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

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*Invited paper
SESSION M1: OVERLAY GROWTH, SURFACE MORPHOLOGY AND NANOSTRUCTURING
Chaim K. Sieradzki and Peter C. Scanzoni
Monday Morning, November 26, 2001
Room 313 (Hynes)

9:00 AM M1.1
MECHANISTIC ASPECTS IN METAL FILM GROWTH - COMPLICATION BEYOND SIMPLE SYSTEMS.
R. Jürgen Behm, Universität Ulm, Abteilung Oberflächenchemie und Katalyse, 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 successively modelled as a sequence of elementary steps. This is true at least for simple systems, where the substrate can be considered as an acceptor template. However, strongly adsorbed coadsorbates or impurities play an important role and growth is largely controlled by kinetic effects such as nucleation and 3D 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 impurities 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 ultrahigh vacuum conditions as well as for metal deposition in electrolytes. Mechanistic ideas will be presented and discussed. Second, the effect of coadsorbed species on nucleation and growth processes will be discussed. Coadsorbates, which are generally present in electrolytes, e.g., as impurities, are known to 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 these cases common aspects will be emphasized.

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

We present the first results for the underpotential deposition (UPD) of a metal on an alloy substrate. This type of information provides key insights into the nature of specific-metal 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 Ag-Au/Cu/CuCl₂ where p was varied between zero and one. Copper is known to underpotentially deposit on elemental Au but not on Ag. The Cu UPD charge density decreased with increasing atom fraction of Ag in the alloy to p equal to 0.26, and for p less than 0.26 no UPD was observed. The potential peak of the UPD stripping 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 nearest-neighbor sites, 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. Ocko and M. Weinert, Department of Physics, Brookhaven National Laboratory, Upton, NY; R.J. Rander and D.M. Kolb, University of Ulm, Ulm, GERMANY; M. Pfeifer, I.K. Robinson, Department of Physics, Un. of Illinois, Urbana, IL.

The structure and behavior of electrodeposited monolayers and thin films have been investigated using surface x-ray scattering techniques under controlled 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 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) with a periodicity of 70 Å (consistent with STM measurements of Cu on Ag(100) and Au(100)). The x-ray measurements conclusively show that the entire copper film structures; that is to say, the surface and underlying gold is also the transformation that occurs with thickness is similar to the temperature dependent martensitic transition observed in some beam 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.

10:30 AM M1.4
STEP AND ISLAND DYNAMICS AT SOLID/LIQUID INTERFACES. Mogens Giese, Sabine Dohmen, Forschungszentrum Juelich, Juelich, GERMANY; Dieter M. Kolb, Abt. Elektrochemie, Universität Ulm, Ulm, GERMANY.

During the last decade much effort has been spent to study atomic-scale processes at metal surfaces in UHV using sophisticated theoretical methods and experimental studies (for an overview see [1]). It is, however, only recently that corresponding studies at the solid/liquid interface have been reported. The reason for this is that model experiments 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 electrochemical 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 focuses on the competition between the solid/liquid and the solid/vacuum interface. Despite many similarities between surface diffusion on surfaces in UHV and in electrolytes, there are some striking differences. Pre-exponential factors for surface diffusion seem to be considerably higher (~10⁻⁴ 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 on the adsorption of K⁺ on Au(111) and Au(100) electrodes. By applying recently developed theoretical methods for island studies on metal surfaces in UHV we determine step and kink energies on Au(100) in contact with a liquid. [1] Prog. Surf. Sci. 68 (2001) 1-253, [2] Preprints available at http://www.fz-juelich.de/iw/Giese/01giese.html#Publications [3] J. Phys. Chem. Phys. 2 (2000) 3675. [4] J. Phys. Chem. Condens. Matter. 13 (2001) S589. [5] Surf. Sci. 384 (1997) 108. [6] Electrochem. Acta. 45 (1999) 523. [7] Surf. Sci., 408 (2000) 149.

11:00 AM M1.5
DISPLAY OF NANO-FEATURES ON GOLD AND SILVER SINGLE CRYSTALS IN CONTACT WITH SULFURIC ACID SOLUTION UNDER THE CONTROL OF POTENTIAL AND TEMPERATURE. Nobuo Hisa, Shigenori Haras, Osaka Univ, Dep. of Materials Science and Processing, Osaka, JAPAN.

Decay of nano-features located on metal surface gives considerable insights in the understanding of stability of nano-features in contact with aqueous solution, as well as vacuum. In this conference, we will present the electrode potential dependence and the temperature dependence of the decay processes of nano-features (islands and holes) located on Au(100), Au(111) and Ag(100) electrodes in contact with sulfuric acid solution, which was observed by means of in-situ electrochemical AFM (EC-AFM) [1-4]. It is found that the size of the top layer of the islands both on Au(100) and Au(111) in sulfuric acid solution decreases linearly with time and that the detachment of atoms from the step edge is the limiting process in this decay. When the potential of Au(100) increases in the potential range between 0.15 V and 1.2 V, the decay of the top layer of nano-islands becomes faster and it is considered that the metal atoms at metal/electrolyte interface are reduced toward electrolyte by the electric field at the interface, which becomes higher at higher applied potential. We have also succeeded in the observation on the decay of nano-holes located on metal electrode under the control of temperature. Activation energy for the decay of the nano-holes on Au(100) terraces in sulfuric acid solution will be discussed.

