

SYMPOSIUM M

Surface Science and Thin-Film Growth in Electrolytes

November 26 – 28, 2001

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* Invited paper

SESSION M1: OVERLAYER GROWTH, SURFACE
MORPHOLOGY AND NANOSTRUCTURING

Chairs: Karl Sieradzki and Peter C. Searson

Monday Morning, November 26, 2001

Room 313 (Hynes)

9:00 AM *M1.1

**MECHANISTIC ASPECTS IN METAL FILM GROWTH -
COMPLICATIONS 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 successfully modelled as a sequence of elementary steps. This is true at least for simple systems, where i) the substrate can be considered as an inert template, ii) strongly adsorbed coadsorbates or anions 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 'unstable' 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 adatoms 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 electrodeposition, e.g., as adsorbed anions, 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

UNDERPOTENTIAL DEPOSITION ON ALLOYS. C. McCall, N. Dimitrov, Karl Sieradzki, Arizona State University, Tempe, AZ.

We present the first results for the underpotential deposition (UPD) of a metal on a foreign metal alloy substrate. This type information provides key insights into the nature of site-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_pAg_{1-p}/Cu^{2+} 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 0.28, and for p less than 0.28 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 average cluster size, 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. Randler 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 phase behavior of electrodeposited monolayers and thin films have been investigated using surface x-ray scattering techniques under in-situ 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 new 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 bcc 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 Angstroms, in agreement with STM measurements of Cu on Ag(100) and Au(100). The x-ray measurements conclusively show that the entire copper film restructures 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.

10:30 AM *M1.4

**STEP AND ISLAND DYNAMICS AT SOLID/LIQUID INTER-
FACES.** Margret Giesen, Sabine Dieluweit, Forschungszentrum
Juelich, Juelich, GERMANY; Dieter M. Kolb, Abt. Elektrochemie,
Universitaet Ulm, Ulm, GERMANY.

During the last decade much effort has been spent to study atomic transport 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 resentment of theorists 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 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 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 ($\sim 10^{16}$ 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 step and island dynamics 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 (preprint available on <http://www.fz-juelich.de/igv/GIESEN/ag-giesen1.htm#Publications>) [2] Phys. Chem. Chem. Phys. 2 (2000) 3675. [3] J. Phys. Condens. Matter 13 (2001) 5009. [4] Surf. Sci., 384 (1997) 168. [5] Electrochim. Acta, 45 (1999) 533. [6] Surf. Sci., 468 (2000) 149. [7] Surf. Sci., to be published.

11:00 AM M1.5

**DECAY OF NANO-FEATURES ON GOLD AND SILVER SINGLE
CRYSTALS IN CONTACT WITH SULFURIC ACID SOLUTION
UNDER THE CONTROL OF POTENTIAL AND TEMPERATURE.**
Nobumitsu Hirai, Shigeta Hara, Osaka Univ, Dept of Materials
Science and Processing, Osaka, JAPAN.

Decay of nano-features located on metal surface gives considerable acknowledges 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 are observed by means of *in-situ* electrochemical AFM (EC-AFM) (1-4). It is found that the area of the top layer of the nano-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 relaxed 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

- (1) N. Ikemiya, M. Nishide, S. Hara, Surf. Sci. 340 (1995) L965.
- (2) N. Hirai, H. Tanaka, S. Hara, Appl. Surf. Sci. 130-132 (1998) 506.
- (3) N. Hirai, K. Watanabe, A. Shiraki, S. Hara, J. Vac. Sci. Technol. B 18 (2000) 7.
- (4) N. Hirai, K. Watanabe, S. Hara, Surf. Sci., in press.

11:15 AM M1.6

**AN ELECTROCHEMICAL AND IN-SITU STM STUDY OF SILVER
DEPOSITION ON MODIFIED GOLD SURFACES.** Maria Jose
Esplandiú, Departamento de Fisicoquímica, Facultad de Ciencias
Químicas, Universidad Nacional de Córdoba, Córdoba, 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 well-defined monolayers on gold and can be functionalized and manipulated according to desired purposes. Aiming at the control of

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 at 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 system. We will report on how the Ag 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 mechanism, the differences with SAM free electrodes and the specific reactivities of metalphilic end groups exposed to the silver electrolyte.

