SYMPOSIUM M
Surface Science and Thin-Film Growth in Electrolytes
November 26 - 28, 2001

Chairs
Dieter M. Kolb
Dept of Electrochemistry
Ulm Univ
Ulm, D-89069 GERMANY
49-731-502-5400

Benjamin M. Ocko
Dept of Physics
Brookhaven National Laboratory
Room 1-15
Upton, NY 11973-5000
631-344-4299

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

Karl Sieradzki
Mechanical & Aerospace Engineering
Arizona State Univ
Tempe, AZ 85287-6106
480-965-8990

Symposium Support
Air Force Office of Scientific Research

*Invited paper
SESSION M1: OVERLAY GROWTH, SURFACE MORPHOLOGY AND NANOSTRUCTURING

Chandra Karmakar, Karl Sieradzki and Peter C. Schwerin
Monday, November 26, 2001
Room 313 (Hynes)

9:00 AM M1.1 MECHANISTIC ASPECTS IN METAL FILM GROWTH: COMPLIANT MATERIALS BEYOND SIMPLE SYSTEMS R. Jürgen Behm, Universität Ulm, Abteilung Oberflächenchemie und Korrosion, Ulm, GERMANY.

The mechanistic understanding of thin film growth processes has considerably improved over the last years and reached a standard where they can be successfully modelled as a sequence of elementary steps. This is true at least for simple systems, where i) the substrate can be considered as a perfect template, ii) strongly adsorbed condensates or monomers play no significant role and iii) growth is largely controlled by kinetic effects such as nucleation and 2D growth phenomena, i.e., the system is sufficiently far from equilibrium. In this talk I will focus on complications which arise when these conditions are not fulfilled. This will include nucleation and growth on “instantaneous” surfaces, where growth competes with exchange processes and surface alloy formation. In such systems growth is not only affected by nucleation and growth on surface heterogeneities, i.e., foreign atoms exchanged into the surface layer, under certain conditions metal deposition also causes a severe restructuring of the substrate, leading to pit formation. Examples for such systems are found for metal growth under ultraviolet excimer laser ablation as well as for metal deposition in electrolytes. Mechanistic ideas will be presented and discussed. Second, the effect of adsorbed species on nucleation and growth processes is discussed. In particular, which are generally present in electrodeposition, e.g., as adsorbed species, but frequently exist also in film growth under UHV conditions, e.g., in the case of chemical vapor deposition (CVD), affect not only the nucleation behavior, but may lead also to the formation of new film structures. Also in this case common aspects will be emphasized.

9:30 AM M1.2 UNDEPOTENTIAL DEPOSITION ON ALLOYS. C. McColl, N. Dimitrov, Karl Sieradzki, Arizona State University, Tempe, AZ.

We present the first results for the underpotential deposition (UPD) of a metal on a metal alloy substrate. This type of surface science provides key insights into the nature of specific chemical interactions between the adsorbate and one of the constituents in the alloy, and is useful in varied problems such as catalysis and alloy corrosion. The system chosen for the investigation was Au_{x}Ag_{1-x}/Cu^{+} where p was varied between zero and one. Copper is known to underpotentially deposit on elemental Ag but not on Ag. The Cu UPD charge density decreased with increasing atom fraction of Ag in the alloy to p equal to 0.29, and for p less than 0.26 no UPD was observed. The potential peak of the UPD stripping wave was also found to depend on p much in the same way as the UPD charge density. Our results are interpreted within a mean-field model based on mean charge state, which does remarkably well in explaining the observed behavior.

9:45 AM M1.3 COPPER ELECTRODEPOSITION ON THE (100) SURFACES OF Ag AND Au. B.M. Osco and M. Weinert, Department of Physics, Brookhaven National Laboratory, Upton, NY, R.L. Rander and D.M. Kolb, University of Ulm, Ulm, GERMANY, M. Pfeifer, I.K. Robinson, Department of Physics, Univ. of Illinois, Urbana, IL.

The structure and behavior of electrodeposited monolayers and thin films have been investigated using surface x-ray scattering techniques under ultrasonic electrochemical conditions. The bulk electrodeposition of copper on Au(100) proceeds in several stages. Whereas the first ten copper layers are pseudomorphic with the Au(100) surface, additional deposition leads to a highly modulated copper structure. The initial pseudomorphic structure (no in-plane reflections) is surprising since the bulk copper lattice constant is 12% smaller than that of the underlying gold. The strained copper unit cell for these thin layers is tetragonal, 2 atoms per unit cell, and is very close to the bulk unit cell. The epitaxial arrangement with the substrate stabilizes this structure despite the additional energy of 38 meV per copper atom. Additional copper deposition leads to additional in-plane reflections characteristic of a one dimensional modulated phase [see below of step and island dynamics on Au(111) and Au(100)]. The x-ray measurements conclusively show that the entire copper film structures and that the resulting strain field propagates into the underlying gold lattice. The transformation that occurs with thickness is similar to the temperature dependent martensitic transition observed in some bcc metals. Similar results were also obtained on the Ag(100) surface for films grown electrochemically and under vacuum deposition conditions. However, under vacuum conditions there appears to be a doubling of the unit cell and this can not be explained by the existing structural model.


During the last decade much effort has been spent to study atomic processes on metal surfaces in UHV using sophisticated theoretical and experimental methods (for an overview see [1]). It is, however, only recently that corresponding studies at the solid/liquid interface have been reported. The renascence of theories and experimentalists to perform quantitative studies at the solid/liquid interface is partly due to the complexity of the interface and due to experimental restrictions. None the less, one may use temperature variable electronic STM [2, 3] to study step and island dynamics on metal electrodes and obtain important energy parameters (as kink and step energies) and pre-exponential factors for surface diffusion. In this talk, recent results on surface diffusion in electrolyte are presented. The talk focus also on the comparison between the solid/liquid and the solid/vacuum interface. Despite many amazing similarities between surface diffusion on surfaces in UHV and in electrolyte, there are some striking differences. Pre-exponential factors for surface diffusion seem to be considerably higher (~10^{15} Hz) at the solid/liquid interface [2, 3]. Furthermore, surface diffusion as well as step energies may be dramatically influenced by the electrode potential and by the specific adsorption of electrolyte anions [4-7]. As an example we present studies of adsorption effects of carbonates on Au(111) and Au(100) electrodes. By applying recently developed theoretical methods for solid states on metal surfaces in UHV we determine step and kink energetics on Au(100) in contact with a liquid [1].

11:00 AM M1.5 ELECTROCHEMICAL AND IN SITU STUDY OF SILVER DEPOSITION ON MODIFIED GOLD SURFACES. Maria Jose Espinash, Departamento de Fisicoquimica, Facultad de Ciencias Quimicas, Universidad Nacional de Cordoba, Cordoba, ARGENTINA.

Metal electrocrystallization on surfaces can be controlled by chemically modified gold electrodes. In this sense, Self-Assembled Monolayers (SAMs) on gold substrates have become one of the most attractive modified metal surfaces, since these organic compounds can form self-assembled monolayers on gold and can be functionalized according to desired purposes. Aim of the control
metal electrodeposition, the phenomena of underpotential deposition (UPD) and overpotential deposition (OPD) are significantly affected by the presence of the thiol layer. In order to have a thorough understanding of these complex processes, we first focused on the stability of the respective organic layer on Au(111) in absence of silver ions. This allowed us to establish the density of the thiol layer and the potential range within which metal deposition can be carried out without any thiol desorption process takes place. Silver deposition on such modified electrodes was subsequently monitored by STM at the potential range where normally the UPD and OPD occur in a SAM-free cell. At the same time, electrodeposition is affected by a variation of the thiol layer thickness and a variation of different thiol-end groups. It is our main motivation to elucidate the substrate/SAM deposited metal configuration, the metal nucleation and growth mechanisms, the differences with SAM-free electrodes and the specific reactivities of metalphile end groups exposed to the silver electrolyte.

11:30 AM M1.7
SI NANOPARTICLE ELECTROCHEMICAL PLATING.
G. Belomoin, A. Smith, S. Chaireb, and M.H. Nogee, Dept of Physics, and Theoretical and Applied Mechanics, Univ of Illinois at Urbana-Champaign; Taysir Nogee, Industrial Engineering, Cleveland State Univ.

We report on a procedure for deposition of ultrasmall ultrabright silicon nanoparticles from an aqueous alcohol colloid using electrochemical plating processes, analogous to metal plating. Unlike metal plating, Si particle plating occurs at the anode, and is self-limiting. Thin particle coatings can be made on metal and silicon substrates are demonstrated. Modulation of the conductivity of the substrate using oxide masking provides selective area depositions. The process is discussed in terms of the formation of complex metal ions with the silicon particles tigering along as "ligands".

11:45 AM M1.8
TIP INDUCED NANOSTRUCTURING OF Au-Cu ALLOYS WITH AN ELECTROCHEMICAL SCANNING TUNNELING MICROSCOPE. Stefan Mauget, Andrew S. Dukkouri, Martin Stratmann, Patrick Schmuki, Dept. of Material Science, LKO, University of Erlangen-Nuremberg, Erlangen, GERMANY.

