

Role of Chloride Ions in Suppression of Copper Electrodeposition by Polyethylene Glycol

Kurt R. Hebert

Department of Chemical Engineering
Iowa State University, Ames, IA 50011

The copper damascene process is currently used in the semiconductor industry to electrodeposit on-chip metallization. The critical ability to produce seam- and void-free deposits in submicron-scale cavities, or “features,” relies on the presence of additives in the electroplating bath (1). The additives in damascene baths include a polymer serving as a “suppressor,” e. g. polyethylene glycol (PEG), an “accelerator,” e. g. sulfopropyl sulfonate (SPS), and Cl^- ions (2). Cl^- is apparently necessary for effective inhibition by PEG, as current-potential curves measured with PEG but no Cl^- are similar to those with no PEG (3).

This work focused on the synergistic role of PEG and Cl^- additives in suppression. Inhibited deposition is achieved over a range of Cl^- concentration around 1 mM. Steady-state voltammetry in solutions with much lower Cl^- concentration displays abrupt activation of deposition, and hysteresis between active and suppressed deposition over a range of potentials (4). This hysteresis suggests multiple steady states over this potential range. Also, during Cu deposition at constant current from baths of similar composition, Hayase et al. observed transient activation from an initially inhibited state, along with incorporated Cl in the deposit (5). This suggests that consumption of Cl^- ions by incorporation initiated activation, consistent with the view that PEG is attached to Cu through adsorbed Cl^- (6).

In the present work, a simple mathematical model of Cu electrodeposition in the presence of PEG and Cl^- additives is reported. The model includes the suppression of deposition kinetics by an adsorbed PEG film, which binds to the surface through a complex involving adsorbed Cl^- ions. Thus, the surface coverage of the PEG suppressor is determined by that of Cl^- . The adsorbed Cl^- coverage is determined by a surface balance accounting for kinetically-limited adsorption and incorporation into the Cu deposit. This balance was shown to be consistent with experimentally obtained depth profiles of incorporated Cl in deposited films, obtained during constant current deposition (5). The model was used to predict steady-state current-potential curves during deposition, for both Cl^- concentrations from 10^{-3} to 1 mM.

The following aspects of model voltammetric behavior were found to be in agreement with experiment: (i) Deposition was suppressed through the entire potential range at 1 mM Cl^- , but there was no suppression at any potential at 10^{-3} mM. (ii) At 10^{-2} and 0.1 mM Cl^- , deposition abruptly activated at potentials cathodic to a critical value, in the neighborhood of which steady-state hysteresis between activated and suppressed deposition was found. (iii) This critical potential was more negative at higher Cl^- concentration. Adsorption of neither PEG nor Cl^- in the model were potential-dependent; the critical potential was simply a consequence of faster incorporation as the potential was made more cathodic. Hysteresis in the model predictions resulted from the high sensitivity of the PEG coverage to the adsorbed Cl^- concentration, owing possibly to a limited number of binding sites for each polymer molecule. In summary, the minimum Cl^- concentration of about 1 mM in copper damascene plating baths is necessary to avoid depletion of adsorbed chloride

by incorporation in the deposit, which if it occurred would lead to loss of suppression.

REFERENCES

1. P. C. Andricacos, C. Uzoh, J. O. Dukovic, J. Horkans, and H. Deligianni, *IBM J. Res. Develop.*, **42**, 567 (1998).
2. T. P. Moffat, J. E. Bonevich, W. H. Huber, A. Stanishevsky, D. R. Kelly, G. R. Stafford, and D. Josell, *J. Electrochem. Soc.*, **147**, 4524 (2000).
3. B.-H. Wu, C.-C. Wan and Y.-Y. Wang, *J. Appl. Electrochem.*, **33**, 823 (2003).
4. V. D. Jovic and B. M. Jovic, *J. Serb. Chem. Soc.*, **66**, 935 (2001).
5. M. Hayase, M. Taketani, K. Aizawa, T. Hatsuzawa, and K. Hayabusa, *Electrochem. Solid-State Lett.*, **5**, C98 (2002).
6. Z. V. Feng, X. Li, and A. A. Gewirth, *J Phys. Chem. B.*, **107**, 9415 (2003).