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Abstract
"Ultrathin" metallization layers on the order of nanometers in thickness are increasingly used in semiconductor interconnects and other nanostructures. Aqueous deposition methods are attractive methods to produce such layers due to their low cost, but formation of ultrathin layers has proven challenging, particularly on oxide-coated substrates. This work focused on the formation of thin copper layers on aluminum, by galvanic displacement from alkaline aqueous solutions. Analysis by atom probe tomography (APT) showed that continuous copper films of approximately 1 nm thickness were formed, apparently the first demonstration of deposition of ultrathin metal layers on oxidized substrates from aqueous solutions. The APT reconstructions indicate that deposited copper replaced a portion of the surface oxide film on aluminum. The results are consistent with mechanisms in which surface hydride species on aluminum mediate deposition, either by directly reducing cupric ions or by inducing electronic conduction in the oxide, thus enabling cupric ion reduction by Al metal.

Disciplines
Chemical Engineering

Comments

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Atom Probe Tomography Characterization of Thin Copper Layers on Aluminum Deposited by Galvanic Displacement

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ABSTRACT: "Ultrathin" metallization layers on the order of nanometers in thickness are increasingly used in semiconductor interconnects and other nanostructures. Aqueous deposition methods are attractive methods to produce such layers due to their low cost, but formation of ultrathin layers has proven challenging, particularly on oxide-coated substrates. This work focused on the formation of thin copper layers on aluminum, by galvanic displacement from alkaline aqueous solutions. Analysis by atom probe tomography (APT) showed that continuous copper films of approximately 1 nm thickness were formed, apparently the first demonstration of deposition of ultrathin metal layers on oxidized substrates from aqueous solutions. The APT reconstructions indicate that deposited copper replaced a portion of the surface oxide film on aluminum. The results are consistent with mechanisms in which surface hydride species on aluminum mediate deposition, either by directly reducing cupric ions or by inducing electronic conduction in the oxide, thus enabling cupric ion reduction by Al metal.

INTRODUCTION

Metallization layers on the order of nanometers in thickness are demanded in technologically significant nanostructures such as semiconductor interconnects, NEMS, and electrocatalysts. Solution-based deposition techniques such as electrodeposition are attractive low-cost strategies to produce such "ultrathin" layers. Electroless deposition involves chemical instead of electrochemical reduction, and thus can be applied to substrates covered by electrically insulating oxide layers, enabling applications to base metals and interconnect diffusion barriers.1,2 Galvanic displacement, a type of electroless deposition in which the substrate or an adsorbed species acts as the reducing agent, can produce nanometer-thickness films on semiconductors and noble metals.3,4 Galvanic deposition of copper layers has been reported on oxide-covered materials such as aluminum, tantalum, as well as TiN and TaN diffusion barriers.5–7 However, it seems that electroless deposition and galvanic deposition have not yet been used to fabricate ultrathin films on oxidized substrates.

Here, we consider the use of galvanic displacement to fabricate thin copper layers on aluminum, as an example of an oxidized metal substrate. Elsewhere, we showed evidence from scanning electron microscopy in combination with quartz crystal microbalance (QCM) measurements that thin Cu films can be deposited from alkaline CuSO4 baths.8 The films consisted of small particles overlying copper layers of order nanometers in thickness. In the same pH range, electrochemical measurements demonstrated that the Al potential lies close to the Nernst potential determining AlH3 stability, suggesting the presence of a hydride-containing surface layer on Al.9–11 The formation of hydride during alkaline dissolution was detected by secondary ion mass spectrometry (SIMS).12 In the copper deposition experiments, QCM and open circuit potential transients revealed a distinct initial stage of deposition occurring near the hydride oxidation potential, in which the mass change was equivalent to a deposited Cu layer of thickness 2–3 nm.8 On this basis, we proposed that Cu2+ ions may be reduced by surface hydride at early times during galvanic deposition, and that this process contributes to the observed thin copper layers. Previous work supports a role of hydride in electroless plating of Cu from alkaline solutions containing NaBH4 additive.13,14 Alternatively, Jennison et al. showed using conductance measurements and first principles calculations that interstitial hydride ions in alumina thin films can induce electronic conduction.15 In this case, Cu2+ ions could be reduced by Al metal, leading to Cu thin film deposition on the oxide.

