A model of copper deposition for the damascene process

C. Gabrielli, J. Kittel, P. Moçoteguy, H. Perrot UPR15 du CNRS, Physique des Liquides et Electrochimie, Université Pierre et Marie Curie 4 place Jussieu, 75252 PARIS CEDEX 05, France

A. Zdunek, P. Bouard, M. Haddix, L. Doyen AIR LIQUIDE, Centre de Recherche Claude Delorme, BP 126, 78354 JOUY en JOSAS, France,

M.C. Clech

ALTIS Semiconductor; 224, Bd J. Kennedy 91105 Corbeil Essonnes Cedex , France

The damascene process for fabrication of copper on-chip metal interconnects requires electrodeposition into two- or three- dimensional cavities (trenches or vias) with width dimensions on the order of 100 nm. To obtain void-free deposits, superconformal deposition, or superfilling, is necessary. These terms refer to the occurrence of more rapid electrodeposition in the bottom of the cavity than toward its entrance. Superconformal deposition is only obtained in the presence of a certain combination on additives in the plating bath.

Among those studies available in the literature, Moffat et al. (1,2,3) showed that baths with three additives in addition to the classical sulfate-sulfuric acid deposition bath, can be used to achieve superfilling in submicrometer cavities. These were a polyether (polyethylene glycol, PEG), chloride ions, and a thiol (3mercapto-1-propanesulfonate, MPSA).

In this work, a model of copper deposition in the damascene process is proposed and analysed in terms of electrochemical impedance. Few publications have reported investigation of the damascene process by impedance techniques (4,5). Experimental results are compared with theory for the sulfate-sulfuric acid bath containing both chloride, PEG and MPSA.

When mass transport is not a limiting step, the proposed model of copper deposition in the damascene process occurs following a two-step reduction of copper ions with the various additives adsorbed on the electrode surface. In this simplified model, the role of chloride is limited to enhancing adsorption of PEG and changing

<u>Figure 1</u> : Calculated impedance.



the transfer coefficient of copper deposition. Competitive adsorption of MPSA, which displaces PEG, is also assumed. Intermediate reaction species such as PEG-Cu⁺(*), and MPSA-Cu⁺(*), which are the adsorbed PEG and MPSA on cuprous ions attached to growth sites (*), are also involved in the deposition mechanism. At last, MPSA is supposed to be incorporated in the copper deposit.



<u>Figure 2</u>: Measured impedance of copper deposition in an aged industrial bath.

The behaviour of this model was analyzed in steady-state and in dynamic regime (electrochemical impedance). Steady-state $(\frac{d}{dt} \equiv 0)$ values of the surface coverages are obtained. The linearization of the state equations leads to the electrochemical impedance that is shown in Figure 1.

The impedance of the electrode was measured during superconformal copper deposition both in the bath proposed by Moffat et al. and in an industrial bath. As an example, Figure 2 shows the impedance obtained in an aged industrial bath. A good agreement was found with the proposed model.

Acknowledgments

The authors would like to acknowledge ALTIS Semiconductor for providing copper baths samples.

References

- ¹ T. P. Moffat, D. Wheeler, W. H. Huber, and D. Josell, Electrochem. And Solid State Let., 4, C26 (2001).
- ² D. Josell, D. Wheeler, W. H. Huber, J. E. Bonevich, and T. P. Moffat, J. Electrochem. Soc. 148, C767 (2001).
- ³ 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).
- ⁴ J. J. Kelly and A. C. West, J. Electrochem. Soc., 145, 3477 (1998).
- ⁵ G. Fabricius and G. Sundholm, J. Applied Electrochem., 15, 797 (1984).