11:30 AM M1.7

Si NANOPARTICLE ELECTROCHEMICAL PLATING. G. Belomoin, A. Smith, S. Chaieb, and M.H. Nayfeh, Depts of Physics, and Theoretical and Applied Mechanics, Univ of Illinois at Urbana-Champaign; Taysir Nayfeh, Industrial Engineering, Cleveland State Univ.

We report on a procedure for delivery 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 on metal or 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 alcohol ions with the silicon particles tagging along as "ligands".

11:45 AM M1.8

TIP INDUCED NANOSTRUCTURING OF AuCu-ALLOYS WITH AN ELECTROCHEMICAL SCANNING TUNNELING MICROSCOPE. Stefan Maupai, Andrea S. Dakkouri, Martin Stratmann, Patrik Schmuki, Dept. of Material Science, LKO, University of Erlangen-Nuremberg, Erlangen, GERMANY.

By tip-induced metal deposition using an EC-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, 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. far 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 AuCu single-crystals of different composition and crystallographic orientation as substrates, opened the possibility to vary the tip-substrate interaction and the influence of adsorbates 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. Ocko
Monday Afternoon, November 26, 2001
Room 313 (Hynes)

1:30 PM *M2.1

Abstract Withdrawn.

2:00 PM *M2.2

COMPOUND FORMATION USING ELECTROCHEMICAL ATOMIC LAYER EPITAXY. John Stickney, Department of Chemistry, University of Georgia, Athens, GA.

The growth of compound semiconductors is being investigated using the electrochemical analog of atomic layer epitaxy (ALE). Initial studies have been on II-VI 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 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 UHV-EC techniques. That is, an electrochemical cell is interfaced directly to a UHV 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. Tiruchirapalli Arunagiri, Thomas Ponnuswamy, 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 electrofilling of damascene features, followed by a chemical mechanical polishing. Ruthenium has almost twice the electrical and thermal conductivities as tantalum and tantalum nitride, i.e. diffusion barriers for 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 CuSO_4 /0.5 M H_2SO_4 . The I-V curve showed a transport-limited growth peak at ca. -175 mV and hydrogen evolution onset occurred around -400 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 heteroepitaxial growth of Cu on Ru with strong Cu(111) texture and no new phase or bimetallic compound formation between the Cu deposit and 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. Takano, National Institute of Science and Technology Policy, Nagata-cho, Chiyoda-ku, Tokyo, JAPAN; Y. Kogure and Masao Doyma, Teikyo University of Science & Technology, Uenohara, Yamanashi, JAPAN.

In the crystal growth from the gas phase, the motion and conversion of ad-atom and their clusters are quite important elementary process. 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 11a, 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). 280 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 moved along different lines, an equi-potential lines were obtained. These calculations were performed for a di-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 an ad-atom along a step 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 II_d (d is the nearest neighbor distance) to II_a and from II_a to II_d 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. Feibelman, 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 decade-long effort to modify thin-film growth by depositing appropriately 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(001), a surface for which Field Ion Microscopy experiments¹ suggest that the low 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 atom on Pt(001) varies linearly with external electric field, changing $\sim 0.1\text{eV}$ per $\text{V}/\text{\AA}$ and increasing for fields oriented to push electrons into the surface. But, with a computed hopping barrier remaining $>0.5\text{ eV}$ higher than that for substitution, the calculations contradict the idea that a change in FIM site visitation at fields of 1.5-2 $\text{V}/\text{\AA}$ and temperatures $\sim 265\text{-}284\text{K}$ 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.

¹G.L. Kellogg, Phys. Rev. Lett. **70**, 1631(1993).

