SYMPOSIUM Z
Mechanisms in Electrochemical Deposition and Corrosion
April 24 – 25, 2003

Chairs

J. Charles Barbour
Sandia Natl Laboratories
MS 1415
Albuquerque, NM 87185-1415
505-844-5517

Peter C. Searson
Dept of MS&E
Johns Hopkins Univ
102 Maryland Hall
Baltimore, MD 21218-2689
410-516-8774

Reginald M. Penner
Department of Chemistry
Univ of California-Irvine
Irvine, CA 92697-2025
949-824-8572

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*Invited paper
SESSION 21: ELECTROCHEMICAL DEPOSITION AND DISSOLUTION
Chair: Reginald M. Penner
Thursday, Morning, April 3, 2003
Salon 4 (Mirriot)

8:30 AM #21.1
ELECTROCHEMICAL SYNTHESIS OF MOLYBDENUM OXIDE THIN FILMS: DEPOSITION MECHANISM AND TEMPLATE-DIRECTED ASSEMBLY OF NANOSTRUCTURED MATERIALS AND COMPONENTS. Keith J Steverson, Todd M McEvoy, Hugo Ocio, 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 catalysis, batteries and electrochromics. In this paper we describe the deposition of molybdenum oxide thin films prepared from aqueous solutions containing peroxo complexes of molybdenum(VI). Electrochemical, microscopic and spectroscopic (EQCM) studies along with supporting spectroelectrochemical experiments have allowed us to elucidate the electrodeposition mechanism. Analysis of EQCM data, 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 gradual reduction of several peroxo components, primarily comprising molybdate anion and di- and tetra-peroxo-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 molybdate anions.

9:00 AM #21.2
SELF-INDUCED VOLTAGE OSCILLATIONS AND DIAMETER MODULATION DURING PORE FORMATION IN Si AND InP. M. Christophersen$^{*,*}$, S. Langer$^a$, J. Christensen$^b$, P.M. Frauchel$^c$.

High pore densities in n-In$_x$P$_{1-x}$ 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 to silicon and In$_x$V (complexes under investigation), which 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 (> 250 mA/cm$^2$ for the free silicon surface, 4 eV% HF in DBMO). The experimental high voltage oscillations as well as the simulated 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 In$_x$P$_{1-x}$ 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 structures 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 In$_x$P$_{1-x}$. The present report will discuss in detail the etching conditions leading to synchronization of pores in In$_x$P$_{1-x}$, In$_x$P$_{1-x}$ 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. Foss, S. Langer, J. Christensen, M. Christophersen, I. Tsigianis, K. Dietzel, Pore Etching in Compound Semiconductors for the Production of Photonic Crystals, L64, MRS Proceedings Vol. 722, 2002.

10:30 AM Z0.1.5
TIN OXIDE THIN FILMS: ELECTRONIC PROPERTIES AND FUNDAMENTAL MECHANISMS UNDER ELECTROCHEMICAL CONTROL FOR GAS SENSING STUDIES. Ray Ding, Issam Dessier-Perez, Pau Gorostiza, Francisco Sainz, University of Barcelona, LTCETM 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$_2$ nanoparticle containing metal catalytic centers that enhances the gas sensitivity of the material [R. Ding et al., Sens. Actuators, B 2008]. 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 metal surface [J. Arbizu et al., Sens. Actuators, B 2008]. 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 Sn(100) single crystals. Following the study of iron oxide films under electrochemical control [I. Dessier-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 relationship 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-STMs 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 Z0.1.4
CORROSION OF NANOCRYSTALLINE TUNGSTEN FILMS USED IN SILICON-BASED MICROSYSTEMS. Kevin R. Zawadl and Paul G. Kotulin, Sandia National Laboratories, Albuquerque, NM.

