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Immersion/Electroless Deposition of Cu on Ta

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Continuous Cu films are deposited on Ta by a two-step process; galvanic displacement of Ta by Cu from ammonium fluoride solutions and subsequent electroless Cu deposition from a formaldehyde-containing bath. The conditions necessary for good adhesion are discussed. The extent of oxide film removal in the HF pretreatment solution is studied by electrochemical impedance spectroscopy. The charge-transfer resistance of about 57 Ω-cm² is several orders of magnitude lower than that measured for the Ta native oxide. These results are consistent with the removal of the Ta₂O₅ portion of the native oxide.

Beginning in the late 1990s, Cu has been replacing Al for deep submicrometer Si device interconnects and vias. Since Cu is a deep level defect, an intervening Ta/TaN diffusion barrier has been employed, and this material appears to be viable for the 90 and 65 nm technology nodes. The relatively high resistivity of this diffusion barrier requires the deposition of a Cu seed layer prior to Cu electrodeposition. Currently, both the barrier and seed layers are deposited in two separate tools by a mixed plasma/physical vapor deposition (PVD) or ion metal plasma (IMP). Electrochemical deposition of either of these layers would provide substantial cost reductions during microelectronic device fabrication and is currently an area of significant interest.

Here we report electrochemical deposition of Cu thin films on Ta with good adhesion by galvanic displacement from fluoride-containing aqueous solutions and subsequent electroless deposition. Since Ta is a refractory metal, Ta electrodeposition processes generally have employed molten salts. Although metals have been electrodeposited atop Ta oxide and local reversible redox sites may be accessible on the Ta oxide film, the authors are unaware of electrodeposition of any metal films on Ta without an intervening oxide film. Fluoride-containing baths have been proposed previously for Cu deposition on Ta by galvanic displacement, but these suffer from adhesion problems. The current research was motivated by reports of adherent Cu thin-film deposition from fluoride-containing solutions on Si by galvanic displacement. Similar to SiO₂, Ta₂O₅ dissolution into fluoride-containing aqueous solutions is driven by the formation of a strongly bound complex TaF₇⁻. Cu wafers coated with 280 nm Ta films were first immersed in a pretreatment solution containing 2.5 M HF and 22.5 M CH₃OH, with continuous Ar deaeration. The main function of this solution is to remove the Ta native oxide. Although the CH₃OH concentration is high, this reagent was necessary to obtain Cu deposition on Ta/Si wafers, although experiments using lower concentrations were also successful. Interestingly, CH₃OH was not needed in the pretreatment bath to obtain Cu deposition on a pure Ta electrode. Discontinuous Cu films were then deposited by galvanic displacement from a bath containing 6.1 M NH₄F, 0.01 M CuSO₄, 0.01 M ascorbic acid, and 7.5 M CH₃OH, with Ar deaeration. The deposit adhesion was rated as level 5B, with no disturbance of either the deposit or the edge of the cuts. In addition, the deposit could not be removed by moderate force applied with a diamond scribe. Preliminary results show that Cu deposition on Si/TaN wafers can also be performed with good adhesion using this bath sequence, but longer immersion time is required in the galvanic displacement bath. The nature of the Ta aqueous interface is critical to obtaining adequate adhesion of the Cu deposit. Good adhesion is obtained only under conditions for which the Ta native oxide either does not form or forms slowly relative to the deposition process. The structure of native Ta oxide has previously been studied using X-ray diffraction, and this research is consistent with the removal of the Ta₂O₅ portion of the native oxide.

Following galvanic displacement of Cu, continuous Cu films were deposited using a room-temperature electroless Cu bath containing 0.05 M CuSO₄, 0.6 M NaOH, 0.007 M Na₂EDTA, and 0.01 M HCOH, with Ar deaeration. The Cu growth rate determined from four-point probe measurements was approximately 5 nm/min. Figure 1 shows an atomic force microscopy (AFM) image of the surface following 10 min of Cu galvanic displacement.

Figure 1. AFM image of the Ta/Si wafer surface following 10 min of galvanic Cu deposition from 6.1 M NH₄F, 0.01 M CuSO₄, 0.01 M ascorbic acid, and 7.5 M CH₃OH, with Ar deaeration.
photoelectron spectroscopy (XPS), revealing an interfacial TaO suboxide beneath a 1-3 nm Ta₂O₅ layer. However, in situ studies of the Ta/aqueous interface in fluoride-containing solutions have been rare. In this work, such studies are complicated by several factors, including the high resistance of the Ta/Si wafer substrate, which necessitates studies on a pure Ta electrode rather than a Ta/Si wafer. In addition, the extent of interfacial oxidation is strongly time-dependent, making steady state analysis difficult, as described below.

Figure 3 shows the time dependence of the open-circuit potential (OCP) following immersion in 2.5 M HF, which is an adequate pretreatment bath for Cu deposition on a bare Ta electrode. For these experiments, a Ta rod embedded in a virgin Teflon mount is employed as the working electrode, a Pt wire spiral or Ag mesh screen as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. Over the time scale of these experiments, the OCP does not reach steady state. The nature of the Ta/aqueous interface can be determined by electrochemical impedance spectroscopy (EIS) only if the entire frequency space can be sampled at steady state, allowing comparison to the results expected from simple equivalent circuit models. In this system, steady-state results can be obtained by immersing the Ta sample in 2.5 M HF at −900 mV SCE with Ar deaeration for 120 min, then setting the potential to the value of interest.

Impedance studies were performed at sequential frequencies using phase-sensitive detection with a Stanford Research Systems model SR830 lock-in amplifier. Figure 4 shows a Nyquist representation of the impedance of the Ta interface in 2.5 M HF at −700 mV SCE, a representative potential taken from Fig. 3. This Nyquist plot can be fit by a capacitive loop with a charge-transfer resistance ($R_{ct}$) of about 57 Ω·cm² in parallel with a constant phase element with a magnitude of 15 mF/cm² and a phase exponent of 0.83. While this constant phase element is typical of double-layer capacitances at metal electrodes, the extent of noncapacitive behavior is somewhat larger than expected. The behavior shown in Fig. 4 is in marked contrast to EIS studies of Ta in 2.5 M NH₄F. In this solution, the $R_{ct}$ is too high to be accurately measured, in agreement with past EIS studies of the Ta native oxide.

Although much of the Ta native oxide can be removed in 2.5 N HF at −700 mV SCE, the surface may be covered with a thin interfacial oxide. This can be demonstrated by cyclic voltammograms of Ta in 2.5 M HF, with and without Cu²⁺ and different complexing agents, where a Cu stripping peak is difficult to observe. This may indicate that an interfacial TaO suboxide remains after HF immersion, and this may be the interfacial suboxide previously seen by XPS. Figure 5 shows time-dependent values for the magnitude of the impedance at 5.2 and 70 Hz for a Ta electrode immersed in 2.5 M HF at −700 mV SCE.
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References

16. ASTM International Standard D 3359-02