By tip-induced metal deposition using an ECG-STM it is possible to generate small metal clusters on a metal surface in an electrochemical environment. This method has been applied with a variety of metals (Cu, Pt, Ag, Pd) on metallic substrates like Au and Ag. Clusters consist typically of 100-500 atoms and, at this size, show an unexpected electrochemical stability to anodic oxidation, i.e. for positive to the reversible Nernst potential the clusters do not show significant signs of dissolution. As existing theory fails to explain this effect, our experimental efforts targeted the elucidation of various parameters influencing cluster stability. A key aspect was to create Cu clusters on binary alloy surfaces instead of pure metal surfaces. Using Au/Cu single-crystals of different composition and crystallographic orientation as substrates, opened the possibility to vary the tip-substrate interaction and the influence of adatoms like the underpotential deposition layers. The experiments give clear evidence that the stability of the metal clusters is not intrinsic but mere an effect of interfacial alloying at the interface between cluster and substrate. Additionally underpotential deposition inhibits Cu surface diffusion and therefore also contributes to the stability of the clusters.

SESSION M2 EPITAXIAL GROWTH, GROWTH MECHANISMS

1:30 PM M2.1
Abstract Withdrawn.

2:00 PM M2.2
COMPOUND FORMATION USING ELECTROCHEMICAL ATOMIC LAYER EPITAXY. John S. Ulleke, Department of Chemistry, University of Georgia, Athens, GA.

The growth of compound semiconductors is being investigated using the electrochemical atomic layer epitaxy (ALE) technique. Initial studies have been on III-V compounds, such as CdTe, although they have recently been expanded to III-VI compounds such as InAs. Work is also progressing on the formation of superlattices; deposition is based on use of underpotential deposition (UPD), a phenomenon where atomic layers of one element can be formed on a second element at a potential under that needed to deposit it on itself. In this way, deposits can be formed essentially under equilibrium conditions. A significant fraction of the work here involves investigations of the surface chemistry of UPD, using UE-ELC techniques and infrared photoelectron spectroscopy. The surface is cleaned directly to a UVH surface analysis instrument, so that deposits can be characterized using LEED, Auger, and XPS, without exposure of the deposits to air. In situ STM is also used to follow surface structure as deposits are formed.

2:30 PM M2.3
INVESTIGATION OF COPPER ELECTRODEPOSITION ON RUTHENIUM METAL SURFACE. Taisonpalah Arunaqiri, Thomas Ponsenwanyi, Oliver Chyan, Univ. of North Texas, Dept. of Chemistry, Denton, TX.

In the sub-0.13 μm generation integrated circuit, the copper interconnects will be prepared by bottom-up Cu electroplating of damascene features, followed by a chemical mechanical polishing. Ruthenium has almost twice the electrical and thermal conductivities as copper and tantulium nitrides, i.e. diffusion barriers, are used as Cu interconnects. In this paper, we report the electrodeposition of Cu on Ru metal surface. The Cu nucleation was found to begin at ca. 0.01 V vs Ag/AgCl in 50 mM CuSO₄ /0.5 M H₂SO₄. The LSV curve showed a transport-limited growth peak at ca. -1.75 mV and hydrogen evolution onset occurred around -0.40 mV. The Cu nucleation and growth process was investigated using a current-transient electrochemical method and compared to SEM and AFM results. Preliminary results showed that the nucleation mode (progressive or instantaneous) was controlled by the applied overpotential. XRD patterns indicated heterogeneous growth of Cu on Ru with strong Cu(111) texture and no new phase or bimetallic compound formation between the two metals deposited on Ru substrate. Cu-Ru interface was investigated by XPS and Auger electron spectroscopy. The potential application of Ru to function as a Cu diffusion barrier will be discussed.

2:45 PM M2.4
MOTION AND CONVERSION ENERGIES OF AD-ATOM AND AD-ATOM CLUSTERS ON GOLD [001]. J. Tanaka, National Institute of Science and Technology Policy, Nagaoka, Chijodawsu, Tokyo, JAPAN; Y. Kogure and Masahiko Doiwa, Tokyo University of Science & Technology, Uenohara, Yamashita, JAPAN.

In the crystal growth from the gas phase, the motion and conversion of ad-atoms and their clusters are quite important phenomena. In this study, the energies required for the motion and conversion have been calculated using molecular dynamics and many body embedded atom potential. Gold (001) surface was chosen as an example. The crystal contains 1584 atoms and was surrounded by (100). The length in the [100] direction was 11 a, that in the [010] was 9a and that in [001] was 4a, where a is the lattice parameter. Ad atom or its clusters were set near the center of (001). 380 atoms near the ad-atom clusters (Region I) were relaxed 1000 time steps. The atom moved along a straight line was relaxed in [001] direction and the all atoms in Region I were relaxed three dimensionally. From the crystal energies mixed along different lines, an equi-potential lines were obtained. These calculations were performed for a ad-atom and tri-ad-atom. Tri-ad-atoms were classified according to the lengths of the bonds between ad-atoms and the bond of the angles. Activation energies of the motion of an ad-atom near [110] were calculated to be 0.33 eV. The activation energy for the motion of an ad-atom on (001) was calculated to be 0.41 eV. The activation energies for the conversion from Hx to Hx and from Hx to Hx were 0.43 eV and 0.16 eV, respectively.

3:30 PM M2.5
SURFACE DIFFUSION MECHANISM VS. ELECTRIC FIELD: Pt/Pt(001). Peter J Porschke, Surface and Interface Science Department, Sandia National Laboratories, Albuquerque, NM.

Identifying macroscopic variables that affect the rates and mechanisms by which surface atoms move should enhance our ability to control surface morphology. The search for new “knobs to turn” is at the root of the decades-long effort to modify thin-film growth by depositing agents purposely chosen “surfactant” species. It also motivates the work reported here, in which ab initio total energy calculations are used to understand how an externally imposed electric field should affect the mechanism and rate of adatom self-diffusion on Pt(111), a surface for which model Ion Microscopy experiments suggest that the energy process, concerted substitution, is supplanted by hopping when the external field is high enough. The result is that theory agrees with FIM that the barrier to concerted substitutional diffusion of a Pt adatom on Pt(001) varies linearly with external electric field, changing ~0.1 eV per V/A and increasing for fields oriented to push electrons into the surface. But, with a computed hopping barrier remaining >0.5 eV higher than that for substitution, the calculations contradict the intuitive change in FIM and variation of fields of 1.5 eV/A and temperatures ~265-284K can be attributed to the onset of hopping.
This work supported by the U.S. Department of Energy under Contract No. DE-AC04-94AL85000. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the U.S. DOE.

4:40 P.M. #M2.6
A THEORETICAL APPROACH TO THE STUDY OF METALLIC MONOLAYER AND SUBMONOLAYER FILMS. C. Sánchez, S. Damas, C. Giménez, M.G. Del Pájaro, M. Rojas, E.P.M. León, Universidad Nacional de Córdoba, Córdoba, ARGENTINA.

We discuss three types of approaches to model different aspects of metal monolayer and submonolayer deposition. These are:

- First principles calculations.
- Computer simulations employing suitable interatomic potentials.
- Lattice models.

We mention here some of the relevant results that we have obtained with these techniques. In the case of condensed matter calculations, as is the present case, the application of the principles of density functional theory allows obtaining reliable results for realistic model systems, involving metals that are of particular interest for electrochemistry. As an example, we present in this work results for systems containing Au, Pt, Pd, and Cu. By means of these calculations we get information concerning the electronic density changes, the work function \Phi and the energetics of the different systems. While this is a relevant quantity for the system since it is closely related to the potential of zero charge of these systems, the relative binding energies are related to the stability of adsorbed monolayers. Computer simulations with an important number of monolayers \textit{n}(t) will be also presented. In this case, semiempirical potentials are used in order to describe the many-body interaction between metallic atoms. The techniques employed are Monte Carlo and atom dynamics. While in the first case the information obtained is related to thermodynamic properties, in the second case dynamic information can also be gained. Then, the latter method is also employed to investigate the formation of nanostructures under different conditions. Finally, lattice models are employed to simulate the growth of 2D phases. While keeping the simplicity of lattice gas models, we introduce the many-body properties of the metallic binding to make the simulations realistic. Thus, several aspects of metal growth in heterogeneity can be analyzed both thermodynamically and dynamically on these bases.

4:30 P.M. #M2.7
STRAIN RELIEF MECHANISMS FOR OVERLAYERS ON RECTANGULAR SUBSTRATES: THE TWO-DIMENSIONAL FRENKEL-KONTOROVA MODEL. John C. Hamilton, Sandia National Laboratory, Livermore, CA.

