

SYMPOSIUM Z

Mechanisms in Electrochemical Deposition and Corrosion

April 24 – 25, 2003

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* Invited paper

SESSION Z1: ELECTROCHEMICAL DEPOSITION
AND DISSOLUTION

Chair: Reginald M. Penner
Thursday Morning, April 24, 2003
Salon 4 (Marriott)

8:30 AM *Z1.1

ELECTROCHEMICAL SYNTHESIS OF MOLYBDENUM OXIDE THIN FILMS: DEPOSITION MECHANISM AND TEMPLATE-DIRECTED ASSEMBLY OF NANOSTRUCTURED MATERIALS AND COMPONENTS. Keith J. Stevenson, Todd M. McEvoy, Hugo Celio, University of Texas at Austin, Department of Chemistry and Biochemistry, Austin, TX.

Thin films of transition metal oxides (e.g., WO_3 and MoO_3) have shown significant promise for application in the contexts of catalysts, batteries and electrochromics. In this paper we describe the deposition of molybdenum oxide thin films prepared from aqueous solutions containing peroxy complexes of molybdenum(VI). Electrochemical quartz crystal microbalance (EQCM) studies along with supporting spectroelectrochemical experiments have allowed us to elucidate the electrodeposition mechanism. Analysis of EQCM, as well as spectroelectrochemical data, has allowed us to identify at least four distinct regimes for film growth. EQCM was used to estimate apparent equivalent molecular weights and corresponding reaction mechanisms were established for films grown at different deposition potentials. We propose a new electrodeposition mechanism that involves the graded reduction of several solution components, primarily comprising molybdic acid and di- and tetra-peroxy-polymolybdates, to form amorphous hydrates of non-stoichiometric, mixed-valent molybdenum oxides. We also describe the electrodeposition of molybdenum oxide from acidified sodium molybdate solutions and demonstrate that film growth proceeds by a similar pathway involving the direct reduction of molybdic acid. However, films grown from acidified sodium molybdate solutions are much less stable, presumably due to incorporation of large amounts of water. Post-deposition sintering in oxygen and vacuum allows for tuning of material properties (e.g., valency, defect concentration, electrical conductivity and optical transparency). When coupled with template-directing methodologies we are able to fabricate a variety of functional materials and configurations. Design strategies will be outlined for creating materials and structures with tailored properties (e.g., thickness, porosity, structure and composition).

9:00 AM *Z1.2

SELF-INDUCED VOLTAGE OSCILLATIONS AND DIAMETER MODULATION DURING PORE FORMATION IN Si AND InP. M. Christophersen^{a,b}, S. Langa^b, J. Carstensen^b, P.M. Fauchet^a, H.Föll^b. ^aCenter for Future Health, University of Rochester, NY; ^bMaterials Science Department, University of Kiel, GERMANY.

High pore densities in n-InP, n-GaP and more recently p-type Si, have been shown to lead to self induced voltage oscillations accompanied by diameter modulation. The origin of these voltage oscillations during pore formation is assumed to be similar in silicon and in III-V compounds. In order to investigate the etching conditions that give rise to the observed voltage oscillations we use p-type silicon with only one open window in a nitride mask at high current densities ($>25 \text{ mA/cm}^2$ for the free silicon surface, 4 wt.-% HF in DMSO). The experimental results for the voltage oscillations as well as the induced diameter modulations can be explained by synchronized pore growth induced by overlapping of the space charge regions around the pores. With this coupling mechanism the stochastic dissolution process at each pore tip can be synchronized in time, leading to the global voltage oscillations and the self-induced diameter oscillations. Only pores in InP can also form self-organized single pore crystals, i.e. have a long range order in space [1]. The main reasons leading to single crystalline pore arrays are the high density of pores, the interaction between them, as well as the so called nucleation layer. The formation of a nucleation layer is a unique feature exhibited only by InP. The present report will discuss in detail the etching conditions leading to synchronization of pores in InP, GaP and Si as well as the reasons why external voltage oscillations have not been observed up to now in other materials, e.g. GaAs or Ge. [1] H. Föll, S. Langa, J. Carstensen, M. Christophersen, I. Tiginyanu, K. Dichtel, Pore Etching in Compound Semiconductors for the Production of Photonic Crystals, L6.4, MRS Proceedings Vol. 722, 2002.

9:30 AM Z1.3

TIN OXIDE THIN FILMS: ELECTRONIC PROPERTIES AND FUNDAMENTAL MECHANISMS UNDER ELECTROCHEMICAL CONTROL FOR GAS-SENSING STUDIES. Raul Diaz, Ismael Diez-Perez, Pau Gorostiza, Fausto Sanz, University of Barcelona, LCTEM Department of Physical Chemistry, Barcelona, SPAIN.

SnO_2 is one of the most studied metal oxides due to its wide applications ranging from electrochemistry to optics, solar cells or gas

sensors. We have recently developed a method to obtain SnO_2 nanoparticles containing metal catalytic centers that enhances the gas sensitivity of the material (R. Diaz et al., Chem. Mater., 2001). SnO_2 displays n-type semiconducting properties, and the presence of oxidizing and reducing agents is known to have dramatic effects on the electronic properties of the material surface (J. Arbiol et al., Sens. Act. B, 2001). Despite the high interest of the close relationship between the electrochemical behavior of these oxides and their applications, only a few electrochemical studies have been reported. These studies have been done on polycrystalline tin and, to our knowledge, there is no published fundamental research on tin single crystals that supports the reported results. We have developed a new chemical etching method to obtain atomically flat surfaces on $\text{Sn}(100)$ single crystals. Following the study of iron oxide films under electrochemical control (I. Diez-Perez et al., J. Electrochem. Soc., 2001), we have started the characterization of tin oxides in borate buffer solution in order to investigate quantitatively the electronic properties of the semiconductor material, and the mechanism responsible for its gas-sensing properties. The results that will be presented include the assignment of the peaks in the voltammogram, and correlation with electrochemical impedance data in the significant potential regions. This, together with in-situ EC-STM studies, allows the characterization of the surface dynamics and the electronic properties of the different oxide layers formed at different anodic potentials. Our data suggest the buildup of an energy barrier at the surface that strongly conditions the electrochemical behavior of the oxide layer, and that may be related to the sensing properties of SnO_2 , as shown in preliminary tests.

9:45 AM Z1.4

CORROSION OF NANOCRYSTALLINE TUNGSTEN FILMS USED IN SILICON-BASED MICROSYSTEMS. Kevin R. Zavadil and Paul G. Kotula, Sandia National Laboratories, Albuquerque, NM.

Tungsten is a particularly attractive metalization and tribological coating for monolithic silicon-based microsystems because it can be deposited using a low temperature CVD process. The resulting ultra-thin, nanocrystalline films represent an interesting material from a corrosion standpoint because the mean grain size in these films is comparable to the passive oxide thickness for this valve metal and this oxide is not thermodynamically stable at near neutral pH. These issues raise concerns of the reliability of tungsten thin films in microsystems under atmospheric conditions where water adsorption and capillary condensation can take place. In this paper, we address the stability of CVD W thin films on Si in both aqueous unadated and atmospheric environments using a combination of electrochemical, surface spectroscopic, electron microscopic and electrochemical scanning probe techniques. The atmospherically formed oxide on W is a mixture of W(IV) and W(VI) oxides. Condensation of or immersion in H_2O produces conversion to the hexa-valent oxide, localized corrosion and large electrochemical impedance changes. Initial dissolution of the W appears to be localized to regions of high disorder where transmission electron microscopy shows grain size is at a minimum and residual contaminants from the pre-deposition Si etch are at their highest concentration. Longer-term exposure to H_2O results in full, local penetration of the W layer and dissolution of the underlying Si. Corrosion product particle formation is found on surfaces subjected to immersion and drying cycles. Recent results using electrochemical scanning probe microscopy to track changes in film microstructure as a function of exposure conditions will be discussed in terms of a complete description of the corrosion mechanism for these films. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. Department of Energy under contract DE-AC04-94AL85000.