4:00 PM M2.6

A THEORETICAL APPROACH TO THE STUDY OF METALLIC MONOLAYER AND SUBMONOLAYER FILMS. C. Sánchez, S. Dassie, C. Giménez, M.G. Del Pópulo, M. Rojas, E.P.M. Leiva, Unidad de Matemática y Física, Facultad de Ciencias Químicas 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 electrochemists. As an example, we present in this work results for systems containing Ag, Au, Pd, Pt and Cu. By means of these calculations we get information concerning the electronic density changes, the work function Φ and the energetics of the different systems. While Φ is a relevant quantity for the system since it is closely related to the potential of zero charge of electrochemical systems, the relative binding energies are related to the stability of adsorbed monolayers. Computer simulations with an important number of atoms (10^2 - 10^3) 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. 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 2-D 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 heteroepitaxy can be analyzed both thermodynamically and dynamically on these bases.

4:30 PM 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 overlayer phenomena including reconstructions, dislocation phenomena, and surface alloying on hexagonal surfaces. Here I discuss overlayer phenomena on rectangular surfaces using a similar model. Previous analytical solutions of the Frenkel-Kontorova model for rectangular substrates implicitly assume that overlayer atoms continue to grow 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(100), Pt(100) and Ir(100) surfaces reconstruct forming hexagonal top layers. Ag grown on Cu(100) or Ni(100) forms hexagonal layers. Cu on Ni(100) grows pseudomorphically with dislocations with locally hexagonal atomic arrangements. In order to understand and model such phenomena, I reconsider the two-dimensional Frenkel-Kontorova model for a rectangular substrate allowing overlayer atoms 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 overlayer atoms occupying non-favored surface sites. However, the energy due to varying coordination of the overlayer atoms in a square or hexagonal overlayer is a critical additional consideration. For model parameters, I present a phase diagram which has hexagonal as well as rectangular overlayer phases and explains the origins of the experimentally observed phenomena including reconstructions, dislocations, and hexagonal overlayer structures on these surfaces.

4:45 PM M2.8

A DELTA-FUNCTION MODEL OF FACETS AND ITS APPLICATION TO GRAIN-BOUNDARY GROOVING BY SURFACE DIFFUSION. Tinghui Xin, Harris Wong, Louisiana State

Univ, 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 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 grooving by surface diffusion. We consider partially to fully faceted surfaces with different facet orientations and 3, 4, and 6 fold symmetry 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. Penner and Margret Giesen
Tuesday Morning, November 27, 2001
Room 313 (Hynes)

8:30 AM M3.1

SUPERCONFORMAL ELECTRODEPOSITION IN SUBMICRON FEATURES. T.P. Moffat, D. Wheeler, W.H. Huber, 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. For dilute concentration of the catalyst precursor in the electrolyte, local coverage in fine features changes more due to interface area change than by accumulation from the electrolyte, yielding superconformal growth. The model is supported by experiments and simulations of copper deposition in 350-100 nm wide features, helping to explain the influence of adsorbates 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. Magtoto, Jinhong Tong, Chen Wang, Xiaopeng 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 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 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 sulfate formation is not the reason for sulfate adsorption at the substrate surface. The oxidation of the Ti substrate during deposition conditions does not appear to be related to sulfate 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 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(I) precursor, Cu(hexafluoroacetylacetonate)(trimethylvinylsilane), or Cu(hfac)(vtms), surprisingly little of this work has focused on the nucleation and growth of Cu on thin films composed of materials that are candidates for diffusion barriers, 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 260°C) nucleation can be described by well-known kinetic models and it proceeds via "complete condensation", where the nuclei 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 diffusivity for Cu on TiN and TaN surfaces. The implication 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. Gwang-Soo Kim, MIT, Department of Chemical Engineering, Cambridge, MA; Larry Gochberg, Novellus Systems, Inc., San Jose, CA; Klavs 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 that link reactor scale and feature scale of electrodeposition process in a self-consistent 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 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.