Tungsten is a particularly attractive materialization 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 neutral pH. These issues raise concerns 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 humidified and atmospheric environments using a combination of electrochemical, surface spectroscopic, electron microscropic and electrochemical scanning probe techniques. The atmospherically formed oxide on W is a mixture of W(IV) and W(VI) oxides. Conduction of or immersion in $H_2O$ promotes conversion to the hydrated 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. Long-term exposure to $H_2O$ results in full penetration of the W layer and dissolution of the underlying Si. Corrosion of the pristine film 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 mechanisms for these films. This work was supported by Sandia Corporation, a Lockheed Martin Company, for the U.S. Department of Energy under contract DE-AC04-94AL85000.
limited by a thin (≈ 1nm), reaction product layer that forms on the surface of the DLC. We conclude that pitting corrosion of hard disks in self-assembly due to the presence of the lower than expected 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 Z1.0
THE EFFECT OF ADDITIVES ON TEXTURE FORMATION AND TWINNING IN Ni ELECTRODEPOSITS FOR MICROSYSTEMS AND CIRCUITS. R. Merkle, C. Bodmer, M. D. LeClair, J. J. Foss, and D. L. Smedley, 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 profound growth of low-energy twin interfaces in electrodeposited Ni films. Using X-ray diffraction (XRD), electron backscatter X-ray techniques (EBSPs), and transmission electron microscopy (TEM), we have examined the effect of texture on the surface morphology and orientation of nanometer-scale twins in Ni films with different grain-refining additives. Our results indicate that while inhibiting grain growth during plating, disperse 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-ascorbate, and Ni-Mn exhibited fiber textures of [100], [100] + [111], and [111] + [110], respectively, and consisted of coarse columnar grains. TEM and analysis indicated that the grains in Ni-Sulfamate and Ni-ascorbate generally 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 different orientations have a mobility influence on 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-ascorbate. [Lithography, Galvanosynthesis (LIGA). This work is sponsored 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. Gayer, W. J. Batteglini, S. J. 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. Further, the 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 variable exists in terms of the governing equations for transport of substances, such as mass and heat. The complexity is due to the nonlinear non-linear field equation is offset by the elimination of the interface boundary conditions that both impose a phase field on the system, limiting the current behavior. 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 analogs between electrochemical and solidification interfaces. Dendrites can form in both systems. The electrolyte potential is analogous to solidification undercoolings, such as diffusional (constitutional), curvature, and interface attachment. Despite these similarities, there is sharp concentration, electrochemical potential, and phase stability on a more complicated interface structure that 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 electrolytic kinetics, such as the exchange current. We will discuss the influence of the chosen phase field evolution equation on the observed current-voltage behavior.

11:15 AM Z1.8
ON THE FORMATION OF ANODIC NIOBIUM OXIDE IN POTASSIUM NITRATE MOLT L. S. Skarzewski, P.C. "Argo" Ltd., Physical Department, Beer Sheva, Israel; V. Gomosnov, 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 (AOX) phase structure showed that the generated film look like sandwich of Nb₂O₅ and NbO₂ and Nb₃N phases (in the direction from oxide surface toward ibium). X-ray photometry made in Kα-radiation of chromium anode permitted to identify the oxide film outer layer as the low-temperature α- modification of Nb₂O₅ 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 by niobium (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 near-constant-adjacent layers and diminishes towards the 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 0% potassium reference. These findings permit to assume the generation of potassium solid solution in niobium oxide during AOX crystallization.

SESSION 22: CORROSION
Chair: J. Charles Barbour
Thursday Afternoon, April 24, 2018
Salle 4 [Marriott]

1:30 PM 22.2.1 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 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 "designed" alloys based on our knowledge of the important factors affecting alloy corrosion behavior.

2:00 PM 22.2.2 DEVELOPMENTS IN CORROSION AND STRESS CORROSION OF SOLID SOLUTION ALLOYS. Roger C. Newman, Benjamin Lynch, Jane Deskin 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 nonporous solids are being explored. These alloys are such a good model system that similar processes in engineering alloys have been modeled neglected recently. In the 1990s, L. Geslins showed 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 overgeneralized, but two key test cases, investigated by our group, have now revealed surprisingly classical de-alloying behavior. These are 1) disordered stainless steel in strong, hot caustic solutions, and 2) Ni-Cu alloys (Medals and copper-nickel) 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 nonporous 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 50Ni-50Fe) 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 nonporous structure.