10:30 AM Z1.5

EFFECT OF 1-5 NM THICK OVERCOATS OF DIAMOND-LIKE CARBON ON THE CORROSION OF MAGNETIC HARD DISKS. Soyoung Jung, Evan T. Dellor, and Thomas M. Devine, University of California, Department of Materials Science and Engineering, Berkeley, CA; Robert Kostecki, Lawrence Berkeley National Laboratory, Division of Energy, Environment and Technology, Berkeley, CA.

Potentiodynamic anodic and cathodic polarization tests and electrochemical impedance spectra were obtained for magnetic hard disks coated with a layer of diamond like carbon and immersed in aqueous borate buffer (pH 8.4) containing 0.1M NaCl. Five thickness of the DLC were investigated: 0 nm (i.e., no DLC), 1nm, 2nm, 3nm and 5nm. At high anodic potentials, the disks were pitted. Inspection of the pitted disks by FESEM indicates that pits occurred through pores in the DLC. Cathodic polarization tests and electrochemical impedance spectra indicate that electrochemical reduction of oxygen occurs on the surface of 1-5 nm thick layers of DLC. Because the DLC, which has very high electrical resistivity, is so thin, cathodic current is able to pass from the metal to reducible species, such as oxygen, in the aqueous solution. In fact, the transport of electrons appears to be

limited by a thin ($\approx 1\text{nm}$), reaction product layer that forms on the surface of the DLC. We conclude that pitting corrosion of hard disks in service is not likely because of the high value of the pitting potential of the magnetic alloy. Corrosion-related failures in service are more likely to result from corrosion enhanced by electrochemical reduction reactions that occur on the surface of the DLC.

10:45 AM Z1.6

THE EFFECT OF ADDITIVES ON TEXTURE FORMATION AND TWINNING IN Ni ELECTRODEPOSITS FOR MICROSYSTEMS APPLICATIONS. Gene Lucadamo, Nancy Yang, and Douglas L. Medlin, Materials and Engineering Sciences Center, Sandia National Laboratories, Livermore, CA.

In order to understand the mechanisms of microstructure evolution during electrodeposition using the LIGA* process, the role of various bath additives on texture formation must be investigated. Accurate modeling of the plating process must also take into account the profuse growth of low-energy twin interfaces in electrodeposited fcc metals. Using X-ray diffraction (XRD), electron backscatter Kikuchi patterns (EBSP), and transmission electron microscopy (TEM), we have examined the effect of texture on the orientation and morphology of nanometer-scale twins in Ni films with different grain-refining additives. Our results indicate that while inhibiting grain growth during plating, dilute concentrations of additives also lead to the formation of different textures and, therefore, restrict the possible orientations of $\{111\}$ twin planes relative to the plating direction. Specifically, 100 μm -thick films of Ni-sulfamate, Ni-saccharin, and Ni(Mn) exhibited fiber textures of $\{100\}$, $\{100\}+\{111\}$, and $\{110\}$, respectively and consisted of columnar grains. TEM analysis indicated that the twins in Ni-sulfamate and Ni-saccharin generally were inclined to the growth direction. By contrast, the Ni(Mn) films contain twins parallel to the growth direction as a consequence of the $\{110\}$ texture. These vertical twins have a low mobility in the plane of the film, which provides a plausible explanation for the inhibited grain growth in Ni(Mn) as compared to Ni-sulfamate or Ni-saccharin. (*Lithographie Galvanoformung Abformung) This work is supported by the US Department of Energy through contract DE-AC04-94-AL85000.

11:00 AM Z1.7

PHASE FIELD MODELING OF THE ELECTROCHEMICAL INTERFACE. J.E. Guyer, W.J. Boettinger, J.A. Warren, Metallurgy Division, National Institute of Standards and Technology, Gaithersburg, MD; G.B. McFadden, Mathematical and Computational Sciences Division, National Institute of Standards and Technology, Gaithersburg, MD.

We present a phase field model of the electrochemical interface. We examine both aqueous and molten salt systems. Our model naturally produces a charged "double layer" and the equilibrium behavior of this interface (Debye length, as well as surface charge and surface energy as functions of potential) is consistent with traditional electrochemical models. Rather than assuming an abrupt change in properties at a mathematically sharp boundary, the phase field approach introduces a new field variable to describe the smooth transition between physical phases of the system. A new governing equation for this phase field is solved along with the governing equations for transport of quantities such as mass and heat. The increased complexity of solving an additional non-linear field equation is offset by the elimination of the interfacial boundary conditions that both influence and depend upon the shape of the evolving boundary. The phase field technique has been successfully applied to a range of solidification morphologies, including dendritic, eutectic, and peritectic systems. We were motivated by the mathematical analogies between electrochemical and solidification interfaces. Dendrites can form in both systems. The electrochemical overpotentials are analogous to solidification undercoolings, such as diffusional (constitutional), curvature, and interface attachment. Despite these similarities, the rich interactions between concentration, electrostatic potential, and phase stability lead to a more complicated interfacial structure than is typically encountered in models of solidification. We will discuss the moving interface, under both plating and corroding conditions. We observe solute depletion, leading to limiting current behavior. We have deduced relationships between the parameters of the phase field equation and the traditional parameters of electrochemical kinetics, such as the exchange current. We will discuss the influence of the chosen phase field evolution equation on the observed current-overpotential behavior.

11:15 AM Z1.8

ON THE FORMATION OF ANODIC NIOBIUM OXIDE IN POTASSIUM NITRATE MELT. L. Skatkov, PCB "Argo" Ltd., Physical Department, Beer Sheva, ISRAEL; V. Gomozyov, National Technical University, Electrochemical Department, Kharkov, UKRAINE.

The work investigates the process of niobium anodization in salt nitrate melts at oxide re-crystallization temperatures. The electron Auger spectroscopy study of anodic oxide film (AOF) phase structure showed that the generated film look like "sandwich" of Nb_2O_5 , NbO₂ and NbO phases (in the direction from oxide surface toward iobium). X-ray photography made in $\text{K}\alpha$ -irradiation of chromium anode permitted to identify the oxide film outer layer as the low-temperature α -modification of Nb_2O_5 with pseudo hexagonal lattice. The studies of possible inclusion of electrolyte components into the oxide led to the result, appearing contradictory at first glance: during its growth the oxide is saturated not only with anions (as might be expected in similarity with anodization in water electrolytes) but with cations as well. Nitrogen concentration in the film is seen to be maximal in the niobium-substrate-adjacent layer and diminishes towards the AOF outer surface, whereas potassium concentration profile is of opposite nature. Potassium quantitative content in oxide was studied by X-ray fluorescent analysis. KCl crystal was used as potassium reference. Potassium concentration value, which amounted to about 9%, was calculated on the assumption of 50% potassium content in the reference. These findings permit to assume the generation of potassium solid solution in niobium oxide during AOF crystallization.

SESSION Z2: CORROSION

Chair: J. Charles Barbour
Thursday Afternoon, April 24, 2003
Salon 4 (Marriott)

1:30 PM *Z2.1

LENGTH SCALES IN ALLOY CORROSION. Karl Sieradzki, Arizona State Univ, Dept of Chemical Eng. and Mat. Sci and Dept of Mech. and Aerospace Eng, Tempe, AZ.

The role of both solid and fluid length scales in determining the corrosion behavior of alloys is considered. For the solid, these length scales are set by alloy microstructure while in the fluid the dominant scale is the diffusion boundary layer thickness. Often, the corrosion/dissolution behavior of an alloy is determined by the coupling of these length scales. We will discuss how the corrosion behavior and resultant corrosion morphology are affected by the various length scales and pose questions regarding the possibility of the development of corrosion resistant "designer" alloys based on our knowledge of the important factors affecting alloy corrosion behavior.

2:00 PM *Z2.2

DEVELOPMENTS IN CORROSION AND STRESS CORROSION OF SOLID SOLUTION ALLOYS. Roger C. Newman, Benjamin Lynch, Jane Deakin and Nicholas Senior, UMIST, Corrosion and Protection Centre, Manchester, UNITED KINGDOM.

