“Seedless” Electrochemical Deposition of Copper on PVD-W_2N Liner Materials for ULSI Devices

MICHAEL J. SHAW[1] and DAVID J. DUQUETTE[2]

1. Sandia National Laboratories, Albuquerque, NM, 87185 mjshaw@sandia.gov
2. Rensselaer Polytechnic Institute, Materials Science and Engineering Department, Rensselaer Polytechnic Institute, Troy, NY duqued@rpi.edu

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 x 10^{10} (nuclei/cm^2) 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 nitride diffusion barriers have been performed. It is shown that very thin copper films can be nucleated directly on a conducting PVD-W_2N liner surface. 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 metal nitride surface

Typical sulfuric acid based plating chemistry produce very little nucleation on air exposed W_2N. The copper nucleation barrier in conventional acid baths is the air formed film, which consists of passivating tungsten oxides. Consideration of conventional potential-pH equilibrium diagrams for the tungsten and copper systems in water suggests that there may be an advantage to the use of higher pH electrolyte baths to reduce the oxide layers and to expose the metal nitride surface to the plating bath[3], see Figure 1.

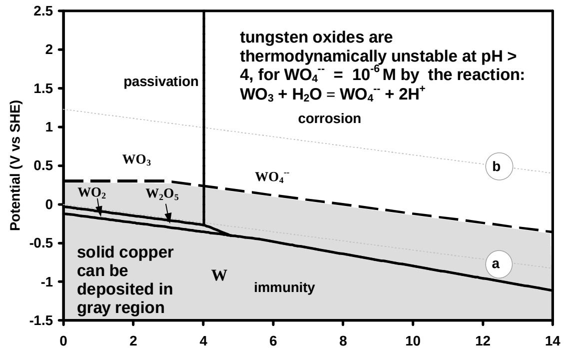

Figure 1. Potential vs. pH diagram for the tungsten-water system showing regions of thermodynamic stability for passivation, corrosion and immunity.

There is also evidence that ammoniacal plating baths may produce a degree of the desirable bottom-up or “super filling” behavior in trenches and vias[4]. 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 for W_2N, 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, at a pH = 7 was developed which produced continuous thin films of 20 nm thickness; below the minimum film thickness required to fill 70 nm features.

The data also demonstrate that the successful ECD of copper on W_2N is also sensitively dependent on the specific reduction potential and mass transport and most heavily influenced by the plating bath chemistry and pH.

It also has been demonstrated that very thin copper films can be nucleated and grown directly on air-exposed, electrically conducting PVD-W_2N liner surfaces. High nucleation densities also have been produced on air-exposed PVD-TaN liner films. Excellent film adhesion has been demonstrated on both 100 nm and 25 nm nominal thickness films of TaN and W_2N. 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.

Complete copper film coverage on incomplete copper seed coatings on planar samples of $Si/SiO_2/W_2N/Cu$ seeded wafers has also been successfully demonstrated, where the seed layer was initially deposited by PVD, and then scratched to the W_2N substrate (barrier layer) in a lattice pattern.

REFERENCES

1. Andricacos, P., Copper On-Chip Interconnections. Electrochem. Soc. Interface, Spring: p. 32-37, (1999).
2. Semiconductor Industry Association, International Technology Roadmap for Semiconductors, SEMATECH: Austin, TX, (1999)
3. Pourbaix, M., Atlas of Electrochemical Equilibria in Aqueous Solutions. Pergamon Press, (1966).
4. Lee, C., Pulsed Electrodeposition of Copper from Alkaline and Acid Baths for Metallization in Integrated Circuits, in Materials Science and Engineering. M.S. Thesis, Rensselaer Polytechnic Institute: Troy. NY, p. 55, (1999).