Nucleation and Growth of Copper Electrodeposits on Barriers

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As feature size approaches the 50-nm node, processes for the direct electrodeposition of copper onto barrier materials may be required due to sub-optimal sidewall coverage of seed layers. The electrodeposition of copper directly onto barrier materials such as TaN or Ta is however not trivial due to complications resulting from 1) adhesion, 2) the island-growth mechanism that prevails under many conditions, and 3) a significant electrical resistance of the barrier material.

The present talk focuses on the island-growth mechanism. Experimental results of copper electrodeposition in various electrolytes, including copper-EDTA, acid-copper, copper-pyrophosphate and copper-citrate baths, are summarized. Both electrochemical and microscopy results are shown. The results are discussed within the context of the process requirements. The importance of scaling fundamental, experimental studies to process conditions is emphasized, and a simulation tool that is an aid for such endeavors is discussed.

The simulation tool is based on the direct numerical simulation of nucleation and growth.[1] It is shown that the simulations are in excellent agreement with previous theories that are valid under certain ideal conditions, namely the assumptions that growth is diffusion controlled and that nucleation rate is constant. It is shown how the simulations can be used to not only interpret current-transient measurements but also microscopy results. Furthermore, the ability to use the simulations to account for deviations from ideality is shown.

Figure 1 shows, for example, simulation results for different growth rate constants for the case of instantaneous nucleation. As the growth rate constant becomes large, growth is diffusion controlled. For comparison, theoretical results[2] for the instantaneous and progressive nucleation limits (assuming diffusion-controlled growth) are shown. For slow growth rates, the transients look akin to the progressive nucleation case.

Figure 1 shows an example of non-ideal growth from the perspective of many theories. It is often assumed that nucleation rate is given by a rate law that is first order in the number of available sites:

$$\frac{dN}{dt} = k_n (N_o - N) \qquad (1)$$

where N is the nuclei density and N_o is the total number of available nucleation sites. While it is commonly acknowledged that the rate constant k_n may be a function of electrolyte composition, the influence of changes in near-surface composition of the electrolyte on nucleation rate is frequently not considered. This is not important when treating rapid nucleation rates, where most nuclei are born nearly instantaneously before significant depletion. However, for the so-called progressive nucleation case, such an effect can be significant.

Figure 2 shows the influence of accounting for the local depletion of metal-ion concentration on nucleation rate. The number of nuclei normalized by the total possible sites is shown as a function of time. The nucleation rate is now assumed to be given by

$$\frac{dN}{dt} = k_n \left(\frac{c_o}{c_\infty} \right)^m (N_o - N) \qquad (2)$$

where c_o/c_∞ is the near-surface concentration over the bulk concentration of metal ion. It is seen that this effect can be significant depending on the value of m.

REFERENCES

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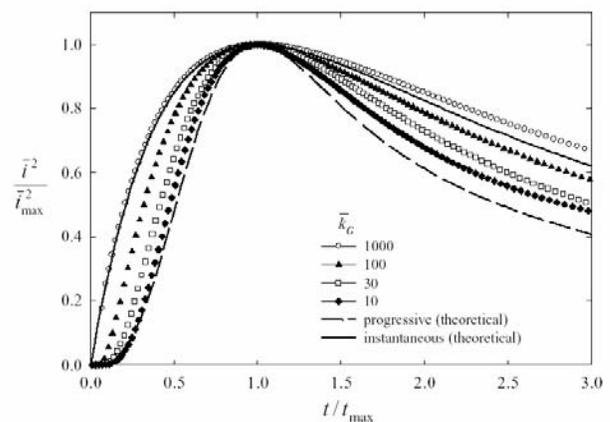
Figure 1. A series of simulated current transients for various growth rate constants. Instantaneous nucleation is assumed for all cases, but the growth is not diffusion controlled.
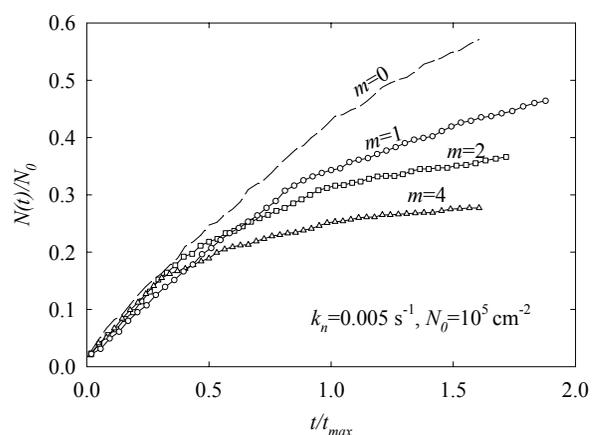
Figure 2. The normalized nucleus density as a function of normalized time for a progressive nucleation case. Results are shown for four values of m in equation 2.