2:30 PM 22.3 UNDERSTANDING THE FUNDAMENTALS OF ATMOSPHERIC CORROSION THROUGH THE DEVELOPMENT OF A HOLISTIC MODEL. Ivan C. A. Scott Smith, Scott Furness, Troy Hughes, Corrosion Science and Engineering, Deakin, CERROGO Manufacturing and Infrastructure Engineering, Melbourne, AUSTRALIA.

A holistic model of atmospheric corrosion has been constructed which models the processes controlling atmospheric corrosion from the micro (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 or the model is divided into small subvolumes (volumes) that are assumed to be chemically homogeneous. All macroscopic events (diffusion, chemical reactions, charge transfer) and their rates (diffusion rates and chemical rates) are converted to stochastic processes. Then, when 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. Even if the model is locked to atomic scale, how the role of redox reactions in inducing a charge imbalance and further generation of potential distributions and charge diffusion. How does the establishment of potential gradients or geometric features between the anode and the 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 22.4 MODELLING 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 atmospheric conditions of corrosion. This extension allows open circuit conditions to be modeled, as well as galvanic galvanic couples to be considered. Kinetics have been added for metallic clad and bare AA2024-T3, including the calculations based on chloride concentration. The model has been applied to studies of the parameters that control the throwing power of metallic cladding (e.g. scratch size, $C^{+}$, $i_{b}$, $i_{c}$). Two geometries were investigated a pseudo 1-D model and a square sample with a cross section 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 case base of electrochemical behavior studied, a loss of protection ability was observed between 0.5 and 2.5 mm. The metallic cladding modeling also allowed the discovery of the equivalence of reducing the $i_{c}$ of the clad or increasing the $i_{b}$ of the AA2024-T3 on the size of the scratch that can be protected. A semiquantitative relation was found between these parameters and the scratch size that can be protected. An order of magnitude reduction in $i_{b}$ (or increase in $i_{c}$) led to a decrease by 60% of the scratch size that was protected. Two competing effects of increasing the chlorides 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 22.5 INITIAL OXIDATION KINETICS OF COPPER (110) FILM INVESTIGATED BY IN SITU UHV-TEM. Guangzhou 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 corrosion reaction, i.e., oxidation, 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 at the macroscale, but the theories do not address the nanoscale 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 on the kinetics of initial stages of Cu(110) and Cu(111) 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 oxide nucleation and growth islands under highly enhanced oxidation rate on Cu(110) surface as compared to Cu(111). 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 as 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 22.6 STRUCTURAL STUDIES OF THE INITIAL STAGES OF COPPER SULFIDE FILM GROWTH: INFLUENCE OF HUMIDITY. M.J. Capien, J.G. Zhu, New Mexico State Univ, Dept. of Physics, Las Cruces, NM J.C. Barbier, J.W. Brighthouse, 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 electrical and electronic devices. This study was performed due to the possibility of multiple sulfide phases and complex corrosion product formation. In this study, we have used focused ion beam (FIB) cross-sectioning, transmission electron microscopy (TEM), high-resolution transmission electron microscopy, and X-ray diffraction ion (XRD), and ion beam scattering to characterize the product formed when thin films of Cu are exposed to a dilute (50-200 ppm) H2S atmosphere at low (0.5%) to high (80%) relative humidity (RH). An important early observation from the CuS grown for long times is significantly higher for sulfides formed 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 formed at low and high RH. Studies were performed to determine whether structural differences in the sulfides could give rise to enhanced structural differences that could be correlated to enhanced structural differences. It was found that for both low and high RH sulfidation, Cu is the dominant diffuser and reacts with S to form the low chloride phase CuS by s-electron and x-electron diffraction. Cross-section and plan-view TEM revealed that the Cu2S grains formed at high RH are 20-50 nm in size, whereas the grains formed at low RH are 70-150 nm and appear to undergo grain growth as the CuS 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 22.7 THE IMPACT OF ANNEALING ON THE CORROSION MECHANISM OF COPPER FILMS. Didem Ernar, Laureen Carbonell, Denis Shmyrny, Karen Moe, IMEC, Leuven, Belgium.