The de-alloying and stress corrosion of noble-metal solid solutions such as Au-Ag is rather well understood, and applications of the resulting nanoporous solids are being explored. These alloys are such good model systems that similar processes in engineering alloys have been somewhat neglected recently. In the 1960s, L. Graf thought that stress corrosion of a wide range of solid solution alloys could be accommodated within a scheme of selective dissolution leading to crack wall protection by a noble metal layer. His scheme has often been thought over-generalized, but two key test cases, investigated by our group, have now revealed surprisingly classical de-alloying behaviour. These are (1) austenitic stainless steel in strong, hot caustic solutions, and (2) Ni-Cu alloys (Monels and cupronickels) in copper sulfate solution. A variety of electrochemical and analytical techniques have been used to explore the surface processes occurring in these systems. A key observation is that 316L stainless steel generates a strong, connected nanoporous layer in caustic solutions, even though the Ni content is only 11%. The space-filling ability is due to the de-alloyed layer having a specific intermediate composition (about 50Fe-50Ni) that gives it a space-filling fraction greater than the continuum percolation threshold. Other systems have been examined, such as Zn-Ni, where an analogous layer eventually falls apart into dust by slow dissolution of Zn, disconnecting the nanoporous structure.

2:30 PM Z2.3

UNDERSTANDING THE FUNDAMENTALS OF ATMOSPHERIC CORROSION THROUGH THE DEVELOPMENT OF A HOLISTIC MODEL. Ivan Cole, Scott Furman, Tony Hughes, Corrosion Science and Surface Design Team, CSIRO Division of Manufacturing and Infrastructure Engineering, Melbourne, AUSTRALIA.

A holistic model of atmospheric corrosion has been constructed which models the processes controlling atmospheric corrosion from the macro (continental scale) to the micron scale. Understanding processes across these diverse scales not only permits development of much more accurate and flexible models but provides new insights

into the processes controlling atmospheric corrosion. One of the key components of the Holistic Model is the stochastic simulator. In this simulator the interface region is subdivided into small sub-volumes (voxels) that are assumed to be chemically homogenous. All macroscopic events (diffusion, chemical reactions, charge transfer) and their rates (diffusion rates and chemical rates) are converted to stochastic probabilities. Then events are randomly applied to the elements in each voxel. Thus in this simulation there is no need to select or define the mechanisms that control oxide growth, diffusion in films or chemical reaction sequences, as these processes will generate themselves. Issue being tackled are how to stochastically model the role of redox reactions in inducing a charge imbalance and further generation of potential distributions and charge diffusion, How does the establishment of membranes or geometric features between the anode and cathode affect these processes. The model framework also permits these fundamental considerations to be linked to processes controlling deposition and segregation of pollutants by solubility consideration on the metal surface

2:45 PM Z2.4

MODELING OF THROWING POWER PROVIDED BY AN ALUMINUM BASED CLAD EXPOSED TO ATMOSPHERIC CONDITIONS. Francisco J. Presuel and R.G. Kelly, University of Virginia, Dept of Materials Science and Engineering, Charlottesville, VA.

A computational mass transport framework originally developed for crevice corrosion modeling was extended to study the interactions of an aluminum clad with its Al-substrate due to a scratch on alloys exposed to the thin electrolytes characteristic of atmospheric corrosion. This extension allows open circuit conditions to be modeled, as well as local galvanic couples to be considered. Kinetics have been added for metallic clad and bare AA2024-T3, including the decrease in pitting potential on chloride concentration. The model has been applied to studies of the parameters that control the throwing power of metallic claddings (e.g. scratch size, $[Cl^-]$, i_{pass} , i_{dl}). Two geometries were investigated a pseudo 1-D model and a square sample with a cross inscribed, analogous to what is done experimentally. A quantitative computation of the throwing power of metallic cladding on AA2024-T3 in thin electrolytes was achieved. For the base case of electrochemical behavior studied, a loss of protection ability was observed between a scratch size of 1.5 mm and 2.5 mm. The metallic cladding modeling also allowed the discovery of the equivalence of reducing the i_{pass} of the clad or increasing the i_{dl} of the AA2024-T3 on the size of the scratch that can be protected. A semilogarithmic relation was found between these parameters and the scratch size that can be protected. An order of magnitude reduction in i_{pass} (or increase in i_{dl}) led to a decrease by 50% of the scratch size that was protected. Two competing effects of increasing the chloride concentration in the thin electrolyte were observed. Higher chloride concentrations increased the throwing power by increases in the conductivity, but it also lowered pitting potential of both the cladding and the base material. In our simulations, the former dominates the latter, indicating better protection of scratches at higher chloride concentrations.

3:30 PM *Z2.5

INITIAL OXIDATION KINETICS OF COPPER (110) FILM INVESTIGATED BY IN SITU UHV-TEM. Guangwen Zhou and Judith C. Yang, Department of Materials Science and Engineering, University of Pittsburgh, Pittsburgh, PA.

Environmental stability is one of the most critical properties for most engineered materials. Furthermore, as engineered materials approach nanoscale, understanding corrosion at this length scale will become necessary. We focused on a simple nanoscale corrosive reaction, i.e. oxidation, by in situ ultra high vacuum transmission electron microscopy (UHV-TEM). Classical theories of oxidation, such as Cabrera-Mott, have proved to be highly successful in predicting oxidation behavior of metals, but these models assume uniform film growth. Due to the increased experimental capabilities in resolution and cleanliness, it is known that early stages of oxidation involve nucleation and growth of metal oxide islands. In situ UHV-TEM is ideal for probing nucleation and initial growth of oxide formation in real time with controlled surface conditions. We report our investigations of the kinetics of initial stages of Cu(100) and Cu(110) oxidation using in situ UHV-TEM. The kinetic data on the nucleation and growth of the 3-dimensional oxide islands demonstrated that oxygen surface diffusion is the dominant mechanism for the oxide formation during the initial oxidation in dry oxygen. The dynamic observation of the nucleation and growth of Cu oxide shows a highly enhanced oxidation rate on Cu(110) surface as compared to Cu(100). Our results indicate that orientations that form a higher density oxide nuclei and have a faster initial oxidation rate, may have a slower long-term growth rate due to the rapid coalescence of the oxide which switches the oxide growth mechanism from surface diffusion to the slower diffusion through an oxide scale.

4:00 PM Z2.6

STRUCTURAL STUDIES OF THE INITIAL STAGES OF COPPER SULFIDE FILM GROWTH: INFLUENCE OF HUMIDITY.

M.J. Campin, J.G. Zhu, New Mexico State Univ, Dept of Physics, Las Cruces, NM; J.C. Barbour, J.W. Braithwaite, P.P. Provencio, Sandia National Laboratories, Albuquerque, NM.

The study of copper corrosion, especially copper sulfidation, is an important area of research because of the widespread use of copper in critical electrical components. Copper sulfidation is challenging to study due to the possible formation of multiple sulfide phases and complex corrosion product morphologies. In this study, we have used focused ion beam (FIB) cross-sectioning, transmission electron microscopy (TEM), high-resolution TEM (HRTEM), x-ray diffraction (XRD), and ion beam scattering to characterize the product formed when thin films of Cu are exposed to a dilute (50-200 ppb) H₂S atmosphere at low (0.5%) to high (80%) relative humidity (RH). An important early observation was that the Cu₂S growth rate for long times is significantly higher for sulfides grown at low RH compared to high RH. This implies that different diffusion mechanisms dominate at low and high RH or that there are morphological differences between the sulfides grown at low and high RH. Studies were performed to determine whether structural differences in the sulfides could give rise to enhanced diffusion. It was found that for both low and high RH sulfidation, Cu is the dominant diffuser and reacts with S to form the low chalcocite phase (Cu₂S) as identified by x-ray and electron diffraction. Cross-section and plan-view TEM revealed that the Cu₂S grains formed at high RH are 20-50 nm in size for all Cu₂S film thickness, whereas the grains formed at low RH are 75-150+ nm and appear to undergo grain growth as the Cu₂S film grows thicker. The connection between the observed Cu₂S grain morphologies and the solid state diffusivity of Cu will be discussed. Sandia National Labs is a multi-program laboratory operated by Sandia Corp., a Lockheed Martin Co., under U.S. D.O.E. contract no. DE-AC04-94AL85000.