The Frenkel-Kontorova model has been widely used in the last decade to explain overlayers phenomena including reconstructions, dislocation phenomena, and surface alloying on hexagonal surfaces. Here I discuss overlayers phenomena on rectangular surfaces using a similar model. Previous numerical studies of the limit of the Frenkel-Kontorova model for rectangular substrates implicitly assume that overlayers form in a rectangular orientation on the substrate, albeit with the possibility of rectangular dislocations. Experimental surface science has shown that this is often not the case. The Au\textit{100}, Pt\textit{100}, Ir\textit{100} and Ir\textit{100} surfaces reconstruct forming hexagonal top layers. Ag grown on Cu\textit{100} or Ni\textit{100} forms hexagonal layers. Cu on Ni\textit{100} grows pseudomorphic with dislocations with locally hexagonal substrates. In order to understand this behavior, we consider a model such phenomena, I consider the two-dimensional Frenkel-Kontorova model for a rectangular substrate allowing overlayers nuclei to adapt non-rectangular configurations. This model incorporates the major three competing factors involved in strain relief in rectangular systems. As in hexagonal systems, the strain energy associated with tensile or compressive film stress competes with the misfit energy associated with overlayers occupying non-favored surface sites. However, the energy due to varying coordination of the overlayers is in a square or hexagonal overlayers is a critical additional consideration. For model parameters, I present a phase diagram which has hexagonal as well as rectangular overlayers phases and exhibits the origins of the experimentally observed phenomena such as reconstructions, dislocations, and hexagonal overlayers on these surfaces.

4:45 P.M. #M2.8
A DELTA-FUNCTION MODEL OF FACETS AND ITS APPLICATION TO GRAIN-Boundary GROUING BY SURFACE DIFFUSION. Tinghui Xin, Harris Wong, Louisiana State University, Mechanical Engineering Dept., Baton Rouge, LA.

Facets appear often on crystalline solids, and need to be accurately modeled in studying surface evolution. A new model of facets is developed recently in which a facet is represented by the Dirac delta function. This model allows arbitrarily strong misorientation in surface energy, but avoids the ill-posedness in evolution problems commonly associated with strong misorientation. We incorporate this new model in a new approach to modeling grain-boundary grooving by surface diffusion. We consider partially to fully faceted surfaces with different facet orientations and 3, 4, and 6 fold symmetries in surface energy. We find that in all cases the groove profile grows with time following a similarity law. We will present the faceted groove profiles and discuss their implications.

SESSION M3: COPPER METALLIZATION
Chair: Reginnik M. Penner and Margret Giesen
Tuesday, November 27, 2001
Room 313 (Hyenas)

8:30 AM #M3.1
SUPERCONFORMAL ELECTRODEPOSITION IN SUBMICRON FEATURES. P.P. Mofii, D. Wheeler, W.H. Haber, D. Josell, National Institute of Standards and Technology, Gaithersburg, MD.

Superconformal electrodeposition is explained based on local growth velocity that increases with coverage of a catalytic species adsorbed on the copper-electrolyte interface. In particular, the addition of a catalyst precursor to the electrolyte, local coverage in finite features changes more due to interface area change than by accumulation from the electrolyte, yielding superconformal growth. The model is supported by experimental results of electrochemically deposited Cu in 350-100 nm wide features, helping to explain the influence of adsorbrates on roughness evolution.

9:00 AM #M3.2
Cu WETTING, NUCLEATION AND GROWTH IN UHV VS. ELECTROCHEMICAL ENVIRONMENTS: ANION EFFECTS ON INTERFACE FORMATION. N.P. Nguyen, Jinhong Tseng, Cheng Wang, Xinpeng Zhao and J.A. Kelber, Department of Chemistry, University of North Texas, Denton, TX.

Achieving conformal growth (5K) of Cu on various substrates is of technological urgency in microelectronics and other areas. Although such growth (wetting) can be readily achieved under UHV conditions, electrodeposition of conformal and thermally stable films without the use of a vacuum-deposited Cu seed layer is extremely difficult. We compare XPS and SEM studies between UHV and electrochemical (UHV-EC) deposition of Cu on reactive metal and modified metal surfaces. UHV-EC studies involve sample transfer between UHV and the electrochemical environment under controlled conditions, permitting detailed real-time analysis of surface properties with minimal atmospheric contamination. These studies reveal that anion incorporation occurs during the formation of the initial Cu nucleus on Ti but is not observed during subsequent growth of the Cu film. Since Cu(0) is observed at low Cu coverages, copper sulfation formation is not the reason for sulfide adsorption on the substrate surface. The oxidation of the Ti substrate during deposition conditions does not appear to be a factor in sulfide incorporation, since anion incorporation has been reported by other groups for Cu deposition on Pt substrates. The chemistry of the anion/substrate interaction and its implications to seedless Cu electrodeposition for ULSI applications will be discussed.

9:15 AM #M3.3
NUCLEATION AND GROWTH OF COPPER VIA CHEMICAL VAPOR DEPOSITION ON TiN, TaN AND SiO\textsubscript{2} SURFACES. Paul F. Ma, Todd W. Schroeder, J.R. Engstrom, Cornell Univ, Dept of Chemical Engineering, Ithaca, NY.

Electrochemical deposition of Cu for use in interconnect technology is always preceded by the deposition of a Cu seed layer via vapor phase methods. Formation of this seed layer can have a profound influence on the nature of the thin film deposited subsequently via electrochemical methods. Despite the fact that considerable research has been conducted on the vapor phase growth of Cu from the Cu(1) precursor, Cu\textsubscript{2}(hexafluoroacetyltrifluoromethane)[(trimethylvinylsilane), or Cu(1)[VMS], surprisingly little of this work has focused on the nucleation and growth of Cu in thin films composed of materials that are candidates for interconnect applications, e.g., TiN and TaN. Moreover, while surface diffusion plays an important role in thin film nucleation, there is essentially no experimental data concerning the diffusion of Cu on TiN and TaN. In the work to be reported here we have applied molecular beam techniques, and ex situ analysis employing atomic force microscopy and scanning electron microscopy to the study of the nucleation of Cu on TiN and TaN (and SiO\textsubscript{2}) surfaces. We find that
for the reaction conditions examined (substrate temperatures between 150 and 260°C) nucleation can be described by well-known kinetic models and it proceeds via “complete condensation”, where the nucleation density passes through a maximum \(N_{max}\), and where this maximum is substrate temperature dependent. The maximum density exhibits an Arrhenius temperature dependence, which we use to infer a surface diffusion coefficient \(D\) and Tanaka surface coverage \(\theta\). These results regarding the formation of seed layers, and their effect on the subsequently electrochemically deposited thin films, will be discussed briefly.

9:30 AM M3.4 
MULTISCALE SIMULATION OF HUMP FORMATION IN COPPER ELECTRODEPOSITION. Gong Seo Kim, MT, Department of Chemical Engineering, Cambridge, MA; Larry Godberg, Novellus Systems, Inc., San Jose, CA; Klaas F. Jensen, MT, Department of Chemical Engineering, Cambridge, MA; 
Copper electrodeposition in the presence of additives shows distinct thin film growth in the feature scale, so-called superfilling or bottom-up filling. More interestingly, it has been experimentally shown that a bump is formed if the film is allowed to grow after feature is completely filled. This bump can form on a single feature or over a multiple features. These phenomena are not observed in other types of thin film process and their understanding requires proper description of surface kinetics in the presence of additives as well as rigorous handling of mass transport both in reactor scale and feature scale. Especially, a self-consistent model of mass transport between reactor and feature scale is possible only with multiscale simulation scheme. We present a multiscale simulation tool that link reactor scale and feature scale and simulate the deposition phenomena in an unified manner. This simulation tool allows the simulation of hump formation under different operating conditions. Experimental data of feature evolution at different times are presented to support the simulation results. A parametric study is presented to illustrate under which conditions the bump can be eliminated.

9:45 AM M3.5 
MOLECULAR DYNAMICS SIMULATION OF Cu THIN FILM GROWTH ON β-Ta [200] SUBSTRATE. Youhong Li and James B. Adams, Arizona State Univ, Dept of Chemical and Materials Engineering, Tempe, AZ; 
Thallium is among the candidates to serve as both diffusion barrier and adhesion promoter for Cu metallization in future VLSI applications. Experimental study by others on Cu/Ta system showed that [200] textured β-Ta enhanced the formation of [111] texture in Cu film grown on it, which is beneficial for the improvement in electromigration resistance of the Cu films. In this work, we use molecular dynamics (MD) simulations to investigate Cu thin film growth on β-Ta surface with our Embedded Atom Method (EAM) copper-tantanium potential developed by the force-matching method. The initial growth mode and surface structure of Cu films on Ta are discussed.

10:30 AM M3.6 
ELECTROPLATED AG THIN FILM FOR ULSI INTERCONNECTION MATERIAL. Jeon-Ae Sung, SooKil Kim, Jea Jeong Kim, Seoul National Univ, School of Chemical Engineering, Seoul, KOREA; 
In ULSI interconnection, Ag is the only candidate next to Cu due to the lowest resistivity and high resistance against both oxidation and silicidation. Furthermore it was shown that self-sacrificing Ag films could generate diffusion barriers like Ti and Al. The characteristics of sub-micron electroplated Ag films for the application of ULSI metallization were investigated. Substrates were sputtered Ag (50 nm)/TiN (40 nm)/Si (p-type 100) wafers and pretreated by nitric acid cleaning solution to get clean and oxide-free AG seed surface. The electrolyte was cyanide-based solution without adding additional process and the current density was 200 mA/cm² for 30 minutes in nitrogen atmosphere. Linear sweep voltammetry indicated that Ag electroplating process window was above -0.144 V (vs. SCE). When applied dc potential was 0.81 V, the deposition rate of Ag was about 200 A/min and the resistivity of non-deposited 1.8 μm thick Ag film was 1.8 μΩ·cm, which were quite comparable to those of electroplated Cu films. Initial nucleation and grain growth of Ag were found to be dense and 3-dimensional from the AFM analysis and RMS value of roughness of the 870 nm thick film was 21 nm. Moreover the electroplated Ag films were found to have strong (111) texture from XRD analysis. AC impedance analysis revealed that double layer capacitance was well correlated with RMS roughness of non-deposited Cu seed film. This implies the possibility of using monitoring of RMS using AC impedance analysis. After the annealing process, the resistivity of electroplated silver films was reduced down to 1.67 μΩ·cm and no agglomeration was observed. Conclusively, it is expected that electroplated Ag films will have high potential as a next generation interconnection material to replace Cu.