Tantalum is among the candidates to serve as both diffusion barrier and adhesion barrier 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-tantalum 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. Joan-Mo Seo, Soo-Kil 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 silicidation. Furthermore it was shown that self-encapsulating 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 organic additives and annealing process was performed at 350°C for 30 minutes in nitrogen atmosphere. Linear sweep voltammetry indicated that Ag electroplating process window was above - 634 mV (vs. SCE). When applied dc potential was - 800 mV, the deposition rate of Ag was about 200 nm/minutes and the resistivity of as-deposited 870 nm thick Ag film was 1.8 $\mu\Omega$ -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 surface 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 as-deposited silver films, which suggests the possibility of in-situ monitoring of RMS using AC impedance analysis. After the annealing process, the resistivity of electroplated silver films was reduced down to 1.67 $\mu\Omega$ -cm and no agglomeration was observed. Conclusively, 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 POLYIMIDE SURFACE WITH SINGLE SHOT IRRADIATION OF ArF LASER. Hiroto Tokunaga, M. Murahara, The Faculty of Engineering of Tokai University, Kanagawa, 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 pre-photooxidation with UV lamp. All aromatic group polyimide has advantages, which are higher mechanical strength, flame 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 polyimides 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 oxidized 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 circuit patterned ArF laser light having 32mJ/cm² was irradiated vertically onto the sample. The dissociated copper atoms form the C-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 24 μ m after immersing the sample into the electroless plating solution for 15 minutes at 60°C. By washing the sample with an ultrasonic washing machine the clear image of the circuit pattern appeared only in the exposed area, with the unexposed copper foils 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, L.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 (dODT), deuterated octadecane disulfide (dODDS), and 3-mercapto-1 propanesulfonate (MPSA) on noble metal surfaces with vibrationally resonant sum frequency generation (VR-SFG). VR-SFG is a surface specific tool that can yield vibrational spectra of molecules at liquid/solid 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 alkane body was studied by in situ monitoring the temporal evolution of the C-D (dODT and dODDS) or C-H (MPSA) stretching modes in VR-SFG spectra. In all cases studied: dODT and dODDS in EtOH on polycrystalline Au, and MPSA in perchlorate on polycrystalline Au and Cu, the uptake of thiol molecules was found to be Langmuir-like. For dODS and dODDS 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 MPSA, it was found that the alkane body was well ordered in an all trans state at all coverages. The ex-situ spectra of the alkanethiol and alkanethiol-sulfonate were quite different. There was little change between the in-situ and ex-situ structures of the alkanethiols. However, the ex-situ spectra of the alkanethiol-sulfonate indicated significant disorder 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 METALLIZATION. Jia-Min Shieh, Bau-Tong Dai, National Nano Device Laboratories, Hsinchu, TAIWAN; Shih-Chieh Chang, Ming-Shiann 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 proposed as the first-step CMP of the typical two-steps Cu-CMP processes to enhance the planarization capability of CMP. Meanwhile, electropolishing also

offer potential advantages of a reduced waste stream, less consumables, no applied pressure to the substrate, and reduced particulate. In this work, a copper electrochemical planarization (ECP) technology involving electroplating followed by electropolishing was achieved in sub-micron multilevel metallization. Superconformal electrodeposition of copper in sub-130 nm vias could be obtained by an acid cupric sulfate electrolyte containing chloride (Cl), polyethylene glycol (PEG), and 2-aminobenzothiazole (2ABT). Continuously, a clean and scratch-free surface was electropolished by using phosphoric acid (85% ortho-phosphoric acid) as the electrolyte. Excellent polishing was obtained under the mass-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 electropolishing 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/H₃PO₄ 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 ELECTRODEPOSITED AT HIGH CURRENT DENSITIES. Guo Xueyi, Liu Zhihong and Zhang Duomo, Central South University, Dept of Metallurgical Science & Engineering, Changsha, P.R. CHINA; Masao Kamiko, Ryoichi Yamamoto, University of Tokyo, Center for Collaborative, Tokyo, JAPAN.

The shape of dendrites is the most important morphological characteristics of electrolytic particle deposits. It is commonly realized that the dendritic appearance and its expansion can be linked to ionic diffusion restrictions during electrodeposition as the top of the dendrite grows 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 electrodeposition 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. Barbour, J.W. Braithwaite, J.P. Sullivan, Sandia National Laboratories, Albuquerque, NM.