4:15 PM Z2.7

THE IMPACT OF ANNEALING ON THE CORROSION MECHANISM OF COPPER FILMS. Didem Ernur, Laureen Carbonell, Denis Shamiryan, Karen Maex, IMEC, Leuven, BELGIUM.

Integration of copper damascene metallization to improve large-scale integration performance necessitates process optimization and understanding of the possible sources of failure. Corrosion of copper is one of the failure mechanisms and has been reported to occur during the Chemical Mechanical Polishing (CMP) process step. The CMP slurry constituents, and the barrier metal have been found to play important roles on the corrosion mechanism of copper. However, little is known about the effect of the copper film properties that might contribute to its corrosion. Copper film properties such as internal stress, grain size, grain orientation, hardness, the amount and the type of impurities present are highly influenced by the plating conditions used during electrochemical plating. Depending on the subsequent anneal temperature, the film properties are further modified. In this study, we investigated the corrosion mechanism of copper films as a function of the annealing temperature. Desorption of the impurities during annealing monitored by Atmospheric Pressure Ionized Mass Spectrometry reveals many desorbing species from the copper films that could originate from the additives in the plating bath. The morphology of the surface was examined by scanning electron microscopy and focused ion beam, showing that with an inorganic acid-based model CMP solution, corrosion is initiated at the grain boundaries. In contrast, for an organic acid-based solution, corrosion starts with no preferential location. Some samples received an additional anneal at different temperatures after the CMP process was completed, and were then treated again with the model CMP solutions. For these post-CMP annealed copper films, a different mechanism governs the initiation and evolution of corrosion. Atomic Force Microscopy images show that samples exposed to inorganic acid-based solution had a rough surface indicating severe corrosion whereas, the ones dipped into the organic acid-based solution show less roughness.

4:30 PM Z2.8

IN-SITU STUDY OF SOLUTION CHEMISTRY DURING LOCALIZED CORROSION IN Al ALLOY 2024-T3. R.G. Copeland, N. Missert, Sandia National Laboratories, Albuquerque, NM; R.G. Buchheit, Y. Kim, The Ohio State University, Columbus, OH.

Localized corrosion in Al alloys has been investigated for many years with diverse experimental approaches. Using a technique refined during earlier corrosion studies with engineered thin film model systems, changes in local solution chemistry during corrosion at second phase particle sites on Al alloy 2024-T3 have now been imaged in real time. The addition of fluorescein to the aqueous chloride solution combined with confocal scanning laser microscopy allows the

in-situ observation of changes in pH at precipitates and on the bulk alloy. An examination of the solution chemistry during the dealloying of S-phase (Al-Cu-Mg) particles and the possible cathodic behavior of other Cu rich second phase particles can be made. This method allows the time evolution of local cathodic and anodic reactions to be observed and makes it possible to study possible particle-to-particle interactions by monitoring the pH of the solution surrounding adjacent second phase particle sites. Simultaneous open circuit potential data can be collected to examine the correlation between changes in solution chemistry and open circuit fluctuations as corrosion events take place. Post exposure characterization of samples using SEM, EDS and AFM provides an extended description of the localized corrosion process in these materials. This work is partially supported by the DOE Office of Basic Energy Sciences. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. Dept. of Energy under Contract DE-AC04-94AL85000.

4:45 PM Z2.9

A STUDY OF LOCALIZED CORROSION IN Al RESULTING FROM THE CONTROLLED INTRODUCTION OF Cl.

Craig Johnson, Doug Wall, Charles Barbour, Kevin Zavadi, Michael Martinez, Sandia National Laboratories, Albuquerque, NM.

High purity Al samples were implanted with 35 keV Cl⁺ then polarized in both Cl⁻-containing and Cl⁻-free electrolytes in order to ascertain corrosion behavior as a function of Cl content. Implant fluences between 5x10¹⁵ and 2x10¹⁶ Cl⁺ cm⁻² resulted in little or no localized attack. Implant fluences of 3x10¹⁶ and 5x10¹⁶ Cl⁺ cm⁻² resulted in significant attack in a Cl⁻-free electrolyte with the severity scaling as a function of implant fluence. The low variability in the behavior of localized corrosion for the 5x10¹⁶ Cl⁺ cm⁻² sample suggests that this implant dosage results in a critical Cl⁻ in the oxide for pit nucleation. The passive current density (*i_{pass}*) decreased with increasing implant fluence. A space-charge effect is proposed to account for this phenomena, although effects from defect interactions and possible oxide thickening are still under consideration. This work is supported by the DOE Office of Basic Energy Sciences, Division of Materials Science. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the DOE under contract DE-AC04-94AL85000.

SESSION Z3: POSTER SESSION INVESTIGATION OF ELECTRODEPOSITION & CORROSION

Chair: Reginald M. Penner
Thursday Evening, April 24, 2003
8:00 PM
Salon 1-7 (Marriott)

Z3.1

PERFORMANCE ASSESSMENT OF ELECTRODEPOSITED EPOXY FILMS. Agustin Santana Lopez and Julia Mirza-Rosca, Las Palmas de Gran Canaria Univ, Dept of Processes Engineering, Tafira SPAIN; Mihai V. Popa, Paula Drob, Ecaterina Vasilescu, Cora Vasilescu, Inst of Physical Chemistry, Dept of Electrochemistry and Corrosion, Bucharest, ROMANIA; Silviu-Iulian Drob, Univ of Bucharest, Dept of Chemistry, Bucharest, ROMANIA.

The paper presents the experimental results concerning the performance assessment of electrodeposited epoxy films using electrochemical techniques (electrochemical impedance spectroscopy - EIS and anodic polarization) assisted by microscopical studies. The films were formed during the cathodic and anodic electrodeposition of the modified epoxy resins (cationic - modified with secondary amine and anionic - modified with carboxylate groups) on carbon steel substrate. After curing and stabilization the experimental specimens were tested in a normal aerated 3% NaCl solution at the ambient temperature for a total period up to 5000 hours. Analysis of the impedance spectra (Nyquist and Bode diagrams) has established an equivalent electric circuit with two time constants fitted to model the electrodeposited epoxy film/carbon steel/electrolyte system. One time constant describes the electrical and barrier properties of the epoxy film (film capacitance and resistance) and the other time constant the electrochemical reactions at the film/metal interface (double layer capacitance and charge transfer resistance). The time monitoring of the principal elements from the equivalent electric circuit were used to determine the water and ions permeability of the electrodeposited epoxy films and the active area of the metallic surface under films. The films porosity and efficiency were calculated from the dissolution current densities of the carbon steel substrate. It results a high performance of electrodeposited epoxy films, characterised by uniformity, insignificant porosity, very low water uptake and few conductive pathways. The electrodeposited epoxy films present a good adhesion to the metallic substrate; microscopical studies shown that no degradation or delamination process during the exposure period

takes place. The electrodeposition technique type has an influence on the protective properties of the epoxy films; the cathodic electrodeposited films exhibit the lower values of the water uptake and the area of the conductive pathways.

Z3.2

SURFACE ANALYSIS OF THE ENVIRONMENTAL CORROSION OF ZINALCO (Zn-22Al-2Cu) ALLOY. Roberto Guerrero-Penalva, Instituto Tecnológico de Tijuana, Centro de Graduados e Investigación, Tijuana, BC, México; M.H. Farias, L. Cota-Araiza, Centro de Ciencias de la Materia Condensada, UNAM, Ensenada, BC, México.

The surface of a set of zinalco (Zn-22Al-2Cu) samples was prepared by mechanical polishing (MP) and by electropolishing (EP). Samples were subjected to environmental corrosion during 56 days and studied by x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Differences in relative atomic concentration ratio of Al/Zn in oxides of the surface layer were obtained and they are related to the bulk microstructure. A different corrosion behavior is observed between MP and EP samples and it is explained in terms of the surface composition and morphology. The initial growth of corrosion products was observed in EP samples and a corrosion model is proposed. The surface of both types of samples can be modified by low-energy argon ion bombardment.