10:45 AM M3.7 
AREA-SELECTIVE NUCLEATION OF COPPER ON PHOTO OXIDIZED POLYIMIDE SURFACE WITH SINGLE SHOT IRRADIATION OF ArF LASER. Hiroto Takahashi, M Murahara, The Faculty of Engineering of Tokyo University, Kawasaki, JAPAN; 
Copper nuclei grow on all aromatic polyimide surface in the presence of copper sulfate water solution with only 10ns single shot of ArF laser. The sample surface are characterized by pro-photosensitization with UV lamp. All aromatic groups have which are higher mechanical strength, film resistance, chemical resistance and heat resistance than that of general polyimide. The general polyimide has been widely used for the flexible electronic circuit printed board. However the all aromatic polyimide has not been used for having chemical stability. If the all aromatic polyimide can be bonded with metal directly, a hybrid material with high heat resistance property can be produced. Firstly, the sample surface was coated with UV light in an oxygen atmosphere. And we have substituted copper atoms with dangling bonds of carbon through the medium of oxygen atoms on the all aromatic polyimide surface. In this study we placed fused silica glass on the sample surface and poured the sulfate water solution into the gap between the silica glass and the sample, forming a thin liquid layer. Then one shot of circular patterned ArF laser light having 32nd J/cm² was irradiated vertically onto the sample. The dislocated copper atoms form the Cu-O-Cu bond with active oxygen on the polyimide surface. In this treatment there was no change on the all aromatic polyimide surface with the naked eye. However, we were able to grow a copper thin film of about 24μm after immersing the sample into the electro less plating solution for 15 minutes as sample with a non-irradiated area. After the processing machine the clear image of the circuit pattern appeared only in the exposed area, with the unexposed copper foil peeled off.

11:00 AM M3.8 
IN SITU STUDIES OF THE KINETICS OF ALKANETHIOL AND ALKANETHIOL-SULFONATE SELF-ASSEMBLY ON NOBLE METALS: C.S. C.Yang, I.J. Richter, Surface and Microanalysis Science Division, National Institute of Standards and Technology, Gaithersburg, MD; K.A. Brigman, J.C. Stephenson, Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD; G.R. Stafford, T.P. Moffit, Metallurgy Division, National Institute of Standards and Technology, Gaithersburg, MD; 
The self-assembly of alkanethiol monolayers on noble metals has been extensively studied, as they are robust model systems for organic surfaces, and have potential applications in diverse areas such as corrosion inhibitors and molecular electronics. Brightening additives in the electrodeposition of noble metals are often small alkanethiol-sulfonate species. We have performed comparative in-situ studies of the adsorption of deuterated octanethiol (d0ODS), deuterated octadecene disulfide (d18ODDS), and 3-mercaptopropanesulfonate (MPISA) on noble metal surfaces with vibrationally resonant sum frequency generation frequency (VR-SFG). VR-SFG is a surface specific tool that can provide vibrational spectra of molecules at liquid/air interfaces. In all studies, the development of the thiolate bond was followed via the non-resonant SFG background, while the conformation and ordering of the thiolate body was studied by scanning the temporal evolution of the GD (d0ODS and d18ODDS) or GH (MPISA) stretching modes in VR-SFG spectra. In all cases studied: d0ODS and d18ODDS in EOH on polycrystalline Au, and MPISA in perdeuterate on polycrystalline Au and Ag were found to be Longchain-like. For dODS and d18ODDS the conformation and ordering of the thiol tail clearly showed a two-step transition from a phase containing considerable chain disorder to a well-ordered all-trans phase during the forming of the monolayer. For MPISA, it was found that the alkyl body was well ordered in an all trans state at all coverages. The ex-situ spectra of the alkethiol and alkanethiol-sulfonate were quite different. There was little change between the in-situ spectra of the alkane sulfonate and the ex-situ spectra.

11:15 AM M3.9 
COPPER ELECTROCHEMICAL PLANARIZATION TECHNOLOGY FOR SUB-MICRON MULTILEVEL MECHANICAL PLANARIZATION. Hau Liu, National Nano Device Laboratory, Hsinchu, TAIWAN; Shi-Chieh Chang; Ming-Shiu Feng, National Chiao-Tung University, Materials Science and Engineering, Hsinchu, TAIWAN; 
In order to eliminate scratches produced by conventional Chemical mechanical planarization (CMP) slurries containing mechanically hard abrasives, electropolishing technology could be introduced as the first-step CMP of the typical CMP process to enhance the planarization capability of CMP. Meanwhile, electropolishing also
offering potential advantages of a reduced waste stream, less 
consumables, no applied pressure to the substrate, and reduced 
processing time. In this work, a copper electrochemical planar 
(CEP) technology involving electroplating followed by electropolishing was achieved in sub-micron multilevel metallization. Superconformal electroplating of copper in sub-130 nm vias was obtained by an acid copper electrolyte containing chloride (Cl\textsuperscript-), polyethylene glycol (PEG), and 2-aminomethylthioanilone (2AMT). Continuously, a clean and scratch-free surface was electropolished using phosphoric acid (85\%) or orthophosphoric acid as the electrolyte. Excellent copper foil obtained under current-controlled dissolution at the limiting current and the anodic surface electrodes after dissolution appeared bright to the naked eye. The electrochemical behavior of phosphoric acid in Cu electroplating was investigated by measuring potentiodynamic polarization and electrochemical impedance spectroscopy. Furthermore, the Nyquist plot at the applied voltage with 1.3 V with respect to the Ag/AgCl reference electrode reveals that two capacitance elements existed in the Cu/Ag/AgCl interface. Besides the double layer capacitance, the second capacitance was derived from the existence of passivation film. As those analyses, the optimized electrolyte and electropolishing dynamics were exploited. In summary, we successfully demonstrated an integral copper planarization processes on 100 nm damascene layouts by a complete electrochemical technology.

11:30 AM M3.10
THE GROWTH MECHANISM AND MORPHOLOGICAL 
CHARACTERISTICS OF NICKEL PARTICLE ELECTRO-
DEPOSITED AT HIGH CURRENT DENSITIES. Guo Xueyi, Liu 
Zhizong and Zhang Doame, Central South University, Dept of 
Material Science and Engineering, Changsha, P.R. CHINA; 
Masato Kamiyo, Miyochi Yamanami, University of Tokyo, Center 
for Collaborative, Tokyo, JAPAN.

The shape of dendrites is the most important morphological 
characteristics of electroplated particle deposits. It is commonly realized that the dendritic appearance and its expansion can be linked to the diffusion restriction during electrodeposition as the top of the dendrite grow faster than other sites in the surface of electrode. However, in this investigation, it is found by the authors that the morphology of the deposited nickel particles was not only influenced by the bath constituents, but also strongly related to the electrolysis parameters, especially the time for deposition. The nickel particles with flake, nodular or dendrite shape may be deposited by controlling the deposition time. The influence of the factors on nickel morphology was analyzed and the growth mechanism of the particle during the electroporation was elucidated.

11:45 AM M3.11
STUDIES OF THE INITIAL STAGES OF COPPER SULFIDE FILM 
GROWTH. M.J. Campin, J.G. Zhu, New Mexico State Univ, Dept 
of Physics, Las Cruces, NM; P.P. Provencio, J.C. Barbier, J.W. 
Braithwaite, J.P. Sullivan, Sandia National Laboratories, 
Albuquerque, NM.