References:

11:15 AM M1.6
AN IN SITU ELECTROCHEMICAL AND IN SITU STM STUDY OF FLAT DEPOSITION ON MODIFIED GOLD SURFACES. Mario José Espinol, Departamento de Físicoquímica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, 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 create self-assembled monolayers of gold and can be functionalized according to desired purposes. Aimed at the control of
metal electrodeposition, the phenomena of underpotential deposition (UPD) and overpotential deposition (OPD) are significantly affected by the presence of the thin 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 thin layer and the potential range within which metal deposition can be carried out. Without any thin film deposition 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 electrode. The deposition process is affected by a variation of the thin layer thickness and a variation of different thin-layer groups. It is our main motivation to elucidate the substrate/SAM deposited metal configuration, the metal nucleation and growth mechanism, the differences with SAM-free electrodes and the specific reactivities of metalophilic end groups exposed to the silver electrolyte.

11:30 AM M1.7
SI NANOPARTICLE ELECTROCHEMICAL PLATING.
G. Belomoin, A. Smith, S. Aseieb, M.H. Nugef, Depts of Physics, and Theoretical and Applied Mechanics, Univ of Illinois at Urbana-Champaign, Tajir Nugef, Industrial Engineering, Cleveland State Univ.

We report on a procedure for depositing ultraslim ultrathin silicon nanoparticles from a aqueous alcohol colloids 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 on metal or silicon substrates are demonstrated. Modulation of the conductivity of the substrate using oxide maskings provides selective anode deposits. The process is discussed in terms of the formation of complex alcohol ions with the silicon particles depending on ligands.

11:45 AM M1.8
TIP INDUCED NANOSTRUCTURING OF Au/Ag ALLOYS WITH AN ELECTROCHEMICAL SCANNING TUNNELING MICROSCOPE. Stefan Maaup, Andreas S. Daskou, Martin Strathman, Paul Schmelz, Dept. of Material Science, LKU, University of Erlangen-Nuremberg, Erlangen, GERMANY.

By tip-induced metal deposition using an EFM 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, Pb, Ag, Au) 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 fail 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 adorbsorbs like the underpotential deposition layers. The experiments give clear evidence that the stability of the metal clusters is not intrinsic but more 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
Chairs: Dieter M. Kolb and Benjamin M. Osoko
Monday Afternoon, November 26, 2001
Room 313 (Hynes)

1:30 PM M2.1
Abstract Withdrawn

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

The growth of compound semiconductors is being investigated using the electrochemical atomic layer epitaxy (EAE). Initial studies have been on In-V compounds, such as CdTe, although they have recently been expanded to III-V compounds such as InAs. Work is also progressing on the formation of nanostructures such as 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 underneath 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 UC techniques. The UPD can be performed directly to a UV 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
INSITU COPPER ELECTRODEPOSITION ON RUTHENIUM METAL SURFACE. Tatsunori Watanuki, Thomas Pons-Fuaz, Thomas C. Otvos, University of North Texas, Dept. of Chemistry, Denton, TX.

In the sub-0.15 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 tantalum nitrides, i.e. diffusion barriers, are employed in the 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 CuSO4/5 M H2SO4. The LV curve showed a transport-limited growth peak at ca. -1.75 mV and hydrogen evolution onset occurred around -0.400 mV. The Cu nucleation and growth process was investigated using a current-transient electrochemical method and compared to TEM and AFM results. Preliminary results showed that the nucleation mode (progressive or instantaneous) was controlled by the applied overpotential. XRD patterns revealed heterostructural growth of Cu on Ru with strong Cu(111) texture and no new phase or bimetallic compound formation between the nucleation and Ru substrate. Cu film properties were investigated using 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. Takanag, National Institute of Science and Technology Policy, Noda-Chou, Chiba-shi, Tokyo, JAPAN, Y. Kogure and Masao Ono, Tokyo University of Science and Technology, Ueno-ku, Yamashita, JAPAN.

In the crystal growth from the gas phase, the motion and conversion of adatoms and their clusters is quite important. 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 1000 free atoms. The length in the [-110] direction was 1.1a, that in the [110] was 9a and that in [001] was 4a, where a is the lattice parameter. Adatom or its clusters were set near the center of [001]. 280 atoms near the ad-atom clusters (Region I) were relaxed 1000 time steps. The atoms moved along a straight line was relaxed in [001] direction and the atoms in Region I were relaxed three dimensionally. From the crystal energies moved along different lines, an equi-potential lines were obtained. These calculations were performed for a ad-atom and tri-ad-atoms. Tri-ad-atoms were classified according to the lengths of the bonds between ad-atoms and the angle of the bonds. Activation energies of the motion of ad-atom alone near [110] on [001] were also 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 Hid (d is the nearest neighbor distance) to In and from In to Hid were 0.45 eV and 0.16 eV, respectively.

3:30 PM M2.5
SURFACE DIFFUSION MECHANISM VS. ELECTRIC FIELD: Pt/Pt(001). Peter J. Fischbein, 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 atoms in carefully chosen "substrate" 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 atom self-diffusion on Pt(001), a surface for which "knob" experiments suggest that the energy process, converted substitution, is supplanted by hopping when the external field is high enough. The result is that theory agrees with FIM that the barrier to converted substitutional diffusion of a Pt atom on Pt(001) varies linearly with external electric field, changing ~ 0.1eV per V/Å 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 tentative change in FIM, in which field variations of 1.2 V/Å 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-AC05-94AL85000. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the U.S. DOE.