Integration of copper dianisocyanate 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 chemistry, and the barrier metal have been found to play important roles in 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 annealing 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. Description of the precipitates during annealing monitored by Transmission Electron Microscopy (TEM) revealed that samples exposed to an organic acid-based solution had a rough surface indicating severe corrosion whereas, the ones dipped into the organic acid-based solution showed smoothness.

4:30 PM 22.8 IN SITU STUDY OF SOLUTION CHEMISTRY DURING LOCALIZED CORROSION IN AI ALLOY 2024-T3. R.G. Copeland, N.L. Mass, Sandia National Laboratories, Albuquerque, NM. G. Buchheit, Y. Kim, The Ohio State University, Columbus, OH.

Localized corrosion in Al alloys has been investigated for many years using diverse experimental approaches. Using a technique defined during earlier corrosion studies with engineered thin film models, 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 fluorescent tracer ion to the aqueous 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 deliquescence of Sphalerite (Zn-Cu) particles and the particles 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 proceeds. Post exposure samples using SEM, EDS and AFM provides an extended description of the localized corrosion process in these materials. This work is partially supported by DOE, 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.

**SESSION IV: CORROSION & ELECTRODEPOSITION**

**Z3.1 PERFORMANCE ASSESSMENT OF ELECTRODEPOSITED EPOXY FILMS**

Chair: Reginald M. Penner

Thursday Evening, April 24, 2008

8:00 PM Salon 1-7 (Merriot)

**Z3.2 SURFACE ANALYSIS OF THE ENVIRONMENTAL CORROSION OF ZINALCO (Zn-2Al-2Cu) ALLOY**

Roberto Guerrer-Penalva, Instituto Tecnológico de Tijuana, Centro de Graduados e Investigación, Tijuana, BC, México; M.H. Parra, L. Coronel, Centro de Ciencias de la Materia Condensada, UNAM, Ensenada, BC, México.

The surface of a set of zinalco (Zn-2Al-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 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**

Agustín Santamaría-Lopez, Julio Mirza-Rosca, Las Palmas de Gran Canaria Univ, Dept of Processes Engineering, Tafira, SPAIN; Iván Redondo, Paula Drob, Emanuela Vasilescu, Corina Vaiaescu, Inst of Physical Chemistry, Dept of Electrochemistry and Corrosion, Bucharest, ROMANIA; Silvia-Julian Drob, Univ of Bucharest, Dept of Chemistry, 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 (7.85, 6.08, 4.35, 2.5) which simulate the conditions of the experiments described previously can be assessed 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 potential 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 +1.85 V. Ti-6Al-4Fe alloy is pitting attack at a pitting initiation potential of 4.35 V in Ringer 1 solution and at +3.9 V in Ringer 2 solution. The hysteresis current loop indicates that the pitting cease, protection potential is about +4.3 V. 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 electron-negative variation of corrosion potential obtained at pH 7.85, the most active at this pH value. The computing of the regression equations permit the prognosis of the potential evolution for longer time than 13,000 hours. The results of the statistical treatment support the 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 hydration of the corrosion products or in the distress periods of the body. So, there is the possibility that the active-passive microcells to be settled down along the metallic surface as a result of the electrolyte non-uniformity; these micro-cells are described by potential gradients. The simultaneous 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 simulated extreme conditions. Impedance spectra (obtained by EIS) illustrate a pure capacitive behaviour, which decreases with time exposure. 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-20%Al ALLOYS**

M. Flores and J.A. Lima, DIP-CUCHE, Universidad de Guadalajara, Zapopan JAL, Mexico; S.R. Casado, L. Huerta, S. Müh and G. Torres-Vilaescer, 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 quenched in ice water. The ingots were warmed to 300°C, in the superplasticity behavior can be explained as a consequence of the finest grain distribution induced during the deformation process. The corrosion resistance of these alloys was studied by means of potentiodynamic polarization and measurements of the evolutions 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 surface region 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.