Many surface redox reactions occurring in condensed phase 
electrodes or ultrahigh vacuum conditions produce uniform and 
well-controlled surface phases. In contrast, the surface redox reactions that occur as a result of exposure to a dilute reactant (i.e. one under gas-phase mass transport control) often lead to complex surface microstructures and morphologies. Unfortunately this complicated surface microstructure is particularly difficult to characterize using only near-surface probes, such as the scanning probe microscopes. In this study, we have used focused ion beam cross-section, transmission electron microscopy (TEM), high resolution TEM, and ion beam scattering to study the surface instability and CuS surface alloying when Cu is exposed to a dilute (~200ppb) H\textsubscript{2}S atmosphere at low (0.5\%) to high (80\%) relative humidity (RH). In the initial stages of exposure, Cu and S react and form the low chalcocite phase (Cu\textsubscript{2}S) as identified by X-ray diffraction and direct lattice imaging. In later stages of sulfidation, Cu diffuses through the Cu\textsubscript{2}S layer forming Kirkendall voids at the Cu/Cu\textsubscript{2}S interface; other Cu and S phases, including sulfates and/or hydroxide hydrates, appear. Surprisingly, for longer times, the Cu\textsubscript{2}S growth rate is significantly higher for sulfides formed at low RH compared to high RH. TEM revealed that the Cu\textsubscript{2}S grains at both low and high RH are 10 nm to 50 nm with no apparent preferred orientation. However, the high RH samples exhibit much larger chalcocite-like structures (250 nm x 75 nm) which tend to be more numerous at higher temperatures and have some grains that span the entire Cu\textsubscript{2}S layer. In addition, the high RH samples appear to have much sharper boundaries between grains. The coupling between Cu\textsubscript{2}S grain morphology and the solid-state diffusivity of Cu will be discussed. Sandia National Labs is operated under U.S. D.O.E. contract no. DE-AC04-94AL85000.

SESSION M4: MORPHOLOGY AND STRUCTURE 
IN ELECTRODEPOSITED THIN FILMS
Chair: Thomas P. O'Keefe and Michael Sierad
Tuesday Afternoon, November 27, 2001
Room 313 (Hyves)

1:30 PM M4.1
GRAIN STRUCTURE EVOLUTION DURING VAPOR 
DEPOSITION AND ELECTRODEPOSITION OF POLY-
CRYSTALLINE FILMS. Carl V. Thompson, R. Krishnan, C. Friesen, 
Massachusetts Institute of Technology. Dept of Materials Science and 
Engineering, Cambridge, MA.

Growth of a polycrystalline film begins with island nucleation and 
growth, and continues through island coalescence to form a 
continuous film and subsequent film thickening. The kinetics of 
nucleation, growth, island or grain coalescing through surface 
diffusion processes or grain boundary motion, and competitive growth 
at the surface of thickening film govern the distribution of grain 
sizes and crystallographic orientations, as well as grain shapes. Grain 
structure characteristics as a function of processing conditions (e.g. 
growth temperature) can be catalogued in the form of zone diagrams. 
Different diagrams apply for different deposition techniques and for 
different classes of materials. Many similarities exist between 
electrochemically and vapor-deposited polycrystalline films, and 
diagrams similar to zone diagrams have been proposed to relate grain 
structures to electrodeposition conditions. We will review these 
diagrams in terms of the underlying physical mechanisms responsible 
for different grain structure characteristics, and compare the 
similarities and differences of the structural phenomenology in 
electro- and vapor-deposited films.

2:00 PM M4.2
IMPURITY DISTRIBUTIONS IN ELECTROPLATED Cu FILMS 
DURING self-ANNEALING. Min Seon Yoon, Young-Chang Joo, 
Seoul National University, School of Materials Science & Engineering, Seoul, KOREA; Young-Joon Park, Nano Devices Research Team, Future Technology Research Division, Korea Institute of Science and Technology, Seoul, KOREA.

Electroplated Cu films have been reported to show self-annealing 
that is referred to as a microstructural evolution at room temperature. 
As for the mechanism of this phenomenon, the explicit role of 
additives in self-annealing has not been understood, while precedent 
redistributions of trapped additives have been supposed to trigger it. 
We have controlled the occurrence of self-annealing by changing 
current densities (1, 7 A/dm\textsuperscript{2}) and film thickness (0.1, 1.0 \mu m), and 
have investigated the impurity distributions. The impurity 
distributions have been measured just after deposition and after three 
weeks using secondary ion mass spectroscopy (SIMS). The amount of 
impurities in electroplated Cu films is reduced throughout the film 
thickness only when self-annealing occurs, while no appreciable 
redistribution of impurities is observed when self-annealing does not 
occur. The redistributed impurities are mainly heavy molecular 
impurities. If impurities should diffuse out prior to self-annealing, we 
can expect the impurity redistributions for all the electroplated Cu 
films after three weeks, regardless of the occurrence of self-annealing. 
Our results suggest that impurity redistributions hardly occur 
spontaneously at room temperature, while they proceed under 
appropriate conditions that lead to self-annealing. Instead grain growth seems to force 
impurities to be redistributed.

2:15 PM M4.3
A NOVEL SELECTIVELY PLATING Cu ON Ta BASED 
BARRIERS BY ELECTROCHEMICAL GALVANIC 
DISPLACEMENT. Yiu-Ping Lee, Ming-Shian Feng, Institute of 
Materials Science and Engineering, National Chiao Tung University, 
TAIWAN, ROC; Ming-Shih Tsai, Bao-Feng Dai, National Nano 
Device Laboratories, TAIWAN, ROC.

In this study, we proposed a novel selective Cu seeding and electroless 
Cu plating method by means of electrochemical Cu contact 
displacement directly from barrier Ta. The galvanic Cu deposition 
which involves the electrochemical redox reaction between cupric ions 
and Ta atoms could be carried out at room temperature in the HF 
anhydrous mental solution corresponding with the following 
electroless Cu plating. This selective Cu metallization is promising for 
overcoming the obstacles in the current damascene process, such as 
the limitation of depositing conformal Cu seed into high aspect ratio 
trenches by PVD for the following void filling Cu electroplating, and 
non-planarity issues after multi-step CMP, like Cu dishing and 
dielectric erosion.

3:00 PM M4.4
STRUCTURE OF Au, Cu, AND Pb ON GaAs(100) AND Si(111)11° SURFACES. Jorg Zegnenbank, European Synchrotron Radiation 
Facility ESRF, Grenoble, FRANCE.
We studied Au, Cu, and Pb on semiconductor surfaces in situ in the electron beam and in high vacuum UHV systems as well as in thin films. We employed X-ray diffraction and sputtering while holding the samples. By scanning electron microscopy and field ion microscopy in UHV. By deposition, epitaxially oriented islands are formed on the metal in contrast to Au deposited films at room temperature. In some cases, e.g., Au on GaAs(100) and Au electrodeposited on Si(111), monolayer amounts of the metals spread on the surface while the islands grow.

3:30 PM M4.5
ASPECTS OF ELECTROCHEMICAL DEPOSITION OF METALS ON SEMICONDUCTOR SURFACES. Chanwoo Ji, Akira Ueda, Radoslav Gerko, and Peter Severson, Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, MD.

The deposition of metallic thin films on semiconductors is usually performed in vacuum from the vapor phase by evaporation or sputter deposition. Electrochemical deposition represents an alternative approach for the deposition of metallic thin films on semiconductor surfaces. However, the deposition of continuous thin films requires a detailed understanding of the mechanism of nucleation and growth and the role of parameters such as solution chemistry and applied potential on the deposition mechanism. We will discuss some of the key features of metal deposition on semiconductor surfaces including Cu on Si, Au on Si, and Bi on GaAs.

3:45 PM M4.6
ORDERED METAL OXIDE NANOSTRUCTURES PRODUCED BY THE THERMODYNAMIC TO KINETIC TRANSITION IN EPITAXIAL ELECTRODEPOSITION. Hitam M. Kothari, Jay A. Switzer, University of Missouri-Rolla, Dept. of Chemistry and Materials Research Center, Rolla, MO.

We have found that it is possible to produce ordered nanostructures of metal oxide semiconductors on single crystal surfaces due to a transition from thermodynamic to kinetic control of crystallographic orientation. The epitaxial film follows the orientation of the substrate (i.e., thermodynamic control) up to a critical thickness, after which the film growth occurs in the kinetically-controlled growth direction. At the transition, the surface is covered with an ordered nanostructure. The thermally-controlled growth direction can be often controlled by varying the solution pH. On polycrystalline substrates, this kinetic preference leads to a fiber texture, in which the film is oriented out-of-plane but not in-plane. In this work, we explore the thermodynamic to kinetic transition in the epitaxial electrodeposition of cuprous oxide on single crystal gold. Cuprous oxide grows fastest in the [100] direction at pH 9; and in the [110] direction at pH 12. At pH 9, cuprous oxide grows on Au(111) with a [110] orientation, but switches to a [001] orientation after an overpotential-dependent critical thickness. The larger the overpotential the smaller the critical thickness. At pH 12, the cuprous oxide grows on Au(100) with a [100] orientation, but switches to a [110] orientation after a critical thickness of about 20 nm. AFM and SEM show that near the critical thickness the films develop very interesting nanostructures. For example, a 50-nm-thick film of cuprous oxide on Au(100) at pH 12 is covered with a 30 by 100 nm, cross-hatched pattern.

4:15 PM M4.7
PREPARATION AND CHARACTERIZATION OF Bi$_2$S$_3$ THIN FILMS WITH PREPARED ORIENTATION BY ELECTRODEPOSITION. Song Ren, Zhongshan Univ, Dept of Physics, Guangzhou, PR China; Li Sun, Chuming Ji, Peter C. Severson, Johns Hopkins Univ, Dept of M&S&E, Baltimore, MD.