The present communication reports nanoscale characterization of deposition by atom probe tomography (APT). APT is a point-projection microscope that uses pulsed field evaporation to remove individual ions from the surface of a needle-shaped specimen. The surface ions are sequentially evaporated and projected into a two-dimensional time-of-flight mass detector. The time-of-flight, location, and sequence of detected ions are then used to reconstruct the atomic-level details of the sample, including the identity and locations of the constituent atoms.16–19 Examples from the literature demonstrate quantitative interpretation of APT data.20 We analyze Al surfaces both before and after galvanic displacement, and demonstrate that nanometer-thick continuous metallization layers can be deposited in this manner.

EXPERIMENTAL SECTION

The substrates for alkaline etching and copper deposition treatments were preshaped aluminum wires suitable for APT analysis. Using procedures described in detail elsewhere,21 tips were prepared from
0.25-mm-diameter Al wires (99.99% purity, Structure Probe Inc.) by electropolishing. Further shaping was carried out by field evaporation in the atom probe microscope (LEAP 3000X SI, Imago Scientific Instruments). Copper coatings were deposited successfully when the tip radius, as estimated from the stopping voltage during field evaporation, was greater than 65 nm. In galvanic deposition experiments, the Al tips were first etched for 2 min in 0.1 M Na₂SO₄ solution at pH 11.75. Based on QCM measurements using Al thin film samples, roughly 10 nm of Al was removed by etching. Then, a 5 min deposition period was initiated by addition of a copper-containing solution at the same pH. The composition of the deposition bath was 0.1 M Na₂SO₄ with 0.1 M EDTA (ethylene diaminetetraacetic acid) and 0.05 M CuSO₄. All aqueous solutions were prepared using 18 MΩ cm resistivity deionized water (NANOpure, Barnstead). After the etching and deposition steps, samples were analyzed with APT, using a combination of thermal and field evaporation. Thermal evaporation was stimulated by laser pulses at a frequency of 250 kHz, and a pulse energy in the range 0.2−5 nJ.

## RESULTS AND DISCUSSION

Alkaline etching produced a mixed oxide/hydroxide surface film containing incorporated hydrogen and hydride. In the ultra-high-vacuum environment that exists in the APT during field evaporation, compound ions typically originate from species in the sample, as opposed to gas-phase recombination. The principal peaks in the cumulative mass spectrum (Figure 1a) are due to hydrates or water molecules in the surface oxide (17 to 19 Da), and aluminum oxide or hydroxide (43 to 45 Da). Peaks for AlH⁺ and AlH₂⁺ were found at 28 and 29 Da. These ions are detected upon exposure of clean Al surfaces to hydrogen, and have been shown to derive from aluminum hydride species formed by reaction of hydrogen with aluminum. Their presence therefore indicates significant levels of hydride in the surface film. Mass spectra after copper deposition were similar to those following alkaline etching, but with two isotopic peaks for Cu⁺ at 63 and 65 Da (Figure 1b). The spectra revealed limited ion signals from copper oxide or hydride.

Reconstructions of etched samples indicated that oxide covered the entire Al surface with a uniform thickness of 1−2 nm, as illustrated by the cross section in Figure 2b. The reconstructions also revealed roughly 3-nm-thick near-surface layers, in which the ion density was about half that found at greater depths. These low-density layers, which were found in samples after both etching and copper deposition, produced the apparent voids below the surface film in Figure 2b and c. In contrast, the as-evaporated tips exhibited uniform ion densities of 30−40 ions/nm³ at all depths, consistent with the atomic density of Al, 60 nm⁻³, and a typical evaporation yield of ~50% (Figure 2a). Surface roughening during corrosion possibly caused these low-density surface layers. The evaporation field is reduced locally on sites with positive curvature, producing preferential evaporation of ions from convex features. These ions would be displaced to smaller depths in the reconstruction than those from flat areas, possibly leading to an apparent low-density layer with thickness determined by the roughness height.