23.5 PASSIVE LAYER BREAKDOWN ON TITANIUM IN DOPED AND UNDOPED ARTIFICIAL SALIVA. Ioana Demetrescu, Belenca Popescu, Daniela Ionescu, Politehnica Univ, Dept of General Chemistry, Bucharest, ROMANIA; Miha V. Popa, Emilian Constantinescu, Bucharest, Romania; Ioana Dobre, Corp. Vantulce, Inst of Physical Chemistry, Dept of Electrochemistry and Corrosion, Bucharest, ROMANIA.

The aim of this work is to investigate the long term (30000 exposure hours) tendency of passive layers on titanium to breakdown in Tani-Zucchi and Carter-Brugiarid artificial saliva undoped and doped with chloride and fluoride ions. The non-uniformity of the saliva pH (from 7.88 to 5.23 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 determination technique were statistical tested. From cyclic polarization curves were determined the breakdown (pitting) potential and the protection potential in Tani-Zucchi saliva. The pitting potential is very noble at about +2.9 V and the protection potential also is very electropositive +2.4 V. The difference between open circuit potential and pitting potential is very large (about 2.4 V); 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 electropositive (+0.5 V) at the beginning of the treatment. But the most important feature is the pitting repassivation potential is very noble of +2.4 V. This potential can not be reach in human body. Monitoring of the open circuit potentials with time (30000 exposure hours) and pH of Carter-Brugiarid saliva have shown some fluctuations; these slight oscillation have kept for the period of 30000 hours. The statistical treatment using the regression procedure permitted to obtain the scattord diagrams expressed by a regression equation; when this equation have a conventional determination coefficient (r 0.7) it is possible to make some prognos concerning the value of the open circuit potential for longer term than the experimental one. Taking into account that the oral cavity is very complex and unexpected phenomenon can take place any time, in our experiments were simulated the conditions of local acidification of the Carter-Brugiarid saliva. The non-uniformity of the pH can generate potential gradients. So, three potential gradient profiles of their various combinations were simulated. The surface potential gradients have low values and can not generate local corrosion till present (30000 exposure hours). Ion release determinations revealed that the fluoride and chloride ions increase the concentration of titanium ions released inrafibular 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.

23.6 PHOTINDUCED CORROSION IN MICROELECTRONIC DEVICES CONTAINING DISSIMILAR METALS. Chuck Belisle, Jagdish Prasad, Mike Molino, Mike English, 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 resistance requires that metal - via overlap be essentially zero. Zero overlap with litho variations and thus misalignment may result in unplugged vias. Since the vias are used to connect various metal levels, a large number of these criss cross many different devices 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 this mechanism of photoinduced galvanic corrosion that occurs between the aluminum and tungsten metal layers during microelectronic manufacturing.

23.7 AN INVESTIGATION OF THE EFFECTS PASSIVITY ON Cu CHEMICAL MECHANICAL POLISHING (CMP). Pushanman Zantye, University of South Florida, Department of Mechanical and Engineering Center for Microelectronics Research, Tampa, FL; Arun Skider,r Florida State University, Department of 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 interconnect technology, which use copper and ultra low-K (K<2.9) 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 I/Os. As controlled etching of Cu to form the interconnect pattern is 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 tribochromatic 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 layer is required during polishing. This research investigates the various effects of surface passivity in not only the usual 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 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 metallicized wafer.

