Phase Field Modeling Applied to the Double Layer

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We present the first application of phase field modeling to electrochemistry. A free energy functional that includes the electrostatic effect of charged particles leads to rich interactions between concentration, electrostatic potential, and phase stability. The present model, explored only for the equilibrium, stationary interface, properly predicts the charge separation associated with the equilibrium double layer at the electrochemical interface and its extent in the electrolyte as a function of electrolyte concentration, as well as the form expected of electrocapillary curves.

The phase field technique has previously been applied to the time evolution of complex dendritic, eutectic, and peritectic solidification morphologies. The present work was motivated by the mathematical analogy between the governing equations of solidification dynamics and electroplating dynamics. For example, the solid-liquid interface is analogous to the electrode-electrolyte interface. The various overpotentials of electrochemistry have analogies with the supercoolings of alloy solidification: diffusional (constitutional), curvature, and interface attachment. Dendrites can form during solidification and during electroplating. It is not surprising, however, that we find significant differences between the two systems.

Electrochemistry has been chosen by the microelectronics industry as the deposition method for “copper damascene” interconnects on microchips because it is capable of “superconformal” filling. In physical vapor deposition on a trench-like surface, material is deposited more readily on the flat than within the trench. This buildup of material will shadow the trench, worsening the condition, and eventually causing the deposited material to “pinch off”, leaving a void within the trench. This void has serious consequences for the current carrying capacity and electromigration resistance of the resulting wire. Chemical vapor deposition is capable of conformal growth, with a uniform thickness deposited on all surfaces. This is superior to the subconformal growth of physical vapor deposition, but still results in a seam where the growth fronts from the trench sidewalls intersect. This seam has been found to have deliterious effects on the conductor. In contrast, while electrochemistry is capable of deposition in both the subconformal and conformal regimes, with the proper combination of additives, superconformal deposition is also possible. Under these conditions, material is deposited faster at the bottom of the trench than on the field and the trench is filled with void-free, seam-free material. This range of morphological evolution, including the possibility of void formation, is well suited to study with the phase field technique.