Copper deposition by galvanic displacement formed coatings with variable thicknesses on different samples. In some cases, copper layers with equivalent thickness of about 10−20 nm were found, suggestive of particulate deposits observed on planar substrates (see Supporting Information, Figure S1). Here, we focus attention instead on thin film deposits found on some samples. For the conditions of the present experiments (50 mM CuSO₄ concentration, 2 min deposition time, tip radii of curvature between 65 to 180 nm), about 40% of the samples produced thin Cu films. This yield is consistent with the fraction of the surface area found to be covered by particles on planar Al samples. Therefore, there were no clear differences in the deposit morphology between flat and high-curvature...
substrates. Smaller concentrations and shorter deposition times produced fewer particles on flat substrates, and thus probably would have increased the fraction of the present samples forming thin films. The images in Figures 2c and 3 illustrate the APT reconstruction of a sample exhibiting an approximately 1-nm-thick continuous Cu layer. Figure 3a is a perspective view of the tip showing the distributions of major species. The three blue columns in Figure 3a mark the locations of the composition vs depth profiles in Figure 3b–d. Figure 3d illustrates the high coverage of the Cu layer, as a significant concentration is found even in this relatively copper-poor area. The profiles exhibit Cu⁺ maxima and AlOHₓ⁺ minima at the same depth. The implications of this apparent displacement of oxide by copper are discussed below. Nearly all the oxygen in the copper-rich layers in Figure 3b–d was detected as AlOHₓ⁺ ions, probably originating from aluminum oxide or hydroxide. The absence of oxygen accompanying the detected Cu⁺ implies that deposited copper was in the metallic state. The ultrathin Cu film morphology in Figures 2 and 3 is distinct from previously reported particulate deposits on Al, formed by reduction of dissolved metal ions by Al metal. Therefore, a different deposition mechanism may be involved, as discussed below.

Quantitative interpretation of the APT results was based on total concentrations of surface species per unit area, which are not affected by possible reconstruction artifacts found sometimes in layered structures. These concentrations were calculated from the total number of ions inside columnar control volumes like those in Figure 3a. On each sample, nine such cylinders were arranged in a square array with their perimeters in contact. The diameter of each column in the array was 6 nm for the alkaline etched sample, and 8 nm for the sample with deposited copper. For each sample, Table 1 lists the average and variability of the local concentrations in the array. The variability ranged from 8% to 15% of the average ion concentration, except for Cu⁺, for which it was 28%. The estimated copper layer thicknesses was about 1.0 nm. The ratio of the combined oxygen concentration to that of AlOHₓ⁺ suggests compositions of the oxide-hydroxide layer close to Al(OH)₃ for the etched sample and Al₂O₃ on the sample with deposited Cu. However, there is appreciable Al⁺ in the surface film after etching, indicating a composition intermediate between oxide and hydroxide (see Supporting Information, Figure S2). The most significant composition change

Table 1. Estimated Surface Concentrations after Alkaline Etching and Copper Deposition

<table>
<thead>
<tr>
<th></th>
<th>after alkaline etching</th>
<th>after copper deposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlOHₓ⁺ (nm⁻²)</td>
<td>27.0 ± 3.4</td>
<td>32.5 ± 2.7</td>
</tr>
<tr>
<td>O (nm⁻²)</td>
<td>47.2 ± 5.0</td>
<td>10.7 ± 1.3</td>
</tr>
<tr>
<td>OHₓ⁺ (nm⁻²)</td>
<td>7.2 ± 0.9</td>
<td>1.6 ± 0.2</td>
</tr>
<tr>
<td>AlHₓ⁺ (nm⁻²)</td>
<td>12.1 ± 1.1</td>
<td>4.6 ± 0.5</td>
</tr>
<tr>
<td>Cu⁺ (nm⁻²)</td>
<td></td>
<td>44.1 ± 12.4</td>
</tr>
<tr>
<td>Oxide thickness (nm)</td>
<td>3.0 ± 0.3</td>
<td>1.6 ± 0.1</td>
</tr>
<tr>
<td>Copper thickness (nm)</td>
<td>1.0 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>(Total O)/AlOHₓ⁺</td>
<td>3.0</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Values represent the mean of 9 sampled concentrations (± 90% confidence intervals), and are based on assumed 50% detector collection efficiency. Sum of the O⁺ concentration and twice the O₂⁺ concentrations. Based on total oxygen concentration and density of anodic alumina. Based on the density of Cu metal.
accompanying copper deposition is the reduced oxygen concentration, as also indicated in Figure 3. The decrease of the total oxygen concentration (36.6 ions/nm²) is comparable to the concentration of deposited Cu (44.1 ions/nm²); the estimated oxide thickness was reduced from 3.0 to 1.6 nm.