Z3.3

CORRELATION BETWEEN THE SUSCEPTIBILITY TO BREAKDOWN AND SURFACE PROPERTIES OF THIN FILMS ON TITANIUM ALLOYS IN PHYSIOLOGICAL FLUIDS. Agustin Santana Lopez, Julia Mirza-Rosca, Las Palmas de Gran Canaria Univ, Dept of Processes Engineering, Tafira, SPAIN; Ioana Demetrescu, Daniela Ionescu, Politehnica Univ, Dept of General Chemistry, Bucharest, ROMANIA; Mihai V. Popa, Ecaterina Vasilescu, Paula Drob, Cora Vasilescu, Institute of Physical Chemistry, Dept of Electrochemistry and Corrosion, Bucharest, ROMANIA.

Correlation between the susceptibility to breakdown and surface properties of thin films on the implant titanium alloys Ti-5Al-4V and Ti-6Al-4Fe in Ringer 1 and Ringer 2 solutions of different pHs (7.82, 6.98, 4.35, 2.5) which simulate the conditions that can appear at the long term (18 months - 13,000 hours) contact between implant and tissues were studied in this paper. The stability and reactivity of the alloy surface films were evaluated from cyclic potentiodynamic and potentiostatic polarization, from variations of the free corrosion potentials in time and electrochemical impedance spectroscopy (EIS). Cyclic voltammograms of titanium and Ti-5Al-4V and Ti-6Al-4Fe alloys, obtained after various exposure periods, show that, their passive films are very stable up to +1.8V; Ti-6Al-4Fe alloy presents pitting attack at a pitting initiation potential of +3.5V in Ringer 1 solution and at +3.9V in Ringer 2 solution. The hysteresis current loop indicates that the pitting cease, protection potential is about +1.75V in both solutions; this is a very noble potential. The variations of the corrosion potential of titanium and its implant alloys for 13,000 exposure hours pointed out that the most electronegative values were obtained at pH=4.35; so, the passive films are most active at this pH value. The computing of the regression equations permits the prognosis of the potential evolution for longer time than 13,000 hours. The results of the statistical treatment support idea that, after a certain period of time, depending of the alloy, the potential trend is the same, trying to reach a stable state. In human body, can arise the local acidification due to the hydrolysis of the corrosion products or in the distress periods of the body. So, there is the possibility that the active-passive macro-cells to be settled down along the metallic surface as a result of the electrolyte non-uniformity; these macro-cells are described by potential gradients. The simulate conditions in this work show that the highest potential gradient can appear for titanium and the most reduced potential gradient presents Ti-6Al-4Fe alloy. However, these potential gradients have very low values, which can not produce any form of local corrosion, in all simulating extreme conditions. Impedance spectra (obtained by EIS) illustrate a pure capacitive behaviour, which denotes high corrosion resistance. These data were modeled with one time constant equivalent electrical circuit, typically for a compact oxide film, for all materials, in all tested solutions. The fitting parameters indicate a long term stability of the passive layers.

Z3.4

THE EFFECT OF Ag ADDITION ON THE CORROSION OF Zn-22%Al ALLOYS. M. Flores and J.A. Luna, DIP-CUCEI, Universidad de Guadalajara, Zapopan Jal., MEXICO; S.R. Casolco, L. Huerta, S. Muhl and G. Torres-Villaseor, Instituto de Investigaciones en Materiales, UNAM, MEXICO D.F., MEXICO.

A new Zn-Al-Ag alloy (ZINAG) with superplastic deformation characteristics has been developed. Four compositions Zn - 22 Al

eutectic doped with 1-4 % Ag were prepared from the melt within a graphite crucible in an electric furnace and subsequently a quenched in ice water. These ingots were warmed and rolled at 360°C. The superplasticity behavior can be explained as a consequence of the fined grain distribution induced during the deformation process. The corrosion resistance of these alloys was studied by means of potentiodynamic polarization and measurements of the evolution in the time of the potential, in a 0.5 M NaCl solution. The corrosion products in the sample surface were analyzed by Rutherford Backscattering and Auger Electron Spectroscopy and the elements dissolved in the electrolyte by Atomic Emission Spectroscopy. The corroded surface was observed by SEM and was found to contain cracks. It was found that the alloy with the higher concentration of Ag has the best corrosion resistance in the electrolyte used, but no clear tendency with the Ag concentration was observed.

Z3.5
PASSIVE LAYER BREAKDOWN ON TITANIUM IN DOPED AND UNDOPED ARTIFICIAL SALIVA. Ioana Demetrescu, Belarisa Popescu, Daniela Ionescu, Politehnica Univ, Dept of General Chemistry, Bucharest, ROMANIA; Mihai V. Popa, Ecaterina Vasilescu, Paula Drob, Cora Vasilescu, Inst of Physical Chemistry, Dept of Electrochemistry and Corrosion, Bucharest, ROMANIA.

The aim of this work is to investigate the long term (3000 exposure hours) tendency of passive layers on titanium to breakdown in Tani-Zucchi and Carter-Brugirard artificial saliva undoped and doped with chloride and fluoride ions. The non-uniformity of the saliva pH (from 7.88 to 5.73 and extreme case 2.15) was simulated. The following techniques were used: atomic force microscopy (AFM), potentiostatic, potentiodynamic and linear polarization, the open circuit potential monitoring vs. exposure time and ion release determinations. All data were statistical treated. From anodic polarization curves were determined the breakdown (pitting) potential and the protection potential in Tani-Zucchi saliva. The pitting potential is very noble at about +2.9V and the protection potential also is very electropositive +2.4V. The difference between open circuit potential and pitting potential is very large (about 2V); so, the tendency of titanium to pitting is very small. The difference between the pitting potential and the protection potential (hysteresis current loop) is very small (about 0.5V) attesting the high pit re-passivation tendency. But the most important fact is that the pitting re-passivation potential is very noble of +2.4V. This potential can not be reach in human body. Monitoring of the open circuit potentials with time (3000 exposure hours) and pH of Carter-Brugirard saliva have shown some fluctuations; these slight oscillation have kept for the period of 3000 hours. The statistical treatment using the regression procedure permitted to obtain the scatted diagrams expressed by a regression equation; when this equation have a convenient determination coefficient (>0.7) it is possible to make some prognosis concerning the value of the open circuit potential for longer term than the experimental one. Taking into account than the oral cavity is very complex and unexpected phenomenon could take place any time, in our experiments were simulated the conditions of local acidification of the Carter-Brugirard saliva. The non-uniformity of the pH can generate potential gradients. So, were obtained three potential gradients and their variation in time. The simulated gradients have very low values and can not generate local corrosion till present (3000 exposure hours). Ion release determinations revealed that the fluoride and chloride ions increase the concentration of titanium ions released in doped Tani-Zucchi artificial saliva. Atomic force microscopy (AFM) performed the surface analysis and average roughness. These characteristics were evaluated for each specimen, after periodically times and were correlated with specific parameters of the corrosion as a measure of the susceptibility to local corrosion.

Z3.6
PHOTOINDUCED CORROSION IN MICROELECTRONIC DEVICES CONTAINING DISSIMILAR METALS. Chuck Belisle, Jagdish Prasad, Mike Molino, Mike Engle, AMI Semiconductor, Pocatello, ID.

Various metals with different galvanic potentials are used to fabricate the microelectronic circuits. One of the most commonly used process during integrated circuit manufacturing is the tungsten via fill. To obtain maximum interconnect density with low via resistance requires that metal - via overlap be essentially zero. Zero overlap with litho variations and thus misalignment may result in unlanded vias. Since the vias are used to connect various metal levels, a large number of these cases may occur causing device failures and thus the yield loss. To study this problem a variety of test structures were studied and a new mechanism of corrosion was found. The tungsten corrosion observed in these structures was found to be photo-induced. In this paper we will discuss the mechanism of photoinduced galvanic corrosion that occurs between the aluminum and tungsten metal layers during microelectronic manufacturing.