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 anisotropy in surface energy, but avoids the ill-posedness in evolution problems commonly associated with strong anisotropy. We incorporate this new model in studying grain-boundary growing by surface diffusion. We consider partially to fully faceted surfaces with different facet orientations and 3, 4, 6 fold symmetries in surface energy. We find that in all the 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
Chairs: Reginald M. Fenner and Margret Giesen
Tuesday, Morning, November 27, 2001
Room 313 (Hyatt)

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

Superconformal electrodeposition is explained based on a local growth velocity that increases with coverage of a catalytic species adsorbed on the copper-electrolyte interface. Focused ion beam and X-ray photoemission spectroscopy of the catalyst precursor in the electrolyte, local coverage in fine features changes due to interface area change thus by accumulation from the electrolyte, yielding superconformal growth. The model is supported by experiments on the electrocodeposition of Cu at 350-100 nm wide features, helping to explain the influence of adsorbates on roughness evolution.

9:00 AM M3.2
Copper Wettability, Nucleation and Growth in UHV vs. Electrochemical Environments: Anion Effects on Interface Formation
N.P. Mogro, Jinzhong Chen, Wen Wang, Xinxeng Zhao and J.A. Kelber, Department of Chemistry, University of North Texas, Denton, TX.

Achieving conformal growth (SK) 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 STEM 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 analytical analysis of surface/interfacial chemistry with minimal atmospheric contamination. These studies reveal that anion incorporation occurs during the formation of the initial Cu adlayer on Ti but is not observed during subsequent growth of the Cu film. Since Cu(0) is observed at low Cu coverages, copper sulfide formation is not the reason for sulfide adsorption at the substrate surface. The oxidation of the Ti substrate during deposition conditions does not appear to be related to 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 SiO2 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 vacuum 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(hexamethyldisilazane) [trimethylvinylsilane], or Cu(hfacet)[(hfac)2] (with surprisingly little of this work focused on the nucleation and growth of Cu on thin films composed of materials that are candidates for interconnect layers, 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 SiO2) surfaces. We find that
for the reaction conditions examined (substrate temperatures between 150 and 200°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 for Cu on TaN surfaces. The implications of 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. Sung-Soo Kim, MIT, Department of Chemical Engineering, Cambridge, MA; Larry Goddard, Novellus Systems, Inc., San Jose, CA; Klaus F. Jensen, MIT, 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 hump is formed if the film is allowed to grow after feature is completely filled. This hump 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 linking reactor scale and feature scale. This multiscale simulation, which is performed in real time, allows us to simulate the 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 hump 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.

Thermal is among the candidates to serve as both diffusion barrier and adhesion layer 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 film. 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-tantalum potential developed by the force-matching method. The initial growth mode and surface structure of Cu films on Ta are discussed.

10:00 AM M3.6 ELECTROPOLISHED Ag THIN FILM FOR ULSI CONNECTION MATERIAL. Jeong-Mo Seo, SooKil Kim, Jae 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 sintering. Furthermore, it was shown that self-etching 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)/TaN (30 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 organic additives. The electroplating process and evaluation methods of thickness, resistivity and the reaction of Ag were described. The resistivity of the Ag-metallic film was 1.8 μΩ cm, which is quite comparable to those of electroplated Cu films. Initial nucleation and grain growth of Ag were found to be dense and three-dimensional from the AFM analysis and RMS value. It is found that the roughness of the Ag film is reduced to 1.67 μΩ cm with no agglomeration observed. Consequently, it is expected that electroplated Ag films will have the high potential as a next generation interconnection material to replace Cu.

10:45 AM M3.7 AREA-SELECTIVE NUCLEATION OF COPPER ON PHOTO OXIDIZED POLYMIDE SURFACE WITH SINGLE SHOT IRRADIATION OF ArF LASER. Hiroto Teikuni, M Murashita, The Faculty of Engineering of Tokai University, Kanzawa, JAPAN.

Copper nuclei grow on all aromatic polyimide surface in the presence of copper sulfate water solution with only 10min single shot of ArF laser. The sample surface is characterized by pre-photocatalyst deposition UV lamp. All aromatic polyimide which has higher mechanical strength, frame 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 been used for hazing 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 covered with UV light in a nitrogen atmosphere. And we substituted copper atoms with dangling bonds of carbon through the medium of oxygen atoms on the all aromatic polyimide surface. In this study we phased fixed silica glass on the sample surface, and poured the surface water solution into the gap between the silica glass and the sample, forming a thin liquid layer. Then one shot of circuit patterned ArF laser light having 32nm/cm² was irradiated vertically onto the sample. The dissociated 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 with 1ml/min reaction rate. We observed the mirror formed on the surface of the layer, the clear image of the circuit pattern appeared on the exposed area, with the unexposed copper layer 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. Yang, I.-J. Richter, Surface and Microanalysis Science Division, National Institute of Standards and Technology, Gaithersburg, MD; K.A. Briggman, J.C. Stephenson, Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD; G.R. Stafford, T.P. Moffat, 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 as diverse as sensors, 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 octadecanethiol (dOCT), deuterated octadecanethiol dioxid (dODS), and 3-mercapto-1-propensulfonate (MPSA) on noble metal surfaces with vibrational resonant sum frequency generation (VR-SFG). VR-SFG is a surface specific technique that can give vibrational spectra of molecules at liquid/liquid 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 monolayer body was studied via the spectral evolution of the C–O (dOCT and dODS) or C–H (MPSA) stretching modes in VR-SFG spectra. In all cases studied: dOCT and dODS in EtOH on polycrystalline Au, and MPSA in perchlorate on polycrystalline Au and Cyclic voltammetry was found to be Lineweaver-Burke. For dODS and dODS 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 formation of the monolayer. For MPSA, a well ordered alkane thiol layer was found along the whole deposition range. However, the in-situ spectra of the alkanethiol-sulfonate exhibited a significant significance in the alkane body, suggesting that solvation of the charged sulfonate head group drives the order of the wet interface.