Many surface redox reactions occurring in condensed phase electrolytes or ultra-high 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 microscopies. In this study, we have used focused ion beam cross-sectioning, transmission electron microscopy (TEM), high resolution TEM, and ion beam scattering to study the surface instability and Cu-S surface alloying when Cu is exposed to a dilute (~200ppb) 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 chalcocite phase (Cu₂S) as identified by x-ray and electron diffraction and direct lattice imaging. In later stages of sulfidation, Cu diffuses through the Cu₂S layer leaving Kirkendall voids at the Cu/Cu₂S interface; also, other Cu and S phases, including sulfates and/or hydroxide hydrates, appear. Surprisingly, for longer times, the Cu₂S growth rate is significantly higher for sulfides 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 bar or plate-like structures (25 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 connection 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.

SESSION M4: MORPHOLOGY AND STRUCTURE IN ELECTRODEPOSITED THIN FILMS

Chairs: Thomas P. Moffat and Michael Rohwerder

Tuesday Afternoon, November 27, 2001

Room 313 (Hynes)

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 coarsening 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 zone 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 REDISTRIBUTIONS IN ELECTROPLATED Cu FILMS DURING SELF-ANNEALING. Min-Seung 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 are referred to as a microstructural evolution at room temperature. As for the mechanism for this phenomenon, the explicit role of additives in self-annealing has not been understood, while preceded 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/dm²) and film thickness (0.1, 1 μm), and have investigated the impurity distributions. The impurity distributions have been measured just after deposition and after three weeks using secondary ion mass spectrometry (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 and do not act as an important role in triggering 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. Yin-Ping Lee, Ming-Shiann Feng, Institute of Material Science and Engineering, National Chiao Tung University, TAIWAN, ROC; Ming-Shih Tsai, Bau-Tong 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 menthol 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-free 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(001) AND Si(111):H SURFACES. Jörg Zegenhagen, European Synchrotron Radiation Facility ESRF, Grenoble, FRANCE.

We studied Au, Cu, and Pb on semiconductor surfaces in-situ in the electrolyte and in ultra high vacuum (UHV) as well as on air exposed samples. We employed x-ray diffraction and x-ray standing waves 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 films 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. Chunxin Ji, Aleksandar Radisic, Gerko Oskam, and Peter Searson, 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. Hiten 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-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 the 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 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 $\text{Bi}_{1-x}\text{Sb}_x$ THIN FILMS WITH PREFERRED ORIENTATION BY ELECTRODEPOSITION. Shan Ren, Zhongshan Univ, Dept of Physics, Guangzhou, PR CHINA; Li Sun, Chunxing Ji, Peter C. Searson, Johns Hopkins Univ, Dept of MS&E, Baltimore, MD.

In this paper we report on the growth of $\text{Bi}_{1-x}\text{Sb}_x$ thin films with (012) preferred orientation by electrodeposition. The electrolytes consisted of BiCl_3 SbCl_3 0.1M, EDTA 0.03M and HCl 2.4M in aqueous medium, with the different molar ratio of bismuth and antimony. 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 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 solution, and have a (012) preferred orientation when the concentration of antimony x is between 0.22 and 1 in bath solution. The composition difference between the film and the bath varies for the different bath composition. The upd of Bi-Sb monolayer and composition of the monolayer were also studied systematically with XPS.

4:30 PM M4.8

SUPPORTLESS THIN FILM GROWTH OF TIN(II)-CONTAINING FLUORIDE-ION CONDUCTORS FROM AQUEOUS SOLUTIONS.

Frédéric Bouget, Jean-René Cotel, Georges Dénès, Marc Le Rouzès, M. Cecilia Madamba and Alena Peroutka, Concordia Univ, Department of Chemistry and Biochemistry, Laboratory of Solid State Chemistry and Mössbauer Spectroscopy, Laboratories for Inorganic Materials, Montreal, Québec, CANADA.