Z3.7
AN INVESTIGATION OF THE EFFECTS PASSIVITY ON Cu CHEMICAL MECHANICAL POLISHING (CMP). Parshuram Zantye, University of South Florida, Department of Mechanical Engineering and Center for Microelectronics Research, Tampa, FL; Arun Sikder, University of South Florida, Center for Microelectronics Research, Tampa, FL; Nivedita Gulati, Department of Mechanical Engineering and Center for Microelectronics Research, Tampa, FL; and Ashok Kumar, Department of Mechanical Engineering and Center for Microelectronics Research, Tampa, FL.

The constant push towards sub-micron miniaturization of device dimensions, increased density of devices, and faster processing power has led to the development of new interconnect technologies that use copper and ultra low-K ($K < 2.2$) polymer based dielectrics. The incorporation of Copper as a replacement for previously used conducting interconnect material, Aluminum, has further reduced the resistance of the metal interconnects and improved the performance of the ICs. As controlled etching of Cu to form the interconnect pattern is a not a worthwhile task, CMP has emerged as the method of choice for global planarization of dielectric and metal films. With the introduction of Cu every wafer is estimated to undergo 15 or more CMP steps before the final device is ready. Thus, there needs to be a better understanding of various phenomena that occur during CMP to improve and optimize this process that would positively affect 30% or more of the 157 billion dollar semiconductor industry. CMP is a tribochemical process which involves simultaneous interaction between the slurry, the semiconductor wafer and the polishing pad. The combination of the mechanical (wear and abrasion) and chemical (surface reaction and corrosion) phenomena contributes to the material removal during the CMP process. In case of patterned Cu wafer, in order to achieve a uniform global planarization of the surface morphology, control over the surface passivation is critical during polishing. This research investigates the various effects of surface passivity in not only the wear accelerated corrosion process but also on the surface mechanical removal rate. This is done with the help of different electrochemical (potentiodynamic) measurements and various surface characterization techniques like AFM, SEM, XPS and Auger spectroscopy. Furthermore the study tries to understand the wear-corrosion synergism to in order to exercise better control on the process by manipulating either one or both of these phenomena. The ultimate objective of this research is to gain a perspective on the microscopic interactions at the surface of Cu metallized wafer.

Z3.8
Transferred to Z2.8

Z3.9
A TECHNIQUE FOR THE NON-INVASIVE IN-SITU STUDY OF CORROSION PROCESSES WITHIN EMBEDDED STEEL STRUCTURES. Peter Haycock, Liam Norcup, Keele Univ, Keele, School of Chemistry and Physics, Keele, Staffordshire, UNITED KINGDOM; Steve Hoon, Manchester Metropolitan Univ, Dept of Environmental and Geographical Sciences, Manchester, UNITED KINGDOM.

Corrosion often occurs where it is difficult to monitor the integrity of the corroded structure. In many cases this is because the structure is completely encased inside another material, for example the steel reinforcing cords inside vehicle tyres or the steel bars within reinforced concrete. Indirect means can be used to evaluate the possibility of corrosion having occurred, or destructive sampling can be undertaken. The former route does not lead to a definitive assessment of the state of corrosion and the latter affects the state of the corroded material such that it cannot be considered truly representative of the in-situ condition. The difficulty in obtaining a true evaluation of the corrosion of buried structures not only makes the reliable non-destructive assessment of their integrity impossible, but also means that direct study of the in-situ corrosion mechanism cannot readily be undertaken. The corrosion products of steel are well known and the results of controlled experiments under various atmospheric conditions are documented. However, the interconversion pathways for these products are complex and depend critically on the exact environment of the steel. The initial state of the interface between steel reinforcing rods and the surrounding concrete is fairly well understood. However, at the onset of corrosion the nature of the interface changes and the chemical environment of the corroding steel is modified by the corrosion process itself. We have developed a non-invasive electromagnetic technique which allows direct detection of the presence of corrosion. A combination of different electromagnetic probes allows identification of the corrosion products present as the process progresses. Hence it is possible by this means both to determine the integrity of a buried structure and also to carry out direct in-situ studies of the corrosion process. Here we present results of a study on reinforced concrete subjected to controlled accelerated ageing.

Z3.10

STUDY ON CORROSION OF UNEARTHED BRONZE RELICS IN SHANG DYNASTY, CHINA. Chen Zhangru, Wen Zhijian, Fan Guang, Liu Yuemiao, Environment Protection Research Center, Beijing Research Institute of Uranium Geology, Beijing, CHINA.

The disposal concept for high level radioactive waste involves isolating the waste from biosphere by a series of engineered and nature barriers. Natural barrier is geological formation in which repository is located. Engineered barrier is composed of vitrified waste, canister and buffer/backfill material. The canister not only provides physical protection for vitrified waste, but also prevents contact between these waste and groundwater. Assessment of the applicability of metal as candidate materials of canister for HLW repository system has been conducted in some countries. Study on the geological disposal of high level radioactive waste has been commenced since 1985 in China. Up to now, site characterization of HLW repository is being conducted in Beishan area, Gansu province, west-northern China. Many bronze relics in Shang Dynasty, China, dated from more than 3500 years ago, have been preserved perfectly. The study on corrosion of bronze relics would contribute to the material selection and design of canister for HLW repository system in China. Samples of unearthened bronze relics collected at Xingan and Wuhan site where are situated in sub-tropic zone with humidity have been chosen for anthropogenic analogue study. Microprobe analyses of bronze relic samples studied show that components of bronze matrix mainly consist of Cu (around 83% and 70%), Sn (around 14.5% and 14%) and Pb (around 1% and 10%) with minor Ag. Composition in corrosion layers of bronze relics greatly varies due to undertake oxidation and migration for copper. Structure of bronze alloy is a cast. Stereo-microscopic studies reveal that malachite, cerussite, cuprite and stannolite can be observed in corrosion layers of bronze samples. Three corrosion sub-layers on the surface of bronze can be described under the mineralogical microscope. The sub-layer next to the bronze matrix is a red oxide sub-layer; then from the inner side to outside one may find a green carbonate sub-layer and a yellow oxide sub-layer in surface. The red oxide sub-layer consists of cuprite (Cu₂O) and tenorite (CuO); green carbonate sub-layer consists of malachite (Cu₂(CO₃)(OH)₂) and cerussite (PbCO₃); yellow oxide sub-layer consists of stannolite (SnO₂). The thickness of corrosion layer of bronze relic studied is about 250-400 μm. The International Atomic Energy Agency (IAEA) and China National Nuclear Corporation (CNNC) are funding the research.

Z3.11

A NEW MECHANISM FOR BRIGHTENING DURING ELECTRODEPOSITION. Daniel Josell, Sam Coriell, Geoffrey McPadden, Thomas Moffat, Walter Schwarzacher and Daniel Wheeler.

This talk presents quantitative analysis detailing how an adsorbed deposition rate enhancing catalyst affects the evolution of surface roughness during metal deposition. Two analyses are presented. A first order perturbation analysis accounts for the impact of accumulation of catalyst from the electrolyte, consumption of the catalyst through incorporation, and changing surface area on the evolution of local coverage of the adsorbed catalyst. Stabilization of the surface is found to be strongly sensitive to the catalyst concentration in the electrolyte, with stabilization under optimum conditions predicted for wavelengths exceeding the 150 micrometer diffusional boundary layer thickness. The second analysis is numerical in nature and accounts for the impact of area change alone to model when catalyst is preadsorbed on the deposit surface prior to metal deposition with no additional accumulation or consumption of catalyst during metal deposition itself. Brightening for these experimental conditions is predicted to occur through formation of extremely small, but finite, amplitude oscillatory perturbations in the steady state. Experimental results are shown to support both predicted mechanisms. The impact of area change on catalyst coverage makes this new mechanism for brightening fundamentally different from traditional leveling models based on spatial gradients in rate-suppressing additives.