In this paper we report on the growth of Bi$_2$S$_3$ thin films with (012) preferred orientation by electrodeposition. The electrolytes consisted of BiCl$_3$, S$_2$Cl$_2$, HCl and EDTA. EDTA 0.5M and HCl 2.4M in aqueous medium with a different mole ratio of BiS$_3$ exposed anion. The composition of the film varies from pure bismuth to pure antimony (x=1 to 0.2). The gold films with (111) preferred orientation sputtered on silicon wafers were used as substrates. The x-ray diffraction analytical study was carried out systematically. The crystal structure and preferred orientation of the films, their composition and morphology were studied as a function of electrochemical parameters and bath composition. It is shown that the obtained thin films represent a continuous series of solid solutions, and have a (012) preferred orientation when the concentration of antimony x is between 0.2 and 1 in bath solution. The composition difference is taken into account to estimate the boundaries of the different bath composition. The up of Bi-Sb monolayer and composition of the monolayer were also studied systematically with XPS.

4:30 PM M4.8
SUPPORTIVE THIN FILM GROWTH OF TiN(1)-CONTAINING FLUORIDE-ION CONDUCTORS FROM AQUEOUS SOLUTIONS. Frédéric Bouget, Jean-René Cotet, Georges Denis, Marc Le Rouzic, M. Cecilia Melchor and Elena Peraud, CORDIFON, University of Solid State Chemistry and Mass spectrometry, Laboratories for Inorganic Materials, Montréal, Québec, CANADA.

Unsupported thin films have been grown from aqueous solutions by two-dimensional polymerization of TiN(1) and fluoride, together with some alkali metal ions (K$^+$ and Pb$^{2+}$), and in some cases, also with nitrate ions. This work has established that the membrane structure is due to highly efficient charge planes that prevent the formation of bonds in the third dimension, and thus imposes a two-dimensional network. The cleavage planes are sheets of stereoactive lone pairs located on the hybrid orbitals of TiN(1).

TiN(1) is covalently bonded, as expected with fluoride. The presence of ions (M$^{2+}$, and sometimes nitrate) is necessary to create structures that have lone pairs cluster in sheets, since the clustering is not sheet-like in TiN(1) fluoride alone. The presence of foreign ions changes the chemical composition of the membranes, and therefore also some of their properties. The TiN(1) lone pair does not have Lewis base properties, and therefore they do not react with Lewis acids to form adducts that could have lost their thin film structure. The membrane can be easily recrystallized, sometimes with a change of chemical composition (insertion of nitrate ions, change of M$^{2+}$/M$^{2+}$/Sn$^{4+}$ ratio), to give surface areas about 1 cm$^2$, while their thickness is in the submicron range. Some possess a large intrinsic stress, that is explained by their ferroelectric properties, created by bonding, the symmetry situation, and the proximity of a phase transition.

SESSION M5/AA6 J连胜 SESSION
SELF ASSEMBLY
Chairs: Peter C. Severson and J. Woods Halley
Wednesday Morning, November 28, 2001
Room 313 (Hyne)
Above the threshold, there is ~0.1 monolayer of Ge atoms moving rapidly on the Pb-covered surface without getting incorporated into existing 2D Ge islands (covered with a Pb layer). [1,2] Now we study Si deposition on Pb-covered Si(111) surfaces at sample temperatures from room temperature to ~250°C, there is also a threshold Si coverage for the nucleation of 3D Si islands (covered with a Pb layer), and the threshold coverage increases with sample temperature. Below the threshold, all Si atoms form 1D nanowires on the Pb-covered surface, and the average length increases with the Si coverage and the sample temperature. Above the threshold, 3D islands are found along with the Si nanowires. This observation of the growth of 2D Si islands at the expense of nanowires after annealing at a higher temperature. This study may help us understand the mechanism of the initial stage of surface reconstruction [1,2].

Electrochemical deposition of FeCo and FeCoV thin films and nanowire arrays Ingo Schönhals, Corinna Steinbacher, Katharina Brachi, and Thomas Gessner, Technische Universität München, GERMANY.

Electrochemical deposition is an important method for the fabrication of thin films and micro-actuators. In this work, we investigated the electrochemical deposition process of FeCo and FeCoV at different conditions. The obtained films were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, and magnetic measurements. The results show that the composition and properties of the deposited films can be controlled by adjusting the deposition parameters. This work is relevant for the development of new materials for sensors and actuators.

11:30 AM *M5.5/A6.7* Cyclic evolution of water/OH molecules on single-crystal surfaces of RuO

SESSION M6: STRESS EVOLUTION: METAL OXIDES

Chair: Karl Sieradzki and Robert C. Cammarata

Room 313 (Hyenas)

1:30 PM *M6.1* Novel methods for the determination of surface stress and energies of defects on surfaces in UHV and in electrolytes

Harald Hackl, Institute of Thin Films and Interfaces-IGF 3, Forschungszentrum Juelich, Juelich, GERMANY.

In recent years, several novel methods have been developed to determine changes in the surface stress [1] as well as the energies of surface defects, such as steps and kinks [2,3]. While these methods have been developed first for surfaces in UHV, they are by no means restricted to clean surfaces in UHV. In the presentation, I will review the developments in the experimental methodology as well as the theoretical background of the methods.

The standard method to measure changes in the surface stress is to determine the small bending of a thin sheet under the influence of a change in the surface stress. With the help of finite element calculations and the theory of elasticity, the method has been expanded to microscopic materials and micromechanical structures.

Recent results of the L2XAS adsorption of Co(110) are shown as an example. Comparison is made to interface charge for induced surface stress in an electrochemical environment. Novel applications of particular concepts of strain microscopy to 3D surface systems have opened the possibility for a qualitative determination of surface defect energies. The step free energy, e.g., can be obtained from the temperature dependence of the equilibrium shapes of 3D islands on surfaces, or from the observations of the shape fluctuations of islands.
3:15 PM #6.5
SELF-CONSISTENT TIGHT-BINDBING DESCRIPTION OF THIN OXIDE FILMS ON METALS. Min Zhang, J.W. Halley, University of Minnesota, School of Physics and Astronomy, Minneapolis, MN; Patrick Schelling, Argonne National Laboratory, Argonne, IL.

To extend first principles studies of thin films grown in electrolytes to scales which permit a full study of the relevant phenomena requires larger simulations than are currently feasible. We report progress on a method for extending the scale of direct dynamics calculations on systems by use of a simplified but still self-consistent description of the electronic structure, recalculated after each relaxation of the atomic structure. Studies of several oxide-metal interfaces as well as progress in modeling the aqueous electrolyte by the same methods will be reported.

3:45 PM #6.6
IN SITU X-RAY SPECULAR REFLECTIVITY STUDY OF THE PASSIVE FILMS FORMED ON STAINLESS STEEL. Do Hyung Kim, Hyun Hwi Lee, Sang Soo Kim, Hyon Chol Kang, Hyo Jung Kim, Do Young Noh, Kwangju Institute of Science and Technology, Dept of Materials Science and Engineering, Kwangju, KOREA; Hyun Jung Kim, Dong Hyo Lee, Sinh Sinh, Argonne National Laboratory, Advanced Photon Source, IL.

The formation of passive oxide films on stainless steel substrates in a pH 8.4 borosilicate buffer solution was investigated by in-situ synchrotron x-ray reflectivity. The thickness of the passive film increases logarithmically in the passive region. The steady state thickness of the passive film, ranging from 18-45 Å, increases with increasing the anodization potentials. We also investigated the depth profile of Fe and Cr oxides in the passive film applying in-situ anomalous x-ray reflectivity technique. In the passive region, the passive film consists of Cr oxide-rich inner region and Fe oxide-rich outer region. In the transpassive region, however, the oxide film is mainly composed of the Fe oxide, because the Cr oxide dissolves in this region. All x-ray reflectivity curves are analyzed in the Parratt's formalism.

4:00 PM #6.7
ANALYSIS OF BARRIER- AND POROUS-TYPE OXIDE LAYERS ON ALUMINUM BY RADIO FREQUENCY GLOW DISCHARGE OPTICAL EMISSION SPECTROSCOPY (Rf-GD-OES). R. Kenneth Marcus, Alwyn B. Anfinsen, Washington, Department of Chemistry, Clemson University, Clemson, SC; Patrick Chapon, John-Yvon, Horiba Group, Longjumeau, FRANCE; Tina Harville, John-Yvon, Horiba Group, Edison, NJ; Kenichi Shimizu, University Chemical Laboratory, Kyoto University, Yoshida, JAPAN.