11:15 AM M3.9 COPPER ELECTROCHEMICAL PLANARIZATION TECHNOLOGY FOR SUB-MICRON MULTILEVEL MCM-INTERCONNECT. Bao-Xian Jia, National Nano Device Laboratory, Hsinchu, TAIWAN; Shih-Chieh Chang, Ming-Shien Peng, 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 proposed as the first-step CMP of the typical microresist Cu film process to improve 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 particle loss. In this work, a copper electrochemical polishing (ECP) technology involving electropolishing followed by electropolishing was achieved in sub-micron multilevel metallization. Superconformal electropolishing of copper in sub-100 nm vias was obtained by an acid copper electroplating containing chloride (Cl), polyethylene glycol (PEG), and 2-aminoethanol (2ABT). Continuous, a clean and scratch-free surface was electropolished by using phosphoric acid (85% orthophosphoric acid) as the electrolyte. Excellent conformal polishing was obtained under the transport-controlled dissolution at the limiting current and the anodic electrode surfaces 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 Cu dendrites elements existed in the Cu/AgPt interface. Besides the double layer capacitance, the second capacitance was derived from the existence of passivation film. As these analyses, the optimized electrolyte and electropolishing dynamics were exploited. In summary, we successfully demonstrated an integral copper passivation process 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, Li Zhihong and Zhang Diouma, Central South University, Dept. of Metallurgical Science & Engineering, Changsha, P.R. CHINA; Masao Kamiko, Ryouichi Yamamoto, University of Tokyo, Center for Collaborative, Tokyo, JAPAN.

The shape of dendrites is the most important morphological characteristic of electrodeposit particle deposits. It is commonly realized that the dendritic appearance and its expansion can be linked to kinetic diffusion restrictions during electroplating at the top of the dendrite grow faster than other sites in the surface of electrode. However, in this investigation, it is found by the author’s 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 electroplating was elucidated.

11:45 AM M3.11

Many solid reactant reactions occurring in condensed phase electrolytes or ultrahigh vacuum conditions produce uniform and well-controlled surface phases. In contrast, the surface reaction mechanisms that occur at a rate 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 complex 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-sectional, transmission electron microscopy (TEM), high resolution TEM, and ion beam scattering to study the surface instability and Cu2S surface alloying when Cu is exposed to a dilute (~2000ppb) H2S 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 clathrate phase (Cu2S) as identified by X-ray and electron diffraction and direct lattice imaging. In later stages of sulphidation, Cu diffuses through the Cu2S layer leading Kirkendall voids at the Cu/Cu2S interface; also, other Cu and S phases, including sulphides and/or hydroxide hydrates, appear. Surprisingly, for longer times, the Cu2S growth rate is significantly higher for sulphides formed at low RH compared to high RH. TEM revealed that the Cu2S grains at both low and high RH are 10 nm to 50 nm with no apparent preferred orientation. However, the high RH samples exhibit many very different-like structures (50 nm x 75 nm) which tend to be more numerous at higher temperatures and have some grains that span the entire Cu2S layer. In addition, the high RH samples appear to have much sharper boundaries between grains. The core/shell behavior between Cu2S 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.
We studied Au, Cu, and Pb on semiconductor surfaces in situ in the electron microscope with high-angle LUEV as well as on LEED samples. We employed x-ray diffraction and sputtering studies with synchrotron radiation and used also scanning tunneling microscopy in UHV. By electrodeposition, epitaxially oriented islands are formed by the metals in contrast to UHV deposited metals at room temperature. In some cases, e.g., Cu on GaAs(001) and Au electrodeposited on Si(111)-H, (sub)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. Clumsy, C.J., A. Marlar, H. Radisic, Gerko Oskam, and Peter Sebree, 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 mechanisms 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. Hiten M. Kothari, Jay A. Szwiren, 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-preferred growth direction. At the transition, the surface is covered with an ordered nanostructure. The kinetically-controlled growth direction can often be 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 onto 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 [111] orientation, but switches to a [100] orientation after a supercritical 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(110) at pH 12 is covered with a 30 by 100 nm cross-hatched pattern.

4:15 PM M4.7
PREPARATION AND CHARACTERIZATION OF Bi2-Sb2. THIN FILMS WITH PREFERRED ORIENTATION BY ELECTRODEPOSITION. Siyu Ren, Zhongshan Univ, Dept of Physics, Guangzhou, PR CHINA; Li Sun, Chuming Ji, Peter C. Sebree, Johns Hopkins Univ, Dept of MDS&E, Baltimore, MD.

In this paper we report on the growth of Bi2-Sb2 thin films with (012) preferred orientation by electrodeposition. The electrolytes consisted of BiCl3, SbCl5, 0.1 M, EDTA 0.6M, and HCl 2.4 M in aqueous solution, with different ratios of Bi:Sb. The composition of the film varies from pure bismuth to pure antimony (x=0 to 1). The gold films with [111] preferred orientation sputtered on silicon wafer were used as substrates. The voltammetric analysis 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 solution, and have a (012) preferred orientation when the concentration of antimony x is between 0.22 and 1 in bath solution. The composition differences between the bath and the films were different bath composition. The uvd 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 Bougat, Jean-René Cotet, Georges Dénis, Marc Le Rouzic, M. Cecilia Malhami and Alena Perucchi, Cordenons Univ.