Unsupported thin films have been grown from aqueous solutions by two-dimensional polymerization of tin(II) and fluorine, together with some alkali metal ions (Sr^{2+} and Pb^{2+}), and in some cases, also with nitrate ions. This work has established that the membrane structure is due to very highly efficient cleavage 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(II). Tin(II) is covalently bonded, as expected with fluorine. 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(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 recrystallized, sometimes with a change of chemical composition (insertion of nitrate ions, change of $\text{M}^{2+}/\text{Sn(II)}$ ratio), to give surface areas about 1cm^2 , while their thickness is in the submicron range. Some possess a large intrinsic stress, that is explained by their ferroelastic properties, created by bonding, the symmetry situation, and the proximity of a phase transition.

SESSION M5/AA6: JOINT SESSION SELF ASSEMBLY

Chairs: Peter C. Searson and J. Woods Halley
Wednesday Morning, November 28, 2001
Room 313 (Hynes)

8:45 AM *M5.1/AA6.1

METAL NANOWIRES BY ELECTRODEPOSITION. Mike Zach, Erich Walter, Reg Penner, Dept. of Chemistry, University of California, Irvine, CA; Fred Favier, 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 obtained by step edge decoration on graphite surfaces. Nanowire electrodeposition is carried out using either of two related procedures: The electrodeposition of a conductive metal oxide at step edges, and the subsequent gas phase reduction of the metal oxide in hydrogen at 500°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 graphite surface by embedding in a polymer film. Topics to be discussed include the kinetics of nanowire growth, the chemical stability of nanowires in air and in aqueous ambients, the grain structure of metal nanowires, and their electrical and mechanical properties.

9:15 AM M5.2/AA6.2

ELECTROCHEMICAL SELF-ASSEMBLY OF $\text{Cu}/\text{Cu}_2\text{O}$ NANOWIRES. S. Kenane, L. Piroux, PCPM, Laboratoire de Physico-Chimie et propriétés des Matériaux de Louvain-la-neuve, BELGIUM.

Arrays of $\text{Cu}/\text{Cu}_2\text{O}$ nanowires were grown by electrodeposition in the nanopores of track-etched polymer membranes. Using appropriate solution, the electrode potential spontaneously oscillates 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 cuprous oxide is deposited at applied current over which oscillations occur. In contrast, pure Cu or pure Cu_2O are obtained at deposition current out of the range of oscillation. Preliminary electrical transport measurements were performed on these $\text{Cu}/\text{Cu}_2\text{O}$ nanowires.

9:30 AM M5.3/AA6.3

SELF-ASSEMBLY OF Si NANOWIRES ON Pb-COVERED Si(111) SURFACES STUDIED BY SCANNING TUNNELING MICROSCOPY. Ing-Shouh Hwang, Tien-Chih Chang, and Tien T. Tsong, Institute of Physics, Academia Sinica, Nankang, Taipei, Taiwan, R.O.C.

Our previous room temperature study of nucleation and growth of Ge at Pb-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 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 $\sim 250^\circ\text{C}$, there is also a threshold Si coverage for the nucleation of 2D Si islands (covered with a Pb layer), and the threshold coverage decreases with the 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, 2D islands are found along with the Si nanowires. We also observed 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 surfactant-mediated epitaxy. [1] I.-S. Hwang, T.-C. Chang, and T.T. Tsong, Phys. Rev. Lett. 80, 4229 (1998). [2] T.-C. Chang, I.-S. Hwang, and T.T. Tsong, Phys. Rev. Lett. 83, 1191 (1999).

9:45 AM M5.4/AA6.4

ELECTROCHEMICAL DEPOSITION OF FeCo AND FeCoV THIN FILMS AND NANOWIRE ARRAYS. Ingrid Shao, P.C. Searson, R.C. Cammarata, Johns Hopkins Univ, Dept of Materials Science and Engineering, Baltimore, MD; P.M. Vereecken, IBM T.J. Watson Center, Yorktown Heights, NY; C.L. Chien, Johns Hopkins University, Dept of Physics and Astronomy, Baltimore, MD.

