Seedless Electrodeposition of Cu on Unmodified Tungsten
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Adherent Cu films were electrodeposited on polycrystalline W foils from a purged 0.05 M CuSO₄ solution in H₂SO₄ supporting electrolyte at pH 1. Films were deposited under constant potential conditions at voltages between −0.6 and −0.2 V vs. Ag/AgCl. The films produced by pulses of 10 s duration were visible to the eye, copper colored, and survived the Scotch tape test. Characterization by scanning electron microscopy and X-ray photoelectron spectroscopy (XPS) confirmed the presence of Cu, with apparent dendritic growth. No sulfur impurity was observable by XPS. Kinetics measurements indicated that the Cu nucleation process is slow compared to recently reported kinetics for Cu electrodeposition on TiN. The adhesion of the deposited Cu strongly suggests the absence of an interfacial oxide.

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The electrodeposition of Cu onto barrier surfaces is of considerable importance in the development of Cu interconnect processes for deep submicrometer devices. Current processing usually involves electrodeposition from a sulfate bath onto a Cu seed layer, which is first deposited by plasma vapor deposition (PVD) or metallorganic chemical vapor deposition (MOCVD). Conformal, uniform seed layer deposition becomes increasing problematic as device dimensions continue to shrink; electrodeposition in the absence of a seed layer is desirable. Surface science studies carried out in ultrahigh vacuum (UHV), however, indicate that the ability of Cu adlayers to wet (grow conformally on) a Ta or W barrier surface is severely degraded by the presence of even monolayer coverages of oxygen. The electrodeposition of Cu onto reactive metal surfaces degraded by the presence of even monolayer coverages of oxygen. Electrochemistry studies.—Cyclic voltammograms (CVs) are shown in Fig. 1 for a W foil in 0.05 M CuSO₄ in supporting H₂SO₄ electrolyte at pH 1, and in the same electrolyte without CuSO₄. The potential scans were started at open-circuit potential (OCP, +0.08 V). A diffusion-limited Cu reduction peak is observed near −0.2 V, while a broader Cu stripping peak is observed at potentials which are noble with respect to 0.2 V. Additional cycling did not produce significant changes in the current-potential curve. The linear behavior (Fig. 2) of peak current (Iₚ) vs. the square root of the scan rate (v½) is consistent with diffusion-limited behavior. The intercept at v = 0 (Fig. 2) is nonzero, however, suggesting that the Cu reduction process also involves a surface-dependent step. The peak voltage also varies linearly with log v (not shown), additional evidence of a diffusion-controlled reaction.

Current vs. time plots at stepped potentials between −0.6 and −0.1 V are shown in Fig. 3. Experiments in Cu-free electrolyte (not shown) indicate that the current attributable to proton reduction or other side reactions comprise <5% of the total current, even at −0.6 V. In each case, a fresh W foil sample was stepped from open circuit to the specific potential for a pulse of 10 s duration. At −0.6 V, the time to maximum cathodic current (tₘₐₓ) cathodic current maximum is obtained at 0.37 s, while at −0.2 V, tₘₐₓ = 1.84 s. At −1.0 V, no maximum is achieved during the 10 s pulse duration. Cu diffusion coefficients can be derived from the data in Fig. 3 using the Leonard-Cottrell equation. The diffusion coefficient obtained at −0.6 V is 4.0 × 10⁻⁶ cm s⁻¹, while the diffusion coefficient obtained at −0.2 V is 2.9 × 10⁻⁶ cm s⁻¹. A comparison of the data in Fig. 3 with corresponding data reported for Cu electrodeposition on...
TiN shows that nucleation kinetics on TiN occur on time scales $<0.1$ s, indicating substantially slower nucleation kinetics on the W surface than on TiN.

Relationships between current and time have been derived for both progressive and instantaneous three-dimensional nucleation, and for the corresponding cases of two-dimensional growth. Attempts to fit the data in Fig. 3 to either model, however, proved unsatisfactory, except at long times ($t/t_{max} > 5$). This suggests that the growth process at these potentials sampled is complex, resembling neither ideal two-dimensional nor three-dimensional models with diffusion as the rate-limiting step.

XPS and SEM measurements.—XPS measurements of the electronic state of the deposited Cu are not a reliable guide to the electronic state of Cu at the sample surface in solution, due to the exposure of the sample to air upon emersion from the electrolyte prior to analysis. Such measurements can, however, determine whether sulfate or sulfate reaction products are included in the deposited film. XPS measurements (not shown) taken prior to and after extensive Ar ion sputtering showed no observable S (2p) signal intensity, indicating no observable sulfate contamination within the surface sampling depth (~40 Å of the film.) EDAX measurements yielded similar results, indicating no bulk S or O contamination. The XPS and EDAX measurements, while indicating that the deposited films are free of bulk sulfate or oxygen contamination, do not serve to characterize the nature of the Cu/W interface.