23.8 TRANSFERRED TO Z3.8

23.9 A TECHNIQUE FOR THE NONINVASIVE IN-SITU STUDY OF CORROSION PROCESSES WITHIN EMBEDDED STEEL STRUCTURES. Peter Haycock, Liam Norcup, Keele Univ, School of Chemistry and Physics, Keele, Staffordshire, UNITED KINGDOM; Steve Houn, 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 embedded structure. If a structure dies from this metallurgical structure is completely ensnared inside another material, e.g. the steel reinforcing rods 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 insitu condition. The difficulty in obtaining a true evaluation of the corrosion to 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 intervention pathways for these products are complex and depend critically on the external environment of the steel. An initial step of how the 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 products. 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 in the process progress of the corrosion. Here it is possible by using 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 weathering.
STUDY ON CORROSION OF UNEARTHED BRONZE RELICS IN SHANG DYNASTY, CHINA. Chen Zhangru, Wen Zhijian, Fan Guang. Liu Yuanming, Environmental 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 & geological formation in which repository is located. Engineered barrier is composed of vitrified waste, canister and buffer/containment. The canister may provide primary protection for vitrified waste, but also prevents contact between these waste and groundwater. Assessment of the applicability of metal as candidate materials for canister for HLW repository system has been conducted in many institutions. Study on the geological disposal of high level radioactive waste has been commenced in 1985 in China. Up to now, site characterization of HLW repository is being conducted in Beidaihe area, Guansu province, west-northern China. Many bronze relics in the region date back to more than 3000 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 unearthed bronze relics collected at Xingang and Wuhua site where are situated in sub-tropic zone with humidity have been chosen for archaeological study. Microprobe analyses of bronze relic samples showed that components of bronze matrix mainly consist of Cu (around 85%) and Pb (around 15%). Sn (around 14.5% and 14%) and Zn (around 1% and 1%) 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. X-ray spectroscopic studies reveal that malachite, cerussite, cuprite and smithsonite 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 surface next to the bronze matrix is a red oxide sub-layer, then from the inner side to outside one can 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)OH2) and cerussite (PbCO3); yellow oxide sub-layer consists of smithsonite (SnO2). The thickness of corrosion layer of bronze relic studied is about 254-400 µm. The International Atomic Energy Agency (IAEA) and China National Nuclear Corporation (CNNC) are funding the research.

A NEW MECHANISM FOR BRIGHTENING DURING ELECTRODEPOSITION. Daniel Josell, Sam Correll, Geoffrey McFadden, Thomas Moeller, Walter Schrinner, 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 film onto the top 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 decreasing 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 along the catalyst layer when catalyst is adsorbed. The results are obtained with no additional accumulation or consumption of catalyst during metal deposition itself. For these experiments, the impacts of the area change along the catalyst layer are predicted to occur through brightening 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 along the catalyst layer makes this new mechanism for brightening fundamentally different from traditional leveling models based on spatial gradients in rate-suppressing additives.

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 a nesous 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 metal which transforms 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. The liquid, highly defective structure of the metal quenched from its liquid state, and intermediate crystalline modifications arising during the superfast cooling of the liquid phase of the polymorphic metal. It is proved by the availability of metallic links in the electrodeposited metal/electrode 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 microstructure, surface structure, structural inhomogeneity and defects of the crystalline structure of metals with an increase in the supercooling rate. 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 4: ELECTRODEPOSITION OF METALS
Chair: Peter C. Searsan
Friday Morning, April 25, 2013
Salon 4 (Marriott)

8:30 AM #24.1 THE MECHANISM OF SUPERCONFORMAL ELECTRODEPOSITION OF SILVER FOR INTERCONNECT METALLIZATIONS. Daniel Josell, Thomas Moeller, Daniel Wheeler, and Britt Baker. Metalurgy 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 electrolyte yielding superconformal silver deposition, also called “superfill”, contain a catalyst but no inhibitor or leveller and are fully disclosed. Essential results are compared with the behavior of features 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 conduction of adsorbed metal-deposition rate to the 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 diffusion-limiting transport on metal deposition rate. The talk will describe how kinetic parameters of the superconformal silver feature fill modeling were obtained from cyclic current-voltage studies (cyclic voltammetry) as well as current-time transient (chronuamperometry) of silver electrodeposition on planar surfaces. 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 metallization are eminently possible because of copper's ability to fill features superconformally during electrodeposition in particular electrolytes. The superconformal filling of fine features with silver metal is predicted to match recent 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 #24.2 REAL TIME IN-SITU STRESS MEASUREMENTS DURING THE ELECTRODEPOSITION OF BISMUTH THIN FILMS. Donglei Fan, Qing Zhu, Ingrid S. Xiao, P.C. Searsan, C.L. Chen, and H.C. Pecht. 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 films were generally deposited in a state of compressive stress, with the magnitude of this stress increasing with 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  24.3
STRESS EVOLUTION DURING ELECTRODEPOSITION OF Ni THIN FILMS

