ANALYTICAL SEMINAR



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"Quantitative Analysis of Voltammetric Data from Semiconductor (Photo)electrodes and Freely Diffusing Redox Species"

This presentation will advance the premise that semiconductor voltammetry has significantly more quantitative information about semiconductor surface and bulk properties than understood in the extant literature. A quasi-analytical model for understanding and assessing voltammetric data collected with freely diffusing redox species and semiconductor electrodes operating in the dark or under illumination will be presented. This model is based on a Gauss's Law description of how an applied potential and injected charge is distributed across the semiconductor/liquid junction. A key advancement of this present work is the inclusion of both equilibrium and kinetic calculation stages that collectively describe dynamics of a semiconductor/electrolyte interface when a *time-dependent* waveform is applied. The use of this refined model with two different current expressions that describe diffusion at macro- and microelectrodes will be presented. First, the model will be discussed in conjunction with a semi-integration algorithm that describes diffusion to a planar surface. Some basic predictions from this form of the model will be discussed to calibrate the audience on how to interpret common voltammetric data shapes as a function of parameters of interest including scan rate, dopant density, presence of a surface oxide, and the density & energy of surface states. This model also will be discussed to address poorly understood factors in semiconductor electrochemistry: a dependence of the Helmholtz layer on the interfacial electric field at a semiconductor electrode and the impact of surface states with different charges. The prevalence of these factors will be articulated by describing data features in the semiconductor voltammetry literature that have previously been undecipherable.

Second, results from the same model in conjunction with a current expression that describes radial diffusion to a point electrode will be introduced. Voltammetric data of this form will be shown from scanning electrochemical cell microscopy measurements of model semiconductor electrode materials. Time permitting, two examples will be shown that illustrate the capacity of voltammetry to be used as a spatially-dependent probe of surface properties. The first example will show how scanning electrochemical cell microscopy can be used to map the chemical properties of Si electrodes under ambient conditions. The second example will highlight the capacity of scanning electrochemical cell microscopy to probe spatially the electrical properties of two dimensional semiconductors like MoS_2.