

“Seedless” Electrochemical Deposition of Copper on Liner Materials for ULSI Devices

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Interconnect reliability is a major issue in the microprocessor industry; and electromigration failures have been linked to interconnect interface defects, which suggests that poor adhesion between the copper and diffusion barrier would be of significant concern^{1,2}. Accordingly, it is essential that adhesion be considered in the initial stages of a seedless deposition strategy. In addition, a high nucleation density of 2.0×10^{10} (nuclei/cm²) is required in order to fill small-scale features of 70 nm with no voiding.

Electrochemical studies designed to identify those processes that provide adequate nucleation and thin film growth directly on ultra-thin, air exposed, PVD-tungsten, tungsten nitride, titanium nitride and tantalum nitride diffusion barriers have been performed. It is shown that very thin copper films can be nucleated directly on conducting refractory metal and refractory metal nitride liner surfaces. A complexing agent chemistry model, based on mass balance and thermodynamic equilibrium, has been applied to several ammoniacal plating bath compositions, and the concentration profiles inserted into the Nernst equation. Comparing experimental results with the model prediction indicates that strong adhesion is associated with the reduction of several copper-ammonia complexes at the liner material surfaces.

Typical sulfuric acid based plating chemistry produce very little nucleation on air exposed W, W₂N, TiN and TaN. The copper nucleation barrier in conventional acid baths is the air formed film, which consists of passivating oxides. Consideration of conventional potential-pH equilibrium diagrams for refractory metals and copper systems in water suggests that there may be an advantage to the use of neutral or even basic electrolyte baths to reduce the oxide layers and to expose the metal or metal nitride surface to the plating bath³.

There is also evidence that ammoniacal plating baths may produce a degree of the desirable bottom-up or “super filling” behavior in trenches and vias⁴. For example, an electrolyte composition of ammonia, copper sulfate, and ammonium sulfate, was shown to be successful in copper plating in previous studies. However, this chemistry was found to be too corrosive to the liner materials, and dissolved the barrier before full copper coverage could be obtained. This work describes the electrochemical and chemical parameters required to optimize nucleation densities and adhesion.

The nucleation density and adhesion were shown to be dependent on pH, potential, and electrolyte chemistry. A “balanced complex bath” composed of equal proportions

of citrate (Cit) and cupric ions (Cu⁺⁺) with ammonia added, was developed which produced continuous thin films of 20 nm thickness; below the minimum film thickness required to fill 70 nm features. The pH of the electrolyte was shown to be a critical variable, both for nucleation and adhesion, with the specific pH being different for each type of barrier film.

Successful ECD of copper, with reduction of the air-formed oxide films on is also sensitively dependent on the specific reduction potential and mass transport properties of the electrolytes.

It also has been demonstrated that very thin, conformal copper films can be nucleated and grown directly on air-exposed, electrically conducting liner surfaces with high nucleation densities (almost layer-by-layer deposition). Excellent film adhesion has been demonstrated on both 100 nm and 25 nm nominal thickness films of each of the barrier layers. Potential controlled deposition has been utilized, and is a significant factor in controlling nucleation. In the electrochemical system under investigation, the copper film resistivity, and film adhesion are dependent on both ECD process parameters and electrolyte bath chemistry, and approach the theoretical value of resistivity for pure copper.

Complete copper film coverage on incomplete copper seed coatings on planar samples of Si/SiO₂/liner/Cu seeded wafers has also been successfully demonstrated, where the seed layer was initially deposited by PVD, and then scratched to the barrier layer in a lattice pattern.

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