A Model of Galvanostatic Pulse with Reverse Plating in the Presence of Additives

K.-M. Yin
Chemical Engineering Department, Yuan-Ze University, Neili, Taoyuan, Taiwan

One of the key plating techniques is to use pulse with reverse (pr) for the interconnections of through holes or blind vias across the multi-board (1). Various addition agents of strong adsorption characteristics are always added in small amounts to increase the throwing power on the far recessed area. However, there is also a need to reduce the usage of organic additives in the printed circuits and in the damascene metallization of sub-micron interconnects in semiconductors (2). The purpose of the present study is to simulate the additive adsorption and incorporation phenomenon as a function of metal deposition and additive adsorption kinetics on the pulse with reverse plating (pr) from first principle. The adsorption rate of the additive at all times is expressed as follows:

$$-N_{add} = D_{add}\frac{\partial C_{add}}{\partial y}\Big|_{y=0} = k_a C_{add,s}\Gamma(1-\theta_{add}) - k_d\Gamma\theta_{add} \quad [1]$$

where k_a and k_d are the respective adsorption and desorption rate constants of additive, Γ is the adsorbed additive concentration of one complete monolayer, and $C_{add,s}$ is additive concentration at interface.

The surface concentration of adsorbed blocking agent is a function of time. During pulse period (t_p), the number of surface accumulated additives is the difference between the rate of additive adsorption onto the surface and the inclusion rate of adsorbed surface additives:

$$\Gamma\frac{d\theta_{add}}{dt} - N_{ip} - (-N_{add}) = 0 \quad [2]$$

where the inclusion rate of additive $-N_{ip}$ during pulse period can be expressed by

$$N_{ip} = \frac{k_i}{F}\theta_{add}\frac{i_p}{1-\theta_{add}} \quad [3]$$

where k_i is the inclusion rate constant, i_p is pulse current density which is a negative value in electrochemical convention. The inclusion rate during pulse period is a function of surface coverage of blocking agent, θ_{add}, and the intrinsic current density $i_p/(1-\theta_{add})$.

In the reverse period (t_r), instead of inclusion, additive is released from the metal matrix. Mass balance on surface adsorbed additive in the reverse period can be expressed similar to Equation 3, The release rate, $N_{ir}(t)$, during t_r can be expressed in Equation 4:

$$N_{ir}(t) = N_{ip}(t^{'})\frac{i_r}{i_p} \quad [4]$$

$N_{ir}(t)$ can be calculated once $N_{ip}(t^{'})$ is determined by interpolation in the previous pulse period.

Figure 1 is the typical periodic adsorption rate and inclusion rate of additive. It is shown that in pulse period, pr mode has a higher inclusion rate than that of pc mode. The inclusion rate decreases along the pulse time since surface coverage of the additive decreases along the pulse time. No additive inclusion during off time in pc mode since no current passed in that period. While in the reverse period of pr mode, additives released from solid phase increase steadily with time. The release rate depends on the history of previous pulse inclusion rate according to Equation 4. The adsorption rate is always higher for pc mode than in pr mode in one complete cycle. Figure 2 depicts the effect of adsorption constant and inclusion constant on the average additive inclusion rate at disk rotation speed 500 rpm. It is shown that the average inclusion rate increases at the increase of k_a and k_i; however, the mass transfer limitation becomes apparent at 500 rpm when the incorporation rate is near -0.85 mol/cm^{2}s.

1. J. Barthelmes, *Trans. IMF*, **78**(4), 135-139 (2000).
2. A. C. West, C.-C. Cheng, and B. C. Baker, *J. Electrochem. Soc.*, **145**, 3070-3074 (1998).

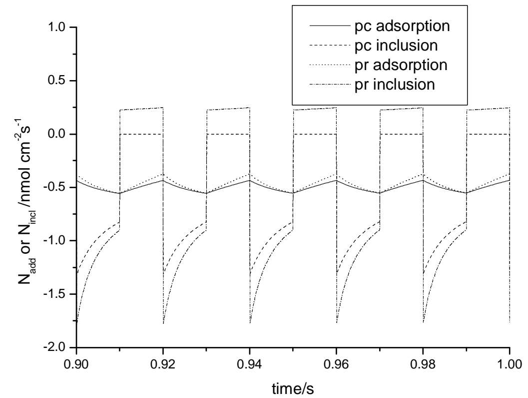

Fig. 1 Additive adsorption rate and additive incorporation rate as a function of time.

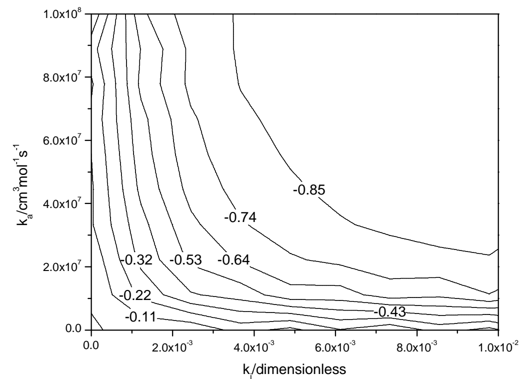

Fig. 2 Effect of average inclusion rate as a function of adsorption constant and incorporation constant. t_p=10 ms, t_r=10ms, i_p= -80 mA cm^{-2},i_r= 20 mA cm^{-2}, 298K.