Unsupported thin films have been grown from aqueous solutions by two-dimensional polymerization of tin(II) and fluoride, together with some alkali metal ions (Li2+ and Pb2+), and in some cases, also with nitrate ions. This work has established that the membrane structure is due to very efficiently cleared planes that prevent the formation of bonds in the third dimension, and thus imposes a two-dimensional network. The cleavage planes are sheets of stoichiometric lone pairs located on the hybrid orbitals of tin(II). Tin(II) is covalently bonded, as expected with fluoride. The presence of ions M2+, and sometimes nitrate, is necessary to create structures that have lone pairs cluster in sheets, since the clustering is not sheet-like in tin(II) fluoride alone. The presence of foreign ions changes the chemical composition of the membranes, and therefore also some of their properties. The tin(II) lone pairs do 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 reconstituted, sometimes with a change of chemical composition (insertion of nitrate ions, change of M2+/Sn2+ ratio), to give surface areas about 1cm², while their thickness is in the submicron range. Some possess a large intrinsic stress, that is explained by the ferroelectric properties, created by bonding, the symmetry relation, and the proximity of a phase transition.

SESSION M5/A6.6 JOINT SESSION
SELF ASSEMBLY
Chairs: Peter C. Sebree and J. Woods Halley
Wednesday Morning, November 28, 2001
Room 313 (Hyatt)

8:45 AM M5.1/A6.1
METAL NANOWIRES BY ELECTRODEPOSITION. Mike Zach, Einar Walter, Reg Penner, Dept. of Chemistry, University of California, Irvine, CA; Fred Payier, CNRS Montpellier, FRANCE.

Metal nanowires with lengths up to 1.0 mm and diameters ranging from 10 nm to 500 nm have been prepared by electrodeposition. These nanowires are edge-decorated step edge arrays fabricated by photo gratings and seed layers. Nanowire electrodeposition is carried out using either of two related techniques: the electrodeposition of a conductive metal oxide at steps edges, and the subsequent in situ phase transformation of the metal oxide in hydrogen at 550°C (molybdenum, iron, copper). Alternatively, for a few noble metals (palladium, gold), nanowires can be obtained directly by electrodeposition in one step. Electrodeposited metal nanowires may be lifted off the substrate with a hydrophobic film to embed in a polymer film to be decorated with metal nanowires. Electrochemical deposition of nanowires in air can be fabricated with many techniques, including the chemical stability of nanowires in air and in aqueous solutions, the grain structure of metal nanowires, and their electrical and mechanical properties.

9:15 AM M5.2/A6.2
ELECTROCHEMICAL SELF-ASSEMBLY OF Cu/Cu2O NANOWIRES. S. Kenes, L. Piraux, P.C. M., Laboratoire de Physico-Chimie et propriétés des Matériaux de Louvain-la-Neuve, BELGIUM.

Arrays of Cu/Cu2O nanowires were grown by electrodeposition in the nanowires of track-etched polymer membranes. Using appropriate solutions, the electrode potential spontaneously oscillations during the application of a constant cathodic current. The period of these oscillations depends on the applied current density. The composition of the nanowires can be simply controlled by varying the applied current. Nanocomposite of copper and copper oxide is deposited at applied current over which oscillations occur. In contrast, pure Cu or pure Cu2O are obtained at deposition current out of the range of oscillation. Preliminary electrical transport measurements were performed on these Cu/Cu2O nanowires.

9:30 AM M5.3/A6.3
SELF-ASSEMBLY OF Si NANO WIRES ON Pt-COVERED Si(111) SURFACES STUDIED BY SCANNING TUNNELING MICROSCOPY. In-Sook Hwang, Tien-Chia Chang, and Tien T. Tseng, Institute of Physics, Academia Sinica, Nankang, Taipei, Taiwan, R.O.C.

Our previous room temperature study of nucleation and growth of Ge at Pt-covered surfaces indicates that there is a threshold coverage for nucleation of two-dimensional (2D) Ge islands to occur [1]. Below the threshold, Ge atoms and clusters are too mobile for STM to image.
Above the threshold, there is ~0.1 monolayer of Ge atoms moving rapidly on the Pb-covered surface without getting incorporated into existing Pb O 2 islands [1, 2]. Now we study Si deposition on Pb-covered Si(111) surfaces at small temperatures from room temperature to ~250°C. There is also a threshold Si coverage for the nucleation of 2D Si islands (covered with a Pb layer), and the threshold increases with decreasing 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 small temperature. Above the threshold, 2D islands are found along with the Si nanowires. As observed in 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 at the initial stage of surface reconstruction [1]. I.S. Huang, C.-T. Chang, I.-S. Hwang, and T.T. Tsong, Phys. Rev. Lett. 80, 4229 (1998). [2] T.-C. Chiou, L.-C. Hsu, P.C. Sensoy, R.C. Cammisuru, Johns Hopkins Univ, Dep of Materials Science and Engineering, Baltimore, MD; P.M. Vereeken, IBM T.J. Watson Center, Yorktown Heights, NY; C.L. Chien, Johns Hopkins University, Dep of Physics and Astronomy, Baltimore, MD.

ELECTROCHEMICAL DEPOSITION OF FeCo AND FeCoV THIN FILMS AND NANOWIRE ARRAYS. Ingrid Shao, P.C. Sensoy, R.C. Cammisuru, Johns Hopkins Univ, Dep of Materials Science and Engineering, Baltimore, MD. FeCo and FeCoV thin-film deposition processes have been developed to generate desirable magnetic materials. The electrochemical deposition is an important processing technology for microfabrication due to its low cost, high yield, low energy requirements, and capability for generating high-impact-size features. However, electrochemical deposition of FeCo alloys has been problematic over the years due to high deposition stress and brittleness of FeCo alloys. We have successfully produced high-quality FeCoV films from aqueous solution using a rotating disk electrode. Samples (7 mm in diameter and about 25 µm in thickness) were deposited at constant current densities between 5 and 400 mA/cm². Knopp hardness, magnetic hysteresis loops, coercivity, microstructure, and composition of these films were characterized. A saturation magnetization about 21 to 22 kG and coercivity about 10 Oe were typical for these as-deposited films. Vanadium has proved to be the most effective element for improving the ductility and maximality of FeCo alloys in the deposition process. We successfully codeposited small amounts of vanadium with FeCo films to further improve the ductility of these electrodeposited films. Magnetic properties of deposited FeCoV alloys were similar to FeCo films. FeCo nanowire arrays were also deposited in a nanoscopic template electrochemically to study the magnetic shape anisotropy due to the geometry of these FeCo nanowires.