ELECTROCHEMICAL DEPOSITION OF FECo AND FECoV THIN FILMS AND NANOWIRE ARRAYS Iron-cobalt alloys near the equiatomic composition have superior soft magnetic properties with the highest known saturation magnetization (24 kG), high permeability and low D.C. coercivity. In the field of micro-devices, such as hard disk drives, micro-actuators and micro-inductors, thin film deposition processes have to be developed to generate desirable magnetic materials. Electrochemical deposition is an important processing technology for microfabrication due to its low cost, high yield, low energy requirements, and capability for generating high-aspect-ratio 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 $\text{Fe}_{50}\text{Co}_{50}$ films from an aqueous sulfamate electrolyte with a rotating disk electrode. Samples (7 mm in diameter and about $25\ \mu\text{m}$ in thickness) were deposited at constant current densities between -5 and $-400\ \text{mA}/\text{cm}^2$. Knoop hardness, magnetic hysteresis loops, resistivity, microstructure, and composition of these films were characterized. A saturation magnetization about 21 to 22 kG and coercivity about 10 Oe was typical for these as-deposited films. Vanadium has proved to be the most effective element for improving the ductility and machinability of FeCo alloys in metallurgical processes. We successfully codeposited small amount 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 nanoporous template electrochemically to study the magnetic shape anisotropy due to the geometry of these FeCo nanowires.

10:30 AM *M5.5/AA6.5

SELF-ASSEMBLY FROM SOLUTION AND UNDER ELECTROCHEMICAL CONTROL COMPARED TO MONOLAYER GROWTH BY VAPOUR PHASE DEPOSITION. Michael Rohwerder, Martin Stratmann, Max-Planck-Institut für Eisenforschung, Dept Interface Chemistry and Surface Engineering, Düsseldorf, GERMANY.

Self-Assembly From Solution And Under Electrochemical Control Compared To Monolayer Growth By Vapour Phase Deposition M. Rohwerder, M. Stratmann Max-Planck-Institut für Eisenforschung Dsseldorf, Germany The growth of monolayer films such as thiol or phosphonate self-assembled films is compared for self-assembly from solution under electrochemical control and for deposition from the vapour phase. The growth kinetics and structure formation of thiol monolayers on gold and iron depends strongly on the electrode potential, owing to the interaction of the solvent and solute molecules with the electric field at the interface. The self-assembly is slow at cathodic potentials, where large domains are formed, and is very fast at intermediate and anodic potentials, where the formed domains are quite small. The difference between film formation from solution as compared to adsorption from the gas phase is greatest in the case of thiol self-assembly on iron surfaces. While thiol molecules adsorb readily - though slowly at the necessarily cathodic potentials- on the reduced iron surface, gas phase adsorption results in a cracking of the thiol molecules at the sulphur/carbon link and well-ordered films are not formed. However, when the iron surface is pre-deposited with a monolayer of oxygen or water molecules, thiol monolayer formation occurs also from the vapour phase. This indicates the important role of one of the main differences between the two environments: the presence of the solvent molecules at the surface.

11:00 AM *M5.6/AA6.6

Cu AND Cd UPD-LAYERS ON Pt(533) STUDIED BY XPS, XAS

AND XRD. Hans-Henning Strehblow, Hartmut Prinz, Institut fuer Physikalische Chemie und Elektrochemie, Heinrich-Heine-Universitaet Duesseldorf, GERMANY.

