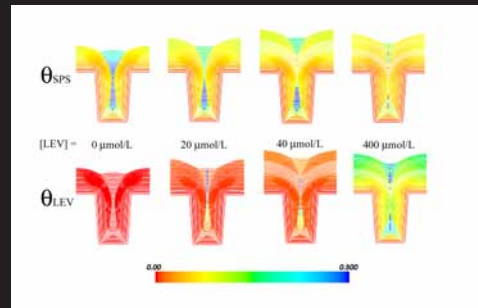


Nanostructure Fabrication Processes

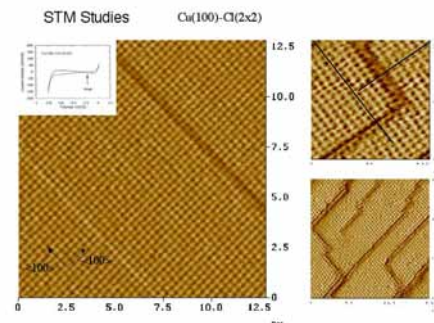
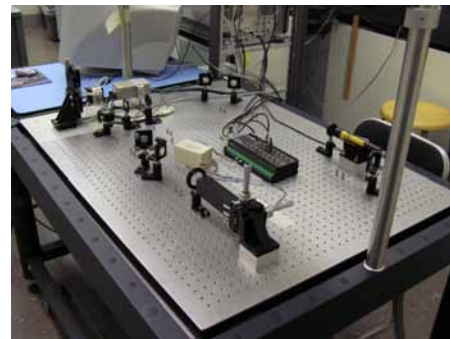
Objective

In this project we are developing *in situ* measurements relevant to the electrochemical fabrication, processing, and application of nanostructured materials and devices. Our effort is focused on the influence of adsorbates, defects, and stress state on the growth, structure, and morphology of complex nanostructures to enable control and optimization of the resulting material properties.



Impact and Customers

- Demonstration of “superfilling” (void-free trench filling) of ferromagnetic materials and the use of Damascene processing (metallization of through-silicon-vias and trenches for on-chip interconnects) to integrate ferromagnetic functionality into ultra large scale integration (ULSI) and microelectromechanical systems (MEMS).
- The NIST model of “superfilling” has been extended to account for the effect of additional electrolyte additives on overshoot phenomena. Also, the effect of adsorbate surface diffusion on feature filling dynamics has been presented. The findings are central to optimizing copper metallization in the fabrication of on-chip interconnects.
- Interactions with industrial, academic, and government partners maximize the utility of our measurement capabilities. Partners include AMD/IBM, Harvard University, Seoul National University, Faraday Technology, UCLA, University of Virginia, and Rohm & Haas.
- Demonstration of alloy co-deposition processes and measurements relevant for producing fuel cell electrocatalyst for oxygen reduction and organics fuel oxidation reactions.



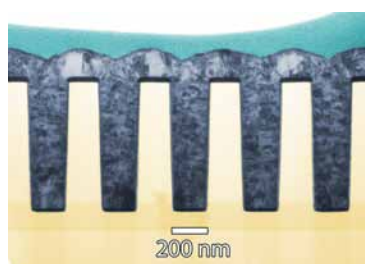
Approach

Progress in optimizing materials processing in wet chemical environments requires the use of in-situ measurements of the structure and dynamics of the metal-electrolyte interface under realistic conditions. These measurements can provide insight into the mechanisms of relevant atomic, molecular, and mesoscale film growth and dissolution processes.

This project has several thrust areas ranging from measurements and modeling of surfactant mediated growth to the investigation of both surface and thin film growth stress. Particular attention has been given to the role of electrolyte additives in the formation and performance of advanced nanoscale and mesoscale interconnects as used in state of the art microelectronic devices. Measurements are also underway that detail the use of underpotential deposition (upd) reactions to precisely control the composition and structure of 2-D and 3-D alloys. This is complemented by measurements of stress changes that accompany alloy formation as well as the inverse dealloying process. An integral part of the program is the development of a mechanistic linkage between atomic and molecular phenomena and rational design of the desired nanostructures.