The stress evolution during electrodeposition of Ni films on bare and patterned gold substrates has been investigated as a function of both chemistry and deposition conditions to examine the microstructural origins of intrinsic stress. We observed 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 initial nucleation / coalescence / phanomorphization 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 at the island nucleation and coalescence of Ni islands during electroplating, by avoiding the complications associated with stochastic island nucleation we can better comprehend the corresponding results 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  24.4
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. We measured the morphological features of the size, shape, density, preference of nucleation sites, and the time evolution of the electrodeposited nickel grains produced while under potential control in dilute Watts and nickel sulfamate electrolytes are described as a function of the additives succhinic, oxamintic, 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-AC04-94AL85000.

10:00 AM  24.5
EVALUATING SURFACE ROUGHNESS DURING ELECTRODEPOSITION WITH AND WITHOUT ADDITIVES.

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 phenomenon is associated with an interfacial instability that is similar to the Marangoni flow. Specifically, we study how this roughening depends on both 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 instability can be suppressed by the additives. Finally, we demonstrate that these predictions are consistent with experimental observations.

10:30 AM  24.6
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 Fowler, 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 with these metals having 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 to dry by ESED was accomplished on highly oriented pyrolytic graphite surfaces by applying two voltage pulses in succession: an oxidizing ‘activation’ pulse, a large amplitude, reducing ‘nucleation’ pulse, and a small amplitude reducing ‘growth’ pulse. The activation pulse provides energy to nucleate 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 3-10 ms. The growth pulse had a small deposition overpotential of less than -100 mV. Nanowire growth was characterized by 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 the application of two voltage pulses that sequentially create parallel arrays of step edges 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  24.7
Abstract Withdrawn.

11:00 AM  24.8
ELECTROCHEMICAL CHARACTERIZATION OF BI-METALLIC Ni-Ti SURFACES GENERATED BY ION IMPLANTATION.
Mina Tan Pham, M.F. Mahtz, H. Reuther, A. Muecklich, F. Prokert, 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, fuel cells, electrochromic and sensor devices [1,2]. As an 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 need for understanding the influence of alloy composition on surface properties and studying the effect of the matrix titanium. In the present work bulk metallic surface layers of Ni and Ti were generated by implanting Ni ions into a Ti substrate surface. The 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 potential dynamic 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) → Ni(III) and Ni(III) → Ni(II) depend on the surface Ni composition. The oxidation of glucose was enhanced, and its oxidation potential shifted more anaerobically 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  24.9
MULTISCALE SIMULATION OF FILM THICKNESS DISTRIBUTION IN COPPER ELECTROCHEMICAL DEPOSITION PROCESSES.
Gwang-Soo Kim and Kiwae J. 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 causes 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-INCIDENT REFLECTIVITY DIFFERENCE STUDY,
Jeremy Gray, University of California-Davis, Dept of Physics, Davis, CA; Walter Schwarzenberger, H.H. Wills Physics Laboratory, Dept of Physics, Bristol, UNITED KINGDOM; Xingfeng 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 pulse deposition has been investigated in-situ by oblique-incidence reflectivity difference (OIR-D). We show that the OIR-D signal is proportional to Pb coverage for the upd 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 OIR-D behavior and subsequently controlling the applied potential, we were able to control the growth mode in-situ.