Oxide layers formed on aluminum surfaces in electrolyte solutions are both industrially important and chemically interesting systems. Thin (<1 µm) barrier-type aluminum coatings are commonly used as protective layers on aluminum surfaces and as dielectric layers in electronic devices. Much thicker (5 - 1000 µm) porous-aluminum is used as keying layers for organic coatings and separation membranes. In many applications, metals ions are doped within the layers to achieve specific chemical or esthetic properties. The combination of the fact that these aluminum coatings are electrolytically induced, and the range of diameters, which range from very small to hundreds of micrometers, allows the depth-resolved elemental analysis of such materials challenging. The development of a method that provides these sorts of information would be extendable to other oxide systems found in electronic and corrosion science research. We describe here the use of radio frequency glow discharge optical emission spectroscopy (rF-GD-OES) for the analysis of diverse aluminum oxide coatings. The rF-GD-OES is uniquely suited for such analyses because it combines the ability to sputter nonconductive materials at high rates (0.1-1 µm/min), deep penetration depths (>300 µm), and high depth-resolving powers (~10 nm). The utility of the rF-GD-OES method is demonstrated in the analysis of both barrier and porous-type coatings. In the first case, the ability to distinguish very thin films demonstrated in a ~7 µm thick Cr layer located ~15 mm beneath the surface of a barrier-type alumina coating that has a total thickness of 180 µm as shown by the x-ray/interference. The second example is a depth profile of a 10 µm thick porous aluminum film where a 2 µm thick layer of Ni has been deposited in the base of the pores. Early in the profile, the composition is clearly Al and O, with only Al being present after the evolution of the Ni coating. It is believed that the rF-GD-OES method will offer a great deal of promise for applications in oxide layer analysis.

4:15 PM #6.8
TITANIUM ELECTROLYTIC CAPACITORS WITH (ALKALI EARTH/TITANATE-DOPED TITANIUM DIOXIDE DIELECTRIC. R. Jain, B. Chou, D. McGeary, G. Welch, MS&E Dept, Case Western Reserve University, Cleveland, OH.

The energy of a capacitor is directly proportional to its capacitance.
and the square of the operating voltage. For a given geometrical configuration the capacitance depends on the dielectric constant of the dielectric material and the operating voltage depends on the dielectric strength. An electrolytic titanium capacitor has a titanium dioxide film that is permanently in contact with an oxidizing electrolyte, enabling self-healing of the dielectric. As a consequence it can perform to higher breaking voltage than it is possible without any electrolyte. The titanium dioxide dielectric film of electrolytic titanium capacitors has dielectric strength of 0.75 V/μm and charge storage capacity of 1.0-100 μC/cm². The present study deals with modification of the dielectric material with metal elements to further enhance its dielectric constant. The aim is to incorporate certain amount of [nickel-eth] into titania to the titania dielectric material, so they can form high dielectric constants. The effect of doping is analyzed in terms of charge density, leakage current, and dielectric strength.

4:30 P.M. M6.9

STUDY OF THE ELECTROCHEMICAL REDOX BEHAVIOUR OF THE LEAD AND IT'S ALLOYS IN SULPHURIC ACID SOLUTIONS: Viorel Branzoi, Polytechnic Univ. of Bucharest, Dept. of Chemical Engineering, Bucharest, ROMANIA; Florin Branzoi, Romanian Academy, Institut of Physical Chemistry, Florestina Golovici, Luka Pihan, Polytechnic Univ. of Bucharest, Dept. of Chemical Engineering, Bucharest, ROMANIA.

Using the potentialodynamic method, the electrochemical redox behaviour of the Pb/PbSO₄ system on the lead alloys electrodes in aqueous H₂SO₄ solutions was studied. The potential sweep of the working electrodes in the given potential ranges (i.e., -1000 mV to +800 mV; 800 mV to 1600 mV and -1200 mV to 1600 mV), was intended to simulate the processes taking place at the positive and negative plates of the lead/acid battery during charge/discharge cycling. Also the anodic and the cathodic polarization behaviours were investigated under the various conditions by changing the potential region, sweeping rate, and concentration of the electrolyte. The characteristic of the polarization curves (i.e., shape and height and potential range in which peaks appear) and the observed changes in the current density were used to calculate the values of the kinetic parameters determined from such curves, enable conclusions to be drawn concerning the electrochemical characteristics of the Pb/PbSO₄ electrodes. The results provide valuable information in attempts to elucidate the processes taking place during Pb/PbSO₄ interface. The mutual electrochemical behaviour of the Pb/PbSO₄ is discussed in detail. The behaviour of lead and lead alloys in alkali solutions (i.e., Pb/PbH₂SO₄) was also investigated to study the characteristics of the Pb/PbSO₄ interface. The results prove that the Pb/PbSO₄ system is a promising candidate for anode materials in lead-acid batteries.

4:45 P.M. M6.10

KINETICS OF PURE ALUMINIUM DISSOLUTION IN PHOSPHoric ACID SOLUTIONS CONTAINING DIFFERENT ANIONIC AND ORGANIC INHIBITORS: Viorel Branzoi, Florestina Golovici, Dept. of Chemical Engineering, University Polytechnic of Bucharest, Bucharest, ROMANIA; Florin Branzoi, Romanian Academy, Institute of Physical Chemistry, Bucharest, ROMANIA.

Effects of aggressive anions additives on dissolution of pure aluminium have been investigated in aqueous solutions of phosphoric acid 1M as a function of anion concentration using electrochemical impedance spectroscopy (EIS) potentiostatic and potentiodynamic methods. The addition of different aggressive anions (like Cl, Br, I, SCN-) lead to in all of the cases to an increase of the corrosion rate. The presence of halide ions creates pitting corrosion in all cases. Characteristic of all systems is that virtually no current flows before some definite potential is reached. The experimental results confirmed that even in solutions containing chloride ions the surface of the metal is covered by oxide film. This film changes its thickness and conductivity of anodic dissolution, being the less resistive the higher the current density. Impedence measurements showed a single capacitive loop in the complex plane plots and one maximum in the phase angle plots at high frequencies. In the presence of hydroxide and sodium hydroxide, the hydroxide ion concentration being maintained constant, the decrease of hydrogen ion concentration down to 0.5 N leads to the increase of the corrosion current density and to the diminution of the corrosion process. The increase of the pH (decrease of the H⁺ ion concentration) leads to the increase of the cathode rate and favours the dissolution of the oxide film, in accordance with the Pourbaix diagram. Electrochemical measurements showed that, the organic inhibitors, like as decyltrimethylammonium bromide, tetradecyltrimethylammonium bromide and heptadecyltrimethylammonium bromide had good inhibiting properties. It has been assumed that the first stage in the action mechanism of the organic inhibitor in aggressive medium is the adsorption onto the metal surface. Physical (electrochemical) and anodic (inhibitors) processes, principal types of interaction between the organic inhibitor and the metal surface. The best efficiencies appear to obtain at concentrations around the critical inhibitor (CI) concentration. The adsorption of the organic inhibitor prevents the adsorption of aggressive anions and the destruction of the aluminium oxide layer.

SESSION M7: POSTER SESSION

Chair: Dieter M. Kolb, Benjamin M. Odo, Peter C. Serns and Karl Sieradzki

Wednesday Evening, November 28, 2001

8:00 PM

Exhibition Hall D (Hynes)

M7.1 ELECTRONICS STRUCTURES OF HVL SEMICONDUCTOR SURFACES: Junho Lee, Dept. of Electrical Engineering, Univ. of Arkansas, Fayetteville, AR; Sangchun Lee, Inho Shin, Dept. of Physics, Kyungnam Univ., Muan, KOREA; Greg J. Salmo, Dept. of Physics, Univ. of Arkansas, Fayetteville, AR.

Empirical tight-binding methods are a common technique to investigate quantum wells, superlattices, and resonant tunneling diodes in heterostructure semiconductors. The surface electronic structure of the materials using the local densities of states (LDOS), the subspace Hamiltonian, and the transfer matrix techniques. From the results, we show that these ideal surfaces can act as interfaces to investigate reconstruction, relaxation, or any defects of semiconductor surfaces for the i-w materials.

M7.2 XPS STUDY OF H-TERMINATED SILICON SURFACE ANNEALED IN NON-OXIDIZING ATMOSPHERE: Kazumasa Kamegai, Junji Yasumura, Hiroshi Kubokawa, Mitsubishi Electric Corporation, Advanced Technology R&D Center, Hyogo, JAPAN; Kenzashi Wako, Akihiro Teramoto, Hiroshi Umeda, Mitsubishi Electric Corporation, ULSI Development Center, Hyogo, JAPAN.

Silicon oxide layers grown at low temperature during temperature rise process are considered to reduce the breakdown voltage of the ultra thin gate dielectrics for MOS devices. Use of H-terminated Si surface treated by HF and non-oxidizing gas atmosphere during pre-process followed by high temperature oxidizing is necessary to prevent the low temperature growth of the layers. The breakdown voltage of the gate dielectric grown with the proposed process, however, is known to be lower than that of the conventional process using O₂-containing atmosphere. We have investigated in detail the chemical state of H-terminated Si (100) surface after different temperature annealing in N₂, Ar and UHV with XPS. It was found that SiC is formed on Si surface annealed at higher 1000°C and remains even after thermal oxidation of 2.2 μm thick. However, SiC was not formed on SiO₂ surface or with O₂-containing atmosphere. On the other hand, the hydrogen atoms terminating the pair of bonds at Si (100) utmost surface were found to desorb at 380°C and 500°C. Dangling bonds generated by hydrogen desorption at 380°C should be deactivated by forming dimers, while dangling bonds generated at 500°C are not able to form dimers. These active dangling bonds would react with organic contamination to form SiC, which should reduce the breakdown voltage of the gate dielectric. It is very important to realize clean contamination-free surface and atmosphere to prevent both low temperature growth of silicon oxide and SiC formation.