Accomplishments

This year we have extended the process for void-free trench filling to include ferromagnetic alloys such as NiFe and CoFe. Feature filling involves a new mechanism of superconformal growth that uses a single inhibitor whose consumption during deposition gives rise to positive feedback. Coupling of the nonlinear dynamics with the nonplanar substrate geometry gives rise to void-free alloy deposition in the recessed surface features, as shown in the cross section TEM images below. Two types of molecules have been shown to yield this effect; cationic N-bearing polymers and more recently certain benzimidazole derivatives. The latter provide feature filling dynamics that offer seamless integration with conventional Damascene processing, and thereby the prospect of introducing ferromagnetic materials into 3-D metallization for ULSI-CMOS and MEMS applications.

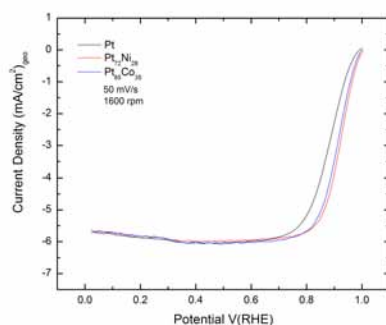


Superconformal Deposition of Ferromagnets

Exploration and measurements developed for upd processes of alloy deposition have received significant attention in the past year. Practical interest in the production of Pt-transition metal alloys for use as either hard magnetic materials for memory applications and/or as potential fuel cell electrocatalysts, has motivated much of this work. In the past year the Pt-Ni, Pt-Co, Pt-Cu, Pd-Cu and Pt-Pb systems have been examined. The bond

enthalpy associated with the formation of Pt and Pd alloys enables codeposition of the more reactive alloying species, e.g., Ni, Cu, etc, at potentials well positive of that required to deposit the elemental form.

Pt-Ni and Pt-Co alloys produced in this manner have been shown to be more catalytic than pure Pt for the oxygen reduction reaction; the latter being a central impediment to improved fuel cell performance.



Rotating disk electrode measurements of enhanced kinetics of oxygen reduction on electrodeposited Pt alloys

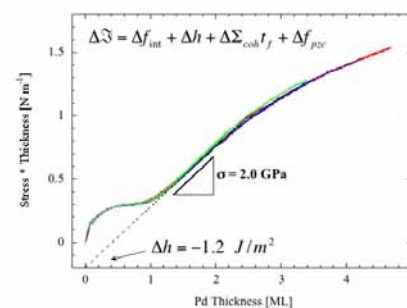
Likewise, electrodeposited Pt-Pb alloys have been shown to exhibit a factor of ten improvement in the formic acid oxidation kinetics relative to Pt.

In order to gain a deeper insight into upd and molecular adsorption processes relevant to a wide range of electrochemical processing issues, a variety of in-situ scanning tunneling microscope (STM), atomic force microscope (AFM), stress and gravimetric measurements are underway.

MSEL has recently constructed an optical bench for in-situ measurement of surface stress during electrochemical processing, using the wafer curvature method. Forces

on the order of 0.008 N/m (23 km radius of curvature) can be resolved, sufficient to study the adsorption of upd and molecular monolayers. This powerful method is capable of monitoring the surface stress associated with thin film deposition.

The figure below shows three independent stress measurements for the first five monolayers of Pd electrodeposited onto (111)-textured Au, which are reported to be pseudomorphic and in registry with the Au(111) surface. If we linearize the portion of the curve immediately following the initial monolayer, we obtain a slope of 0.48 N/m/ML which corresponds to a coherency stress of about 2.0 GPa, considerably less than the theoretical value of 14.2 GPa based on the +4.9 % lattice misfit. This is likely due to anion adsorption, which can stabilize an expanded Pd structure. The y-intercept of -0.2 N/m yields an interface stress, Δh , of -1.2 J/m^2 , indicating that the Pd-Au interface favors expansion. It is also clear that the stress-thickness curve deviates from linearity as the Pd film thickens, suggesting that the Pd begins to lose coherency with the Au substrate. Further work is underway to explore these timely and exciting issues.



Stress-thickness product for Pd deposition onto (111)-textured Au

Learn More

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Publications

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