SESSION M6: STRESS EVOLUTION: METAL OXIDES
Chairs: Karl Sieradzki and Robert C. Cammisuru
Room 303 (Hynes)

1:30 PM *M6.1
NOVEL METHODS FOR THE DETERMINATION OF SURFACE STRESSES AND ENERGY OF DEFECTS ON SURFACES IN UHV AND IN ELECTROLYTES. Harold Bache, Institute of Thin Films and Interfaces-IGS 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 now also applied to clean surfaces in vacuum environment. In my 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 nanometric surface stresses. Recent results of the effect of Li adsorption on Mo(110) are shown as an example. Comparison is made to interface charge induced surface stresses in an electrochemical environment. Novel applications of particular concepts to structural model of 2D surface systems have opened the pathway to an intuitive determination of surface defect energies. The step-free energy, e.g., can be obtained from the temperature dependence of the equilibrium shapes of 2D islands on surfaces, or from the observations of the shape fluctuations of islands.

2:00 PM M6,2 SURFACE STRESS AND ITS INFLUENCE ON THIN FILM GROWTH AND ELECTROCAPILLARITY OF SOLID ELECTRODES. R.C. Cammarata, Johns Hopkins University, Department of Materials Science and Engineering and Department of Mechanical Engineering, Baltimore, MD.

Associated with every free solid surface and solid-solid interface are two thermodynamic quantities: the surface free energy and the surface stress. Both of these quantities can strongly affect stress evolution during thin film growth. Recently, a variety of models have been proposed that suggest the surface free energy and surface stress are critical parameters in determining the stress behavior of thin films during the early stage of thin film growth. Examples include the stress evolution during electrodeposition of ultrathin, epitaxial films by underpotential deposition as well as during the early stage of island growth of nonmetallic films produced by physical vapor deposition. A review of recent experimental and theoretical studies of these issues will be presented with particular consideration given to how a correct understanding of the influence of the surface parameters on thin film growth and structure can be used to experimentally obtain values for these surface parameters. In addition, the role surface properties play in the proper interpretation of wafer curvature measurements in electrocapillarity experiments involving solid electrodes will be discussed. The change in surface properties associated with double layer effects and with the potential-induced surface reconstruction in Au(111) will be presented.

2:15 PM M6,3 SURFACE STRESS EVOLUTION DURING UPD. K. Sieradzki, Nicholas Dimitrov, Arizona State University, Tempe, AZ; Cody Friesen, Massachusetts Institute of Technology, Cambridge, MA; Robert Cammarata, Johns Hopkins University, Baltimore, MD.

We develop thermodynamic arguments that describe proper interpretations of wafer curvature experiments that are typically used in electrocapillarity experiments of solid electrodes and stress evolution during underpotential deposition. The sources of stress relate to electrocapillarity differences between overlayer and substrate, interface stress, and coherency stress. Experimental results are presented for the systems Pt/Ag/Au(111), Pt/Ag/Au(111) and Ag/Au(111). We show how it is possible to use the experimental data to extract results for the interface stresses in each of these systems. The following values of interface stress were determined: for the incommensurate systems Au(111) interface, Σ/2 = 0.04 N/m; for the incommensurate Pb/Ag/Au(111) interface, 0.9 ± 0.04 N/m; and for the coherent Ag/Au(111) interface, -0.02 ± 0.04 N/m.

2:30 PM M6,4 STRESS EVOLUTION DURING INTERFACE FORMATION. B.M. Clemens, V. Ramaswamy, W.D. Nie, J.M. Freitag, and B.L. Peterson, Stanford University, Department of Materials Science and Engineering, Stanford, CA.

The stress behavior during the initial stage of growth is influenced by many factors, including coherency stresses, intermixing, and surface or interface effects. In growth of multilayer thin film interfaces these effects can complicate to complex behavior with the magnitude and sign of stress changing from layer to layer even during growth of a single layer. The net average stresses can be large and can strongly affect film crystalline and magnetic properties. Furthermore, stress monitoring is essential for sorting out the origins of this behavior, although at atomic length scales the distinction between interface and bulk stress effects is somewhat arbitrary. We present stress behavior for a variety of metal/metal multilayer systems which illustrate these effects. In growth of Ag on a variety of transition metals we see that the stress behavior can be explained by either changes in surface tension or bulk coherency stress or perhaps both working in concert. We present some evidence for surfactant-driven intermixing in the Ag/Ni system, which has strong implications for some measurements of interface stresses. We also show that intermixing can lead to complex interface stress behavior. For example, in the Mo/Si system, a common system for extreme-ultraviolet lithography mirrors, the intermixing at the interface plays a strong role in the observed large compressive stresses. Lastly, we discuss the effect of surfactant layers on stress and its relationship to growth processes.

