Ligand Complexation in Electrodeposition and Copper Superfilling of Interconnects

Jacob Jorne and Eli E. Jorne*
Department of Chemical Engineering
University of Rochester, Rochester, NY 14627
*Department of Applied Physics
Caltech, Pasadena, CA 91125

The electroplating of copper in high-aspect-ratio trenches and vias is a challenge facing the emerging technology of copper on-chip interconnect. Super filling, or bottom-up filling, is currently achieved by the addition of organic additives to the electrolyte. However, the monitoring and control of additives in the electrolyte are difficult tasks, thus an additive-free electrolyte is highly desirable. Bottom-up electroplating can be achieved by complexing the copper ions and reducing it in two steps, thus forcing the electroplating towards the bottom of the trench. A mathematical model, which determines the conditions under which bottom-up electroplating occurs, is presented and experimentally verified.

Uncomplexed Copper: Pinch-Off Formation

Consider a trench with high aspect ration h/a, where h is the depth and a is the width of the trench., The following electrochemical reaction occurs between the metal ion A and the wall of the trench:

$$A \xrightarrow{k_1} M$$

where A for the case of copper electrodeposition is the copper ion in solution and M is the electrodeposited copper metal. The metal ion diffuses into the trench and reacts there. The conservation equation for A is:

$$d^2A/dx^2 - (k_1/D_1)A = 0$$

where x is the distance from the mouth of the trench, k_1 is the reaction rate and D_1 is the diffusivity of A. k_1 is related to the true heterogeneous rate constant k_1^t by $k_1 = k_1^t/(a/2)$ Defining a dimensional coordinate z=x/h, one obtains:

$$d^2A/dz^2 - \Phi_1^2 A = 0$$

Where the Thiele modulus is defined by $\Phi_1^2 = k_1h^2/D_1$ and represents the ratio of the reaction kinetics to diffusion. The boundary conditions are: z = 0 $A = A_0$ and z = 1 $-dA/dz = \Phi_1^2/(h/a)\,A$. The first boundary condition implies bulk concentration at the top, while the second boundary condition implies that the flux to the bottom surface is equal to the rate of the electrochemical reaction.

The solution for the distribution of A along the depth of the trench is obtained (1) and the distribution of the electrodeposition rate is given by

$$R = k_1 A = k_1A_0(C_1 \sinh \Phi_1 z + \cosh \Phi_1 z)$$

and is presented by the dotted line in Fig. 1, Where C_1 is a constant determined by the boundary conditions. It can be seen that the electrodeposition is preferred at the top of the trench, resulting in undesirable pinch-off and void formation.

Complexed Copper: Bottom-Up Super Filling

If the metal ion is complexed now by a ligand, then the electrodeposition is carried out in two subsequent steps:

$$A \xrightarrow{k_1} B$$

$$B \xrightarrow{k_2} M$$

where A is again the metal ion, B is an intermediate species (i.e. the ligand-complexed ion) and M is the electrodeposited metal. The conservation equations for both species A and B are:

$$d^2A/dz^2 - \Phi_1^2 A = 0$$
$$d^2B/dz^2 - \Phi_2^2 B + \Phi_3^2 A = 0$$

where Φ_1^2 and Φ_2^2 are the Thiele parameters for A and B, respectively and Φ_3^2 is a mixed Thiele modulus difined by $\Phi_3^2 = k_1h^2/D_2$, which represents the ratio between the kinetics of the first reaction and the diffusion of B.

The following boundary conditions apply: z=0: $A=A_0$, $B = B_0$ and at z=1 $-dA/dz = \Phi_1^2/(h/a)A$ and $-dB/dz = \Phi_2^2/(h/a)B$. The boundary conditions at z=0 imply bulk concentrations there. The boundary conditions at z=1 imply that the reaction rates of A and B are equal to their respective diffusion fluxes there.

The analytical solution is obtained (1) and the rate of electrodeposition along the depth of the trench is given by:

$R_2=k_2B_0[C_3\sinh\Phi_2 z+C_4\cosh\Phi_2 z+C_5\sinh\Phi_1 z+C_6\cosh\Phi_1 z]$

where C_1, C_3, C_4, C_5 and C_6 are constants, determined by the boundary conditions and are functions of the three Thiele parameters and the aspect ratio h/a. The rate distribution is presented by the solid line in Fig. 1 for the various Thiele modulus: Φ_1^2 =2, Φ_2^2 =1 and Φ_3^2=5. Species B accumulates faster than it can diffuse out. Consequently, the electrodeposition is preferred at the bottom, resulting in the desirable super-filling (bottom-up). Recently, super filling was achieved in high aspect ratio h/a=5 from specifically complexed copper electrolyte, in the absence of additives, as shown in Fig. 2.

References

1. J. Jorne and E. E. Jorne, Cupricon Internal Report: Additive-Free Electro-deposition of Copper in High-Aspect-Ratio trenches and Vias," Cupricon, Inc., Rochester, NY (1999).

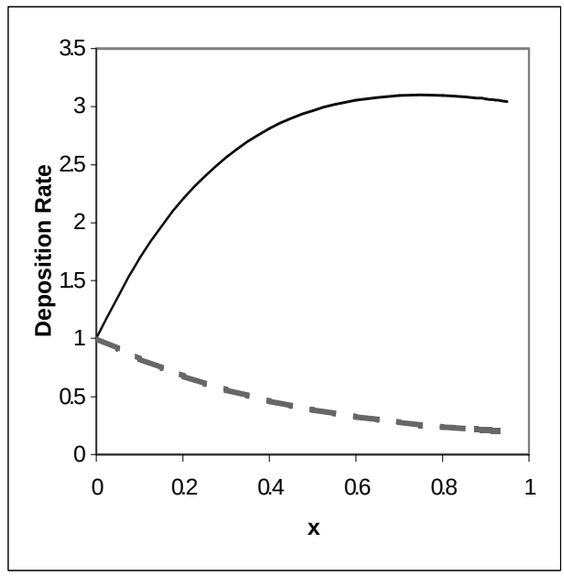

Fig. 1: Distribution of deposition rate in uncomplexed (pinched-off) and complexed (super-filling) electrolyte.
---------- Uncomplexed _____ Complexed
$\Phi_1^2 = 2$, $\Phi_2^2 = 1$, $\Phi_3^2 = 5$.

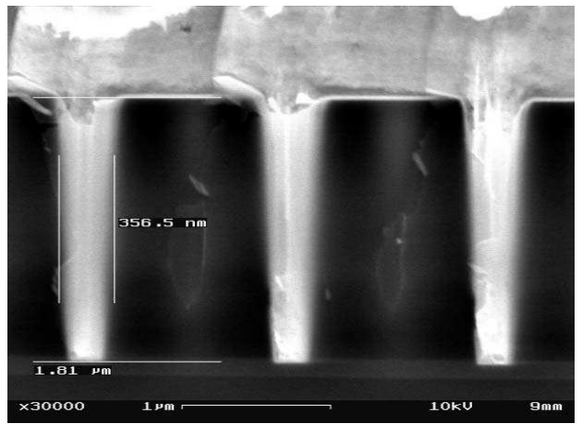

Fig. 3: Supper-filling of copper in high aspect ratio vias from complexed copper sulfate electrolyte.