM of alkane thiol on the Cu surface greatly decreased the rate of Cu deposition on this surface so that it occurred preferentially on the barrier layer

which did not appear to absorb the thiol. The Cu deposited on the Ta surface was rough compared to the shiny Cu structures that are unavoidably overexposed in images taken with an optical microscope (Fig. 2D). Note the sub-micrometer wide Cu line that clearly separated the two deposited Cu zones (Fig. 2E) that were higher than the pre-existing Cu structure but did not appear to bridge over it, although the mechanical polishing introduced defects on the Cu line (Fig. 2B) and the resolution limitations of the microscope made the boundary somewhat fuzzy. This indicated a complete passivation of the thin Cu surface rather than an anisotropic plating. Also, note that Cu at the edges of structures in the original sample after polishing were also passivated during the chemical treatment, as no Cu was electrodeposited there as shown in Fig. 2F. These images, as well as images with a number of other samples, clearly demonstrate that the chemical treatment for selective deposition of Cu on a barrier layer in the presence of Cu structures works well.

Finally, the passivated Cu surface could be reactivated again by applying a negative potential pulse such as  $-1.3$  V for 0.2 s that restored the chemically modified Cu surface to its original properties. Cathodic treatment of Au surfaces is known to remove SAMs. This action removed the SAM and electrodeposition of Cu on the reactivated Cu layer could be carried out. Both the Cu deposition current and the surface appearance were about the same as those of the original (untreated) Cu surface. For example, when one third of a deactivated sample ( $2.5 \times 5$  cm) was reactivated and the whole sample was placed back into the plating bath, Cu was plated only on the reactivated area and no trace of deposited Cu was seen on the remaining two-thirds of the sample. Such an externally controlled reversible change in Cu surface chemistry toward Cu deposition should be useful in the fabrication of interconnects and contacts for electronic devices.

#### Acknowledgment

This project was supported by Sematech and the National Science Foundation (CHE-9876855). We thank Aaron Frank for providing the test samples and the adhesion measurements.

*The University of Texas at Austin assisted in meeting the publication costs of this article.*

#### References

1. A. E. Braum, *Semicond. Int.*, April (1999).
2. G. Oskam, P. M. Vereecken, and P. C. Searson, *J. Electrochem. Soc.*, **146**, 1436 (1999).
3. N. L. Jeon, R. G. Nuzzo, Y. Xia, M. Mrksich, and G. M. Whitesides, *Langmuir*, **11**, 3024 (1995).
4. A. Ulman, *An Introduction to Ultrathin Organic Films from Langmuir-Blodgett to Self-Assembly*, Academic Press, New York (1991).
5. S. M. Driver and D. P. Woodruff, *Langmuir*, **16**, 6693 (2000).