3:15 PM M6,5 SELF-CONSISTENT TIGHT BINDING DESCRIPTION OF THIN OXIDE FILMS ON METALS. M. Zhang, J.W. Halley, University of Minnesota, School of Physics and Astronomy, Minneapolis, MN; Patrick Schilling, 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 such systems by use of a simplified but still self-consistent description of the electronic structure, recalculation 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 M6,6 IN SITU X-RAY SPECULAR REFLECTIVITY STUDY OF THE PASSIVE FILMS FORMED ON STAINLESS STEEL. Do Hyung Kim, Hyeon Hwi Lee, Sang Soo Kim, Hycen Chol Kang, Hyo Jung Kim, Do Yong Noh, Kwangju Institute of Science and Technology, Dept of Materials Science and Engineering, Kwangju, KOREA; Hyeon Jung Kim, Dong Ryeol Lee, Sung Shin, Argonne National Laboratory, Advanced Photon Source, IL.

The formation of passive oxide films on stainless steel substrates in a pH 8.4 borate 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 profiles 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 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 M6,7 ANALYSIS OF BARRIER- AND POROUS-TYPE OXIDE LAYERS ON ALUMINUM BY RADIO FREQUENCY GLOW DISCHARGE OPTICAL EMISSION SPECTROSCOPY (RF-GD-OES). R. Kennel-Marcus, Alwyn B. Anfonow, Wisnake Lienawong, Department of Chemistry, Clemson University, Clemson, SC; Patrick Chapon, John-Yeon, Horiba Group, Longjumeau, FRANCE; Tina Harville, John-Yeon, Horiba Group, Edison, NJ; Kenichi Shimizu, University Chemical Laboratory, Keio University, Yokohama, JAPAN.

Oxide layers formed on aluminum surfaces in electrolyte solution are both industrially important and chemically interesting systems. Thin (~10 nm) barrier type aluminum coatings are commonly used as protective layers on aluminum surfaces and as dielectric layers in electronic devices. Much thicker (~5 - 100s of μm) porous-aluminum is used as key layers for organic coatings and separation membranes in many applications. Metals ions are doped within the layers to achieve specific chemical or aesthetic properties. The combination of the fact that these aluminum coatings are electrically insulating and range in thicknesses from micrometers to hundreds of micrometers makes 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 systems. 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 very high rates (0.1-1 μm/min), deep penetration depths (>300 μm), and high depth-resolving powers (>10 μm). 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 dopant layers demonstrated as ~7 μm thick Cr layer located ~15 μm beneath the surface of a barrier-type alumina coating that has a total thickness of 180 μm as shown at the oxide/substrate interface. The second example is a depth profile of a 14 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 has sufficient accuracy to meet all of the demands of promise and flexibility for applications in oxide layer analysis.

4:15 PM M6,8 TITANIUM ELECTROLYTIC CAPACITORS WITH ALKALI EARTH/TITANATE-DOPED TITANIUM DIOXIDE DIELECTRIC. R. Jain, B. Chou, D. McGiver, 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 voltage applied to it. An electrolytic titanium capacitor has a titanium dioxide film that is permanently in contact with an oxidizing electrolyte, enabling self-heating of the dielectric. As a consequence it can perform to higher breakdown voltage than 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 10-200 µC/cm². The present study deals with modification of the dielectric film with metallic elements to further enhance its dielectric constant. The aim is to incorporate certain amount of (nikele-eth) into the titanium dioxide films, so as to modify the film to have high dielectric constants. The effect of doping is analyzed in terms of charge density, leakage current, and dielectric strength.

4:30 PM M6.9
STUDY OF THE ELECTROCHEMICAL REDOX BEHAVIOUR OF THE LEAD AND ITS ALLOYS IN SULPHURIC ACID SOLUTIONS, Viroel Branzoi, Polytechnic Univ. Bucharest, Dept. of Chemical Engineering, Bucharest, ROMANIA; Florin Branzoi, Romanian Academy, Inst. of Physical Chemistry, Florestina Golovici, Lusia Pilin, Polytechnic Univ. of Bucharest, Dept. of Chemical Engineering, Bucharest, ROMANIA.

The use of the potentiodynamic method, the electrochemical redox behaviour of the Pb/PbO/SO₄ system on the lead alloys electrodes in aqueous H₂SO₄ solutions was studied. The potential sweep of the working electrode, given potential range (-1500 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 behaviour parameters were investigated under the various conditions by changing the potential region, sweeping rate, and concentration of an electrolyte. The characteristic of the polarization curves (i.e. shape and height and potential range in which peaks appear), as well as the values of the kinetic parameters determined from such curves, enable conclusions to be drawn concerning the electrochemical characteristics of the Pb/PbO/SO₄ system. The results also provide valuable information in attempts to elucidate the processes taking place at the Pb/H₂SO₄ interface. The mutual electrochemical behaviour of Pb/PbO/SO₄ is discussed in detail. The behaviour of lead and lead alloys during oxygen evolution in H₂SO₄ solution has been studied by electrochemical impedance spectroscopy. A reaction model of anodic processes is presented, which quantitatively fits the experimental data. Lead and lead alloys have been shown that with increasing anodic polarization, first an insulating layer of PbO is formed, then a conductive layer of PbO₂, are successively formed on the electrode. In the PbO₂ potential domain, different crystallographic phases (alp and beta) can be formed, the alpha phase of PbO₂ being in fact a non-stoichiometric alpha-PbO₂ layer, with n = 1.4 - 1.5, i.e., consistent with the Paweł's model of Pb/PbO/SO₄ electrode, and the alpha behaviour appeared to be essentially determined by the electrolysis time. It is in the alpha phase that the layer growth is first controlled by the solid-state diffusion of sulphate ions, and then by a chemical step associated with a charge in charge carriers taking place at the PbO/PbO₂ interface.