Deposition of the ultrathin Cu layer should require modification of the protective oxide film on aluminum. While alkaline solutions dissolve the surface oxide layer, a thin oxide remains on the Al surface, as revealed for example by quartz crystal microbalance measurements. Such a film if composed of pure alumina would be electrically insulating; thus, direct reduction of Cu²⁺ ions by Al could occur only at isolated conductive defects, producing Cu particles rather than the observed thin continuous film. However, the presence of hydride in the surface layer is demonstrated by the present APT results, as well as the electrochemical potential and SIMS measurements discussed above. In solution, this hydride might be in the form of a continuous AlH₃ layer, or interstitial ions such as H⁺ in the oxide. Upon addition of CuSO₄ to the alkaline bath, either type of hydride could reduce cupric ions directly to copper metal, for example

\[
2\text{AlH}_3 + 8\text{OH}^- + 3\text{Cu}^{2+} \rightarrow 3\text{Cu} + 2\text{Al(OH)}_4^- + 3\text{H}_2 \quad (1)
\]

In experiments with no copper addition, upon emersion of the sample, water vapor or oxygen would oxidize the hydride layer to aluminum oxide or hydroxide, in a reaction such as

\[
\text{AlH}_3 + \frac{3}{2}\text{O}_2 \rightarrow \frac{1}{2}\text{Al}_2\text{O}_3 + \frac{3}{2}\text{H}_2\text{O} \quad (2)
\]

Thus, the oxide thickness on the alkaline etched sample would be greater than that on the sample with the copper deposit, as is consistent with the APT results Table 1. From the perspective of ex situ characterization, the copper metal formed by eq 1 seemed to “replace” the oxide produced by eq 2; in fact, both oxide and copper would be formed by conversion of the hydride layer present in solution.

A second possible deposition mechanism involves enhancement of electronic conduction of alumina thin films by interstitial hydride ions, as suggested by previous density functional theory calculations and conductance measurements. In this situation, cupric ions could be reduced by Al metal, mediated by electron transport through the oxide. If the oxide is uniformly conductive, the observed continuous copper layer would be formed. Oxidation of interstitial hydride by Cu²⁺ ions would eventually restore the insulating character of the oxide, thus limiting the thickness of the deposited copper film. Air oxidation after emersion of the alkaline etched sample could account for its greater oxide thickness compared to the sample with deposited copper (Table 1). Thus, either mechanism, acting alone or in combination, appears to be consistent with the experimental results presented here and in ref 8.

### CONCLUSIONS

Atom probe tomography was used to investigate the deposition of thin copper layers on Al from alkaline solution, by a galvanic displacement process. Copper deposits on some samples consisted of continuous layers of approximately 1 nm thickness, thus demonstrating that ultrathin metallization layers can be deposited on oxidized metal substrates from aqueous solutions. Overlying copper nanoparticles are also produced. The ultrathin Cu film is distinct from the entirely particulate deposits found in other investigations of galvanic displacement of dissolved metal ions by aluminum. Quantitative comparison of samples after alkaline etching and copper deposition revealed that part of the surface oxide layer is replaced by copper metal. The detection of hydride in the surface film suggests mechanisms in which surface hydride species mediate deposition, either by directly reducing Cu²⁺ ions, or by inducing electronic conductivity in the oxide layer, thereby permitting reduction of cupric ions by the substrate metal. Further research should explore methods to limit the nucleation of particles, so that uniform ultrathin metal layers can be realized.

### ASSOCIATED CONTENT

#### Supporting Information

Atom probe tomography reconstruction showing evidence of nonuniform copper deposits found on some samples. Concentration depth profiles of major detected species on ultrathin Cu layers on Al from alkaline solution, by a galvanic displacement process. Copper deposits on some samples consisted of continuous layers of approximately 1 nm thickness, thus demonstrating that ultrathin metallization layers can be deposited on oxidized metal substrates from aqueous solutions. Overlying copper nanoparticles are also produced. The ultrathin Cu film is distinct from the entirely particulate deposits found in other investigations of galvanic displacement of dissolved metal ions by aluminum. Quantitative comparison of samples after alkaline etching and copper deposition revealed that part of the surface oxide layer is replaced by copper metal. The detection of hydride in the surface film suggests mechanisms in which surface hydride species mediate deposition, either by directly reducing Cu²⁺ ions, or by inducing electronic conductivity in the oxide layer, thereby permitting reduction of cupric ions by the substrate metal. Further research should explore methods to limit the nucleation of particles, so that uniform ultrathin metal layers can be realized.

#### ACKNOWLEDGMENTS

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#### REFERENCES