Z3.12

PHENOMENON OF ELECTROCHEMICAL DEPOSITION OF METALS VIA A SUPERCOOLED METAL LIQUID. Oleg B. Girin, Ukrainian State University of Chemical Engineering, Department of Materials Science, Dnipropetrovsk, UKRAINE.

An earlier unknown phenomenon of electrochemical deposition of metals via a supercooled metal liquid has been found using new in situ methods. The phenomenon resides in the fact that while a metal is electrodeposited on a solid cathode in an aqueous solution, a supercooled metal liquid is being formed and solidified at the deposition temperature, producing a crystalline or amorphous structure. It is caused by an extremely rapid (explosive) character of metal precipitation due to a chain reaction of electrochemical formation of atoms and a transition of the atom associates from a liquid state to a more stable solid state. The phenomenon is confirmed

by the existence in the electrodeposited metals of metastable structures corresponding to: an amorphous structure of the solidified metal liquid, highly defective crystalline structure of the metal quenched from its liquid state, and intermediate crystalline modifications arising during the superfast cooling of the liquid phase of the polymorphous metal. It is proved by the availability of metallic links at the electrodeposited metal/cathode interface, and by the formation of primary solid solutions and intermediate phases resulting from the electrodeposition of metals alloyed by metals and non-metals. This phenomenon manifests itself in the predictable changes of the macrostructure, microstructure, substructure, structural condition, crystallographic texture, surface morphology, structural inhomogeneity and defects of the crystalline structure of metals with an increase in the supercooling rate while they are being electrodeposited. Guidelines for practical utilization of the found phenomenon are proposed for the development of technologies of producing electrochemical coatings with advanced properties.

SESSION Z4: ELECTRODEPOSITION OF METALS

Chair: Peter C. Searson
Friday Morning, April 25, 2003
Salon 4 (Marriott)

8:30 AM *Z4.1

THE MECHANISM OF SUPERCONFORMAL ELECTRODEPOSITION OF SILVER FOR INTERCONNECT METALLIZATIONS. Daniel Josell, Thomas Moffat, Daniel Wheeler and Brett Baker, Metallurgy Division, National Institute of Standards and Technology, Gaithersburg, MD.

This talk presents experiments and modeling of superconformal electrodeposition of silver in fine trenches and vias. The electrolytes yielding superconformal silver deposition, also called "superfill", contain a catalyst but no inhibitor or leveler and are fully disclosed. Experimental results are compared to predictive simulations of feature filling from models based on the CEAC mechanism. Agreement is seen to be excellent, with the experimentally observed fill or failure to fill of a given feature in a given electrolyte as well as the experimentally observed incubation period of conformal growth, the bottom-up filling characteristic of "superfill", and the formation of an overfill bump all predicted; this is particularly impressive because the CEAC mechanism has no fitting parameters. The CEAC mechanism is based on conservation of adsorbed metal-deposition rate enhancing catalyst during surface area change; i.e., the local coverage changes with the surface area on which it is adsorbed by simple mass conservation. The CEAC mechanism leads to increasing catalyst coverage, and thus local deposition rate, on concave surfaces such as the bottoms of fine features (hence the name of the mechanism). A significant strength of the CEAC mechanism is that its applicability to all geometries means that all kinetics required for modeling of feature filling can be obtained from experiments on planar substrates. Specifically, these include the kinetics for adsorption of the catalyst from the electrolyte, the impact of adsorbed catalyst on the interface kinetics affecting the metal deposition rate, and the role of diffusional transport on metal deposition rate. The talk will describe how kinetic parameters for the superconformal silver feature fill modeling were obtained from cyclic current-voltage studies (cyclic voltammetry) as well as current-time transient (chronoamperometry) of silver electrodeposition on planar substrates. Note that, while aluminum alloy metallizations are being replaced by copper in integrated circuits due to the lower resistivity of the latter metal, surface scattering effects are becoming quite significant as dimensions move beyond the 130 nm node. Silver metallizations, with their intrinsically lower resistivity (bulk value slightly lower than copper), and potentially lower surface scattering properties are being considered by many as the next metallization of choice. However, the high aspect ratio, dual damascene geometries now used with copper metallizations are possible only because of coppers ability to fill features superconformally during electrodeposition in particular electrolytes. The superconformal filling of fine features with silver and quantitative prediction of the filling results with kinetics from independent studies on planar substrates presented here thus overcome perhaps the most substantial hurdle toward industrial use of silver metallizations.

9:00 AM *Z4.2

REAL TIME IN-SITU STRESS MEASUREMENTS DURING THE ELECTRODEPOSITION OF BISMUTH THIN FILMS. Donglei Fan, Qing Zhu, Ingrid Shao, P.C. Searson, C.L. Chien, and R.C. Cammarata, Johns Hopkins University, Baltimore, MD.

Bismuth, a semi-metal with very long electronic mean free path and large magnetoresistance, is a promising material for future spintronic devices. In order for bismuth to be utilized in this manner, it is necessary to fabricate it in the form of a single crystal thin film. Electrochemical deposition followed by annealing has yielded single crystal bismuth films on various substrates, with different orientations

depending on the substrate and the deposition and annealing conditions. In order to investigate and characterize the growth process, highly sensitive real time in-situ stress measurements have been conducted. The stress was measured using a substrate curvature apparatus and showed that the bismuth films were generally deposited in a state of compressive stress, with the magnitude of this stress increasing with increasing deposition rate. This behavior will be discussed in terms of current models for thin film stress evolution. In addition, the influence of the thin film stress state on post-deposition annealing in order to achieve single crystal material will be presented.

9:30 AM Z4.3

STRESS EVOLUTION DURING ELECTRODEPOSITION OF Ni THIN FILMS. Sean J. Hearne, Jerry Floro, Todd Christenson, Graham Yelton, Chris Dyck, Dean Dibble^a, and James Kelly^a, Sandia National Laboratories, Albuquerque NM, ^aSandia National Laboratories, Livermore, CA.

The stress evolution during electrodeposition of Ni films on bare and patterned gold substrates has been investigated as a function of bath chemistry and deposition conditions to examine the microstructural origins of intrinsic stress. We observed striking similarities between the stress evolution during electrodeposition of Ni and that of vacuum deposited metals such as Ag, Cu, and Au. Specifically, both systems display a rapid tensile stress rise during the island nucleation / coalescence / planarization phase of growth. This phase is followed by rapid decrease in tensile stress that often results in net compression. We will discuss the similarities in the stress behavior and the possible common mechanisms for stress generation. In order to better quantify the tensile stress arising from island coalescence, patterned substrates were used to geometrically and temporally constrain nucleation and coalescence of Ni islands during electroplating. By avoiding the complications associated with stochastic island nucleation we can better compare experimental results with existing theories for stress generation during coalescence. This work is partially supported by the DOE Office of Basic Energy Sciences. Sandia is a multiprogram laboratory of the United States Department of Energy operated by Sandia Corporation, a Lockheed Martin Company, under contract DE-AC04-94AL85000.

9:45 AM Z4.4

IN-SITU SCANNING PROBE MICROSCOPY OF THE EFFECTS OF ADDITIVES ON ELECTRODEPOSITED NICKEL.

Dean C. Dibble, James J. Kelly, Sandia National Laboratories, Livermore CA.

The physical properties of electrodeposited nickel and nickel alloys used for functional coatings and electroformed micromachine parts can be controlled over a wide range by addition of various additives to a base plating bath. Additives for control of stress, texture, nanostructure, tribological, magnetic, and other properties are known but are frequently empirically developed. In-situ scanning probe microscopy enables the direct observation of the effects of additives at nanometer length scales to help elucidate their mechanism of action. Using in-situ STM and AFM, we have studied the nucleation, coalescence and growth of nickel films to a thickness of 200 nm on well-ordered Au(111) terraces. Our measurements of the size, shape, density, preferred nucleation sites, and morphological evolution of the electrodeposited nickel grains produced while under potentiostatic control in dilute Watts and nickel sulfamate electrolytes are described as a function of the additives saccharin, coumarin, manganese and other materials known to control stress, texture and nanostructure. Our observations are compared with those of other groups and with the bulk properties of materials produced from plating baths containing the additives used in this study. This work is supported by the U.S. Department of Energy under contract number DE-AC-04-94-AL8500.

