Simulated additive behavior in a copper-deposition bath using molecular dynamics

Clint G. Guymon and Dean R. Wheeler
Department of Chemical Engineering
Brigham Young University

In the fabrication of copper interconnects, additives in the electrodeposition bath make it possible for high-aspect-ratio trenches to be filled without voids. The mechanistic behavior of the additives is not well understood at the molecular level. Little is known how additives such as bis-[3-sodiumsulfopropyl disulfide] (SPS) and polyethylene glycol (PEG) interact with chloride and other surface species to alter the polarization of the copper surface. Complicated interactions between the additives and the Cl^- determine for instance, the orientation and location of PEG and SPS in the surface layer.

The purpose of this study is to investigate molecularly the Cu(111) solid - solution interface using molecular dynamics simulations. As electron-transfer events are rare at the length and time scales modeled here, they are not included. The competition between solution species for energetically favorable positions near the surface dominates the dynamics and structure of the interface. We will report on the differences in additive behavior in a model copper-deposition bath with and without chloride present. The model bath contains various combinations of PEG, SPS, NaCl, and water.

We have developed a variation of a charge equilibration scheme [1, 2] to model the ability of the conduction electrons in the metal to respond to charge density fluctuations in the fluid. The model yields a smooth transition from copper-cluster ab initio calculations to large-scale electrode surfaces and reproduces the image-charge result at long range.

Approximately 10,000 atoms are modeled in a 4 x 4 x 7 nm periodic cell. Using simple inter-atomic potentials, Newton's equations of motion are solved to obtain the position and momenta of all simulated species. From the evolution of positions and momenta, fluid and interfacial properties are calculated. Shown in Figure 1 is a snapshot of a PEG, NaCl, and water simulation between Cu(111) electrodes. For clarity the water isn't shown. The copper atoms are shaded according to their respective charges: white is positive, black is negative, and grey is neutral.

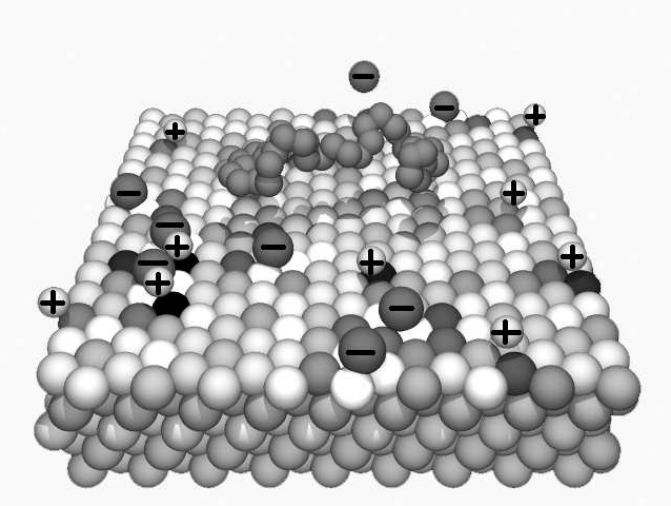

Figure 1: Simulated bath with chloride (large gray spheres w/ neg. sign), sodium(small light gray spheres w/ pos. sign), and PEG (array of spheres) with water omitted from view. Copper atoms are shaded according to their respective charges: white is positive, black is negative, and gray is neutral.

References

[1] Rick, S. W.; Berne, B. J. *Journal of the American Chemical Society* **1996,** *118,* 672–679.

[2] Rappé, A. K.; Goddard III, W. A. *Journal of Physical Chemistry* **1991,** *95,* 3358–3363.