SEM images of Cu films at potentials of $-0.5$ and $-0.2$ V are shown in Fig. 4. An integration of the net charged passed (derived from total current less that observed for the same pulse in a Cu-free electrolyte) yields equivalent Cu thicknesses of 190 monolayers after 10 s pulse at $-0.5$ V, and 144 monolayers after 10 s pulse at $-0.2$ V. The SEM of the film grown at $-0.2$ V (Fig. 4a) shows the formation of Cu nuclei with a complex geometry, generally larger.
than \( \sim 1.0 \, \mu \text{m} \) in diam. There also appears to be some orientation of the clusters with the striations visible in the W surface. (The striations may be due to rolling of the W foil.) The film grown at \(-0.5 \, \text{V}\) (Fig. 4b) is sufficiently thick as to obscure substrate irregularities. Both large clusters, \(-1.0 \, \mu \text{m} \) diam, and smaller, irregularly shaped clusters \(-0.1 \, \mu \text{m} \) diam are observed, whereas no such small clusters are observed for the film grown at \(-0.2 \, \text{V}\). In addition, the large clusters observed for the film grown at \(-0.5 \, \text{V}\) have a more three-dimensional structure than those grown at \(-0.2 \, \text{V}\). The overall impression of the SEM images is that the growth appears more three dimensional at more cathodic over voltages, consistent with a faster diffusion of Cu ions to the film surface.\(^{10}\)

**Discussion**

This is of interest because the thermodynamic potential for W oxide formation falls in the middle of this range

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\begin{align*}
\text{WO}_2 + 4\text{H}^+ + 4\text{e}^- & \rightleftharpoons \text{W} + 2\text{H}_2\text{O} + \text{E} \\
& = -0.375 \, \text{V/Ag/AgCl (pH 1)}
\end{align*}
\]

Because UHV results indicate poor Cu adhesion to oxidized W surfaces,\(^4\) one would expect to produce adhesive films only at potentials cathodic to \(-0.375 \, \text{V}\), if the formation/dissolution of the oxide were under thermodynamic control. The results reported here therefore suggest either that oxide stability is dominated by kinetic factors under these conditions, or that Cu/substrate adhesion is affected by factors other than Cu/surface chemical interactions, such as mechanical interactions between the oxide and the Cu. (Additionally, the Scotch tape test is only a rough assessment of interfacial adhesion.) Also of interest is that the time scale for nucleation observed in these experiments (\(-3 \) to \(10 \, \text{s}\), Fig. 3) is greater by over one order of magnitude than corresponding observations for Cu electrodeposition on TiN under roughly comparable conditions (pH 1.4, 0.025 M CuCO\(_3\), nonsulfate electrolyte.) The reasons for this are not apparent from the existing data, but may be related to either hydrogen or sulfate coordination to the W surface.

The observation of Cu/W interfacial adhesion therefore makes the chemical nature of the Cu/W interface one of broad scientific as well as technical interest. The presence of an interfacial oxide or hydroxide or sulfate region would suggest that factors governing Cu nucleation and growth during electrodeposition may differ fundamentally from those deduced in UHV surface science experiments.\(^3,4\) In contrast, the absence of such an interfacial region at voltages positive to about \(-0.4 \, \text{V}\) indicates that kinetic factors (e.g., H-surface interactions or sulfate chemisorption) may be critical in controlling oxide/hydroxide formation, and therefore metal nucleation and adhesion.

**Conclusions**

These data demonstrate that Cu films can be directly electrodeposited on a W surface from an acidic CuSO\(_4\) solution at potentials between \(-0.2 \) and \(-0.6 \, \text{V}\), without significant sulfate contamination. Films grown under these conditions are adherent in that they survive the Scotch Tape test. In summary, the CuSO\(_4\)/W system is of practical interest for the electrodeposition of Cu interconnects on barrier materials without the use of a Cu seed layer. The system is also of scientific interest because the thermodynamic vs. kinetic control of surface oxide formation, the coordination of cations and anions to the surface, and the effects of these on metal nucleation and growth are issues of paramount importance in obtaining a fundamental understanding of metal electrodeposition on reactive substrates.

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**References**