4:45 PM P6.10
KINETICS OF PURE ALUMINIUM DISSOLUTION IN PHOSPHORIC ACID SOLUTIONS CONTAINING DIFFERENT PHOSPHORIC ACID SOLUTIONS, Viroel 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) potentialistic and potentiodynamic methods. The addition of different aggressive anions (like Cl, Br, I, SCN ) lead to 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 a thin oxide film changes its properties by acidity of anodic dissolution, being the less resistant the higher the current density. Impedance measurements showed a single capacitive loop in the complex plane plots and one maximum in the phase angle Bode plots at high frequencies. In the mixture phosphoric acid and sodium phosphate, the phosphate ion concentration being maintained constant, the decrease of hydrogen ion concentration down to 0.5 N leads to the decrease 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 corrosion rate and favours the dissolution of the oxide film, in accordance with the Pourbaix diagram. Electrochemical measurements showed that, the organic inhibitors, like as dodecyltrimethylammonium bromide, tetradecyltrimethylammonium bromide and hexadecyltrimethylammonium bromide had good inhibiting properties. It has been assumed that the first stage in the action mechanism of the organic inhibitor in aggressive media is the adsorption onto the metal surface.

SESSION M7: POSTER SESSION

8:00 PM

Exhibition Hall D (Hynes)

M7.1
ELECTRONICS STRUCTURES OF C-V SEMICONDUCTOR SURFACES: Junho Lee, Dept. of Electrical Engineering, Univ of Arkansas, Fayetteville, AR; Sangchun Lee, Inho Son, Dept. of Physics, Kyungnam Univ, Myan, KOREA; Greg J. Salamo, 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 properties of silicon, which have been mostly studied over the last two decades, have been successfully studied for two decades. Most researches in these fields are focused on the electronic structure of GaAs and GaAs. In this paper, we discuss the tight binding model for the electronic structure of silicon. We use the electronic structure of silicon for the materials using the local densities of states (LDOS), the subspace Hamiltonian, and the transfer matrix techniques. From the results, we show that the electronic bands can act as resonant states in the silicon. We show the effects of defects in semiconductor surfaces for the i-i-v materials.

M7.2
XPS STUDY OF H-TERMINATED SILICON SURFACE ANNEALED IN NON-OXIDIZING ATMOSPHERE, Kazuhisa Kurosawa, Junji Tsujiura, Hiroshi Kurokawa, Mitsubishi Electric Corporation, Advanced Technology R&D Center, Hyogo, JAPAN; Kazutoshi Wako, Akinobu Teramoto, Hiroshi Umeda, Mitsubishi Electric Corporation, ULSI Development Center, Hyogo, JAPAN.

Silicon oxide layers grown at low temperature are difficult to grow at high temperature due to 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 with 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 500°C and remains even after thermal oxidation of 2.2 mm 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)most surface were found to desorb at 300°C and 500°C. Dangling bonds generated by hydrogen desorption at 300°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 react with organic contamination in the surface atmosphere to prevent both low temperature growth of silicon oxide and SiC formation.

M7.3
ROUGHNESS IMPROVEMENT OF THIN SO₂/S Interfaces PREPARED BY RADICAL OXYGEN GROWTH TECHNIQUE, Koji Utaka, Masahito Nagamine, Hiroshi Itobi, Corporate Research &
irradiated by UV light. It was used for blurring free mirror of car attachment and the coal application for sterilization. TiO2 coating microspheres show self-cleaning functions which are also "insensitiveincible free" semipermanently. Namely, it generates effects of sterilization and blurring free of TiO2 film. Then, photo-catalytic reaction induced super-hydrophobicity and super-oleophobicity of the TiO2 surface simultaneously. However, it takes a long time for UV irradiation to improve the super-hydrophobic conversion. On the other hand, the blurring-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 blurring free property of amine phase of TiO2 thin film. The sheet electron beam irradiation was homogeneously applied with an electron gun type: CB1715/15/18IL, Energy Science Inc., Woburn, 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 amine phase of TiO2 thin film. Namely, sheet electron beam irradiation increased surface energy of amine phase of TiO2 thin film.

**M7.11**

**ELECTROCHEMICAL GROWTH OF THIN OXIDE FILM ON SINGLE CRYSTALLINE SILICON WAFER.** Chi-Woo Lee, Sang-Eun Bae, In-Cheol 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 physicochemical characteristics for device fabrication have been the main advantageous 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 through interfacial diffusion of oxides 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 motion of O atoms by simple diffusion induced by the presence of surface 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 gate oxide thickness thinner than 3 nm may be recognized. The properties of layer oxide films are known. As compared with the Pd/Pd cluster, electron transfer from the Pd-Au cluster to an adsorbed CO is restrained. The adsorption energy of the Pd-Au clusters is also restrained. We will show whether the effect of the Pd-Au cluster on the surfaces or the electronic effect of the second layer atom is stronger.

**M7.12**

**GROWTH OF BARRIER ANODIC ALUMINUM OXIDE FILMS.** Ura N. Lednik, Vacuum Microelectronic Laboratory, Institute of Electronics, Belarus Academy of Science, BELARUS.

Barrier type anodic aluminum 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 aluminum oxide grow with width depending on the anodization conditions. In this work we have made an attempt to investigate the structure and properties of anodic aluminum oxide in dependence on the electrolyte temperature and to connect critical current density and temperature by relationship. Anodic aluminum oxide films were formed in 0.1 % aqueous solution of citric acid. Anodization was carried out at the constant current and under the constant voltage up to 450 V. Current density was found to decrease with the raise of the temperature. Anodization constant also 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 to oxide with temperature raising. Investigation of chemical stability in strong acids of barrier anodic aluminum 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 values of electrolyte temperature, higher temperature results in the formation of an ideal anodic aluminum oxide (barrier oxide).