M7.3 ROUGHNESS IMPROVEMENT OF THIN SiO₂/S SURFACES PREPARED BY RADICAL OXYGEN GROWTH TECHNIQUE: Koji Usada, Mitsuo Nagamine, Hiroshi Tobu, Corporate Research &
Development Center, Toshiba Corporation, Kanagawa, JAPAN; Akira Toriumi, The University of Tokyo, Department of Materials Science, School of Engineering, Tokyo, JAPAN.

To realize sub-100 nm gate MOS devices, highly reliable very thin SiO₂ film in the nm order is required. A newly developed SiO₂ growth technique, the radial oxidation method, has several advantages compared with conventional thermally grown film, such as lower process temperature, higher oxide growth rate, etc. [1]. These advantages are thought to derive from the radical oxygen reaction (RO₂) on the Si surface. To investigate the advantage of the radial oxygen reaction on the Si surface, characterization of both radial and thermally grown SiO₂/Si interfaces was carried out in detail, first with TM-AFM (tapping-mode atomic force microscopy). It was established that roughness of the radial SiO₂/Si interface decreased monotonically with thicker oxidation, and was superior to that attainable with conventional dry oxidation. Atomic order parameters and terraces emerged on interfaces with bilayer steps of 0.3 nm in height from Si[111], and single steps of 1.4 nm in height for Si[001] after the radial oxidation. Furthermore, we investigated other SiO₂/Si interfaces that were grown directly on an atomicly flat Si surface prepared by UHV-CVD. It was found that the interface improvement discussed above did not depend on the roughness of the pre-oxidized Si surface, and that, in any case, the radial process produced a flatter interface. Improvement of the SiO₂/Si interface might be required for fabricating high-performance MOS devices as the thickness of SiO₂ film becomes thinner. Hence, the conclusion is that the radial oxidation process is ideal for the thin SiO₂ film growth technique to realize a flat SiO₂/Si interface in the nm order. [1] M. Nagamine, H. Ito, H. Susane, and A. Toriumi, JEDM Tech. Dig. (1998) 293.

M7.4 Abstract Withdrawn.

M7.5 THEORETICAL STUDY ON THE ELECTRONIC STRUCTURE OF POLYMER ON LAYER ON AS ELECTRODE. Masatake Aoyagi, Kohji Yatsuda, The Univ of Tokyo, Graduate School of Engineering, Tokyo, JAPAN.

We have studied theoretically the electronic structure of a Poly(allylamine) (PAA) film on metal electrodes, and how the density functional theory. These electrode surfaces have been modeled by clusters consisting of 7 atoms on the first layer and 6 atoms on the second and third layer, and by slab models. We have adopted a CO molecule as an adsorbate. The properties of cluster models are calculated at the level of H3LYP, while the properties of slab models are calculated using a plane wave basis set and ultrasoft pseudopotentials. The calculated charge on the first layer of the PAA clusters is more positive than that of the PAA cluster. As compared with the Pd-Pd cluster, electron transfer from the Pd-Pd cluster to an adsorbed CO is restrained. The adsorption energy of the Pd-PAA clusters is also restrained. We will show whether the effect of the PAA film on the surfaces or the electronic effect of the second layer atom is stronger.

M7.6 Abstract Withdrawn.

M7.7 Abstract Withdrawn.

M7.8 Abstract Withdrawn.

M7.9 NIOBIUM OXIDE FILM FORMATION BY ANODIZATION. Hiroshi Moriyama, Toshiyuki Ikuki, Ryosuke Osada, Youichiro Asou, Toho University, Department of Chemistry, Funabashi, JAPAN; Takashi Morizuki, Sunshin Ltd, Shiojiri, Nagano, JAPAN.

Oxide films on niobium metal with various kinds of colors due to interference were formed by anodization of niobium [99.99%] plates in aqueous ammonium solution solutions. Interference colors of the films were found to depend dominantly on applied voltage. Analysis of the oxidized niobium films by means of SEM, EPM, AUGER, and ESCA revealed that mixed oxide films of Nb(II), Nb(IV), and Nb(V) with various composition were formed on the surface.

M7.10 INFLUENCE OF SHEET ELECTRON BEAM IRRADIATION ON BLUR FREE PROPERTY OF ANATASE PHASE OF TiO₂ THIN FILM. Kumiyu Oguri, Yamaumi Hagiwara, Rie Fujii, Akira Tonomura, Takashi Ichikawa, Tokyo Univ, Dept of Materials Science, Kanagawa, JAPAN.

Photoelectrocatalytic reaction is well known on the TiO₂ film surface irradiated by UV light. It was applied for blurr free mirror of car attachment and the toilet paper application for sterilization. TiO₂ coating mirrors show self cleaning function which are also "promotion of anisotropic thin film" semipermanently. Namely, it generates effects of sterilization and blurr free of TiO₂ film. Then, photocoagulation reaction induced super-hydrophilic and super-oilphobic conversion of the TiO₂ surface simultaneously. However it takes long time for UV irradiation to improve the super-hydrophilic conversion. On the other hand, the blurr free has been developed by sheet electron beam irradiation treatment. The effect is due to an enhancement of the interfacial energy between the TiO₂ and water. Thus we studied the effect of sheet electron beam irradiation on blurr free property of anisotrope phase of TiO₂ thin film. The sheet electron beam irradiation was homogeneously applied with 7 keV electron gun (electron source: Cu-polytype: CBIB15/15/18/10, Energy Science Inc., Wolum, MA; Iwasaki Electric Group Company, Tokyo). It is important for the sheet electron beam irradiation to treat homogeneously under protective nitrogen gas. The surface condition was evaluated by contact angle of water drop on the surface. The sheet electron beam irradiation decreased the contact angle on anisotropic phase of TiO₂ thin film. Namely, sheet electron beam irradiation increased surface energy of anisotropic phase of TiO₂ thin film.

M7.11 ELECTROCHEMICAL GROWTH OF THIN OXIDE FILM ON SINGLE CRYSTALLINE SILICON WAFER. Chi-Woo Lee, Sung-Eun Bae, In-Chool Lee, and Nam-Ki Min, College of Science and Technology, Korea University, Jochiwon, Chungnam, KOREA.

Facile formation of oxide films on silicon surfaces and their desirable photochemical characteristics for device fabrication have been the main advantages driving force for the present development of modern silicon technology. Silicon dioxide films thicker than 20 nm are believed to be grown by two independent mechanisms in gaseous environments at high temperatures (1) and intercalation diffusion of oxidents such as molecular oxygen or water through oxide network to react with Si atoms at the pure silicon/silicon oxide interface and (2) step-by-step pair and 0 atom step-by-step motion of O atoms by simple diffusion induced by the presence of network defects near the external surface. As planar integrated circuit dimensions have been reduced, the gate oxide thickness has also been reduced. It has been predicted that oxide gate thickness as thin as 3 nm will be required in the near future. Nuclear horizontal dimension reaches 0.1 µm. Thermal growth of very thin (less than 10 nm) films of silicon dioxide or ambient growth of native oxide on Si is anomalously high. There are many proposed mechanisms with no consensus for the anomalous growth range. For thinner oxides the wafer cleaning process becomes a key step in obtaining high quality oxides in dry process. It has been reported that HF/ethanol led to only 0.25 nm of silicon oxide after 4 hours of exposure to air and 0.9 nm after 22 days, while HF/H₂O presented the incorporation of oxygen to 0.45 nm after 4 hours and up to 1.4 nm after 22 days. Apparently different Si stabilities are evidenced by being introduced by two wet cleaning procedures. Despite the importance of device fabrication procedures, the wet cleaning process has been largely a matter of trial and error. Recently, the cleaning process has been less studied in the ambient laboratory conditions at the room temperature. We have been investigating the electrochemical formation of thin oxide films on single crystalline silicon wafers in aquagases as well as on gaseous solutions under inert and reducing atmospheres. In this work we would like to present the similarities and differences between the electrochemically and thermally grown silicon oxides and among the monodic oxides.

M7.12 GROWTH OF BARRIER ANODIC ALUMINIUM OXIDE FILMS. Urs N. Lednik, Vacuum Microelectronics Laboratory, Institute of Electronics, Belarus Academy of Science, BELARUS.

Barrier type anodic aluminium oxide films are formed at the current density higher or equal to some critical value. At the current density lower than critical one pores of anodic aluminium grow with characteristic depending on the anodization conditions. In this work we have made an attempt to investigate the structure and properties of anodic aluminium oxide on dependence on the electrolyte temperature and to connect critical current density and temperature by relationship. Anodic aluminium oxide films were formed in 0.1 % aqueous solution of citric acid. Anodization was carried out at the constant current and under the finish voltage up to 450 V. Current density was found to decrease with the raise of the temperature. Anodization current constant decreases with the electrolyte temperature increasing and reaches 1.3 mm/V. This confirms our assumption about decreasing of amount of interfacial impurities from electrolyte oxide to oxide with temperature raising. Investigation of chemical stability in strong acids of barrier anodic aluminium oxide was carried out and it was shown that perfect film with high density and high chemical stability can be formed only under the high temperature. We determined critical value of electrolyte temperature, higher temperature results in the formation of an ideal anodic aluminium oxide (barrier oxide).