10:00 AM Z4.5

EVOLVING SURFACE ROUGHNESS DURING ELECTRODEPOSITION WITH AND WITHOUT ADDITIVES.

Mikko Haataja, and David J. Srolovitz, Princeton Materials Institute and Dept. of Mechanical & Aerospace Eng., Princeton University, Princeton, NJ; Andrew B. Bocarsly, Dept. of Chemistry, Princeton University, Princeton, NJ.

The surfaces of electrodeposited metals grown from baths without additives are typically rough, while the addition of appropriately chosen additives can suppress this roughening. This roughening phenomena is associated with an interfacial stability that is similar to the Mullins-Sekerka instability. We first examine how this roughening depends on bath composition and growth rates. Next, we propose a mechanism by which additives can reduce or suppress this instability. We present a stability map which shows the experimental conditions under which instabilities can be suppressed by the additives. Finally, we demonstrate that these predictions are consistent with experimental observations.

10:30 AM *Z4.6

METAL NANOWIRES BY ELECTRODEPOSITION. Reginald M. Penner, Erich Walter, Benjamin Murray, Dept. of Chemistry, University of California, Irvine, CA; Gisela Kaltenpoth, Michael Grunze, Department of Physical Chemistry, Univ. of Heidelberg, GERMANY; Fred Favier, CNRS Montpellier, FRANCE.

A general method is described for the electrodeposition of long (> 500 μm), nanowires composed of noble or coinage metals including nickel, copper, silver, and gold. Nanowires of these metals, with diameters in the range from 60 nm to 750 nm, were obtained by Electrochemical Step Edge Decoration (ESED); the selective electrodeposition of metal at step edges. Nanowire growth by ESED was accomplished on highly oriented pyrolytic graphite surfaces by applying three voltage pulses in succession: An oxidizing "activation" pulse, a large amplitude, reducing "nucleation" pulse, and a small amplitude reducing "growth" pulse. The activation pulse potential was optimized to oxidize step edges on the graphite surface just prior to deposition. The nucleation pulse had an overpotential for metal deposition of between -200 and -500 mV and a duration of 5-10 ms. The growth pulse had a small deposition overpotential of less than -100 mV. Nanowire growth was characterized by a time-independent deposition current and consequently, the nanowire radius was proportional to the square root of the deposition time in accordance with the expected growth law. We also describe a method for preparing long (> 100 μm) bimetallic nanowires that are compositionally modulated along the axis of the nanowire. Essentially, the new method described here involves "wiring" together particles of one metal using nanowires of a second. This is accomplished by combining two new electrodeposition methods that we have recently described: "Slow growth" for preparing metal nanoparticles that are narrowly dispersed in diameter, and nanowire growth. Using this approach, beaded bimetallic nanowires that are up to a millimeter in length can be prepared in parallel arrays on a graphite surface. These wires can then be transferred onto a second, insulating surface (e.g., glass) using a method we have previously described.

11:00 AM Z4.7

Abstract Withdrawn.

11:00 AM Z4.8

ELECTROCHEMICAL CHARACTERIZATION OF BIMETALLIC Ni-Ti SURFACES GENERATED BY ION IMPLANTATION.

Minh Tan Pham, M.F. Maitz, H. Reuther, A. Muecklich, F. Prokert, E. Richter, Forschungszentrum Rossendorf e.V., Institute of Ion Beam Physics and Materials Research, Dresden, GERMANY.

Ni presents an electroactive material employed in many electrochemical technologies - batteries, catalysts, electrochromic and sensor devices [1,2]. As electrocatalyst material the Ni-Ti alloy has been shown to be more advantageous than pure Ni. So far only one composition Ni-Ti (55:44) provided by a bulk alloying process has been studied [3]. There is a great interest in optimising the material surface properties and studying the effect of the matrix titanium. In the present work bimetallic surface layers of Ni and Ti were generated by implanting Ni ions into a Ti substrate surface. Surface Ni-Ti compositions confined to thicknesses below 100 nm were prepared of surface Ni content ranging from 60 down to 1 at%. The material was characterized by XRD, TEM, and XPS. Electrochemical properties in 0.1 N NaOH were studied using cyclic voltammetry and potentiodynamic polarization. The electrocatalytic activity was examined by the anodic oxidation of glucose. For comparison the Ni-Ti (55.9:44.08) alloy was included in the study. The electrochemical characterization revealed Ni to be electroactive on all surface compositions. The electrochemical conversion of Ni (II) to Ni(III) occurred more efficiently on ion beam generated surfaces than on the reference alloy. The Faradaic efficiency of the redox reactions Ni(II) \rightarrow Ni(III) depended on the surface Ni concentration. The oxidation of glucose was enhanced, and its oxidation potential shifted more anodically with reduced surface Ni content. The corrosion resistance in NaOH was improved as the surface concentration of Ti increased. The results were interpreted associating with surface characteristics generated by ion bombardment. The material was shown to consist of Ni and Ni oxide embedded within a Ti oxide matrix with a depth dependent distribution of Ni, Ti, and O over a thickness of 60 - 80 nm. The Ni containing phase was amorphous.

11:15 AM Z4.9

MULTISCALE SIMULATION OF FILM THICKNESS DISTRIBUTION IN COPPER ELECTROCHEMICAL DEPOSITION PROCESSES. Gwang-Soo Kim and Klavs F. Jensen, Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA.

Different factors influencing electrodeposition of copper in small features (~100 nm) on patterned wafers are analyzed using a

multiscale simulation tool. The major factors include the terminal effect along with mass transport and pattern density effects. The terminal effect creates a highly nonuniform growth rate distribution at the early stage of the deposition especially when the seed layer is thin, and this nonuniformity decreases as the seed layer grows. Mass transport variations stemming from nonuniform boundary layer thickness created by uneven flow distribution in the electrochemical cell have a strong influence on growth rates of the copper film, and the effects persist even after long periods of deposition time. Ideally, the electrochemical cell should be designed to produce even boundary layer thickness distribution, but when the reactor chamber cannot be altered other ways to improve the uniformity must be implemented. Different options to enhance mass transport in the electrochemical cell are suggested and validated with the multiscale simulations. Finally, an uneven pattern density on the wafer creates growth rate variation across the wafer, and its effect changes as features grow and effective surface area changes over time. In order to mitigate the pattern density effect, the multiscale simulation tool is used to identify the operating conditions that result in even growth rate distribution. The multiscale simulation tool serves to identify main causes of the film growth rate uniformity and to suggest geometry and operating changes to improve process performances.

11:30 AM Z4.10

PB ELECTRODEPOSITION ON Cu: AN IN-SITU OBLIQUE-INCIDENCE REFLECTIVITY DIFFERENCE STUDY.
Jeremy Gray, University of California-Davis, Dept of Physics, Davis, CA; Walther Schwarzacher, H.H. Wills Physics Laboratory, Dept of Physics, Bristol, UNITED KINGDOM; Xiangdong Zhu, University of California-Davis, Dept of Physics, Davis, CA.

The growth of submonolayer, monolayer, and multilayer Pb films electrodeposited on Cu(100) during cyclic voltammetry (CV) and pulsed deposition has been investigated in-situ by oblique-incidence reflectivity difference (OI-RD). We show that the OI-RD signal is proportional to Pb coverage for the up of one monolayer. We then show that subsequent overpotential growth, resulting in multilayer Pb films, can proceed in two distinctly different modes. The two growth modes are a function of the applied potential and, during CV scans, the potential ramping rate. Most likely, at higher overpotentials and/or scan rates, the growth proceeds in a three dimensional process, while at lower potentials and/or scan rates, a progressive two dimensional nucleation and growth process dominates. By observing the OI-RD behavior and subsequently controlling the applied potential, we were able to control the growth mode in-situ.