The Pt (533) surface consist of a sequence of 3 atomic rows of Pt in (111) direction followed by a (100) oriented step. Potentiodynamic polarisation curves in Cu_2 containing H_2SO_4 suggest a first decoration of the steps by Cu atoms at $E = 0.63\ \text{V}$ followed by the coverage of the (111) terraces at $E = 0.4\ \text{V}$. The measured charges of both peaks (175 and $581\ \text{mC}/\text{cm}^2$) of the CV yield the expected ratio of 1:3 for the step and terrace sites. Quantitative XPS investigation of emersed Pt electrodes support these results (0.24 and $0.8\ \text{nmole}/\text{cm}^2$). Parallel to Cu a coadsorption of sulphate is found. According to in situ XAS studies the near range order of Cu deposits at the steps ($E = 0.55\ \text{V}$) yields a coordination number 2 for the Cu-Pt ($d = 268\ \text{pm}$) as well as the Cu-Cu distance ($d = 277\ \text{pm}$) and a coordination 1 for the Cu-Pt distance of $d = 464\ \text{pm}$. These results support a linear alignment of the Cu atoms at the edge with a coadsorption of sulphate anions in the energetically preferred angle position as supported by XPS results. The evaluation of XRD truncation rods and their comparison with the data obtained by simulation confirm these results for the long range order structure. For more negative potentials, $E = 0.3\ \text{V}$, with increasing coverage the coordination number of the Cu-Pt and Cu-Cu shells is increasing to 3.2 or 5.8 respectively corresponding to the growth of 2-dimensional islands on the (111) terraces. The adsorption of Cd leads to an alignments at the steps with a coordination number 2 for the first Cd- ($298\ \text{pm}$) and of 1 for the Pt-neighbours ($303\ \text{nm}$) as a consequence of their larger radius with respect to the Pt-substrate.

11:30 AM *M5.7/AA6.7

CYCLIC EVOLUTION OF WATER/OH MOLECULES ON SINGLE-CRYSTAL SURFACE OF RuO_2 : ORIGIN OF ULTRA-CAPACITANCE. H. You, Y.S. Chu, T.E. Lister, W.G. Cullen, Z. Nagy, Argonne National Laboratory, Argonne, IL.

Ruthenium dioxide is a widely used electrode material for industrial applications because its special properties such as ultra- capacitance (approximately 10 times the double-layer capacitance). The origin of the ultra-capacitance, however, has not been understood because the molecular-level surface-structure studies were not available. Our synchrotron surface x-ray scattering technique combined with STM and cyclic voltammetry measurements unveils that the ultra-capacitance is a result of surface redox processes accompanying structure transformations of the surface by adsorption/desorption of the water and OH molecules. Two distinctive cyclic-voltammetry features associated with surface redox processes were observed in NaOH solution on the $\text{RuO}_2(110)$ surface and the corresponding structural models are proposed. Also features associated with surface redox processes of other crystallographic surfaces in basic and also in acidic solutions will be discussed.

SESSION M6: STRESS EVOLUTION: METAL OXIDES

Chairs: Karl Sieradzki and Robert C. Cammarata
Wednesday Afternoon, November 28, 2001
Room 313 (Hynes)

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 Ibach, Institute of Thin Films and Interfaces-ISG 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 vacuum environment. In this 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 anisotropic materials and anisotropic surface stresses. Recent results of the effect of Li-adsorption on $\text{Mo}(110)$ are shown as an example. Comparison is made to interface charge induced surface stresses in an electrochemical environment. Novel applications of particular concepts of statistical mechanics to 2D surface systems have opened the pathway to a quantitative 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

as a function of the island size at an arbitrary temperature. Once the step energy is known, the kink energy can be determined from the mean minimum curvature of the island perimeter at a fixed temperature. The methods will be illustrated with examples from silver, copper and gold surfaces. [1] H. Ibach, Surf. Sci. Rep. 29 (1997) 193. [2] M. Giesen, C. Steimer, H. Ibach, Surf. Sci. 471 (2001) 80. [3] C. Steimer, M. Giesen, L. Verheij, H. Ibach, Phys. Rev. B, in press (2001).

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 nonepitaxial 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 stress behavior 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. Karl Sieradzki, Nikolay 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, $Pb^{2+}/Au(111)$, $Pb^{2+}/Ag(111)$ 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 $Pb/Au(111)$ interface, 1.76 ± 0.04 N/m, for the incommensurate $Pb/Ag(111)$ 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. Nix, 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 conspire to give complex behavior with the magnitude and sign of stress changing from layer to layer or even during growth of a single layer. The net average stresses can be large and can strongly affect film stability and magnetic properties. In-situ 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 surface-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, important for extreme ultra-violet 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. Min Zhuang, 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 such systems by use of a simplified but still self consistent treatment 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 M6.6

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 Ryeol Lee, Sunil K. Sinha, 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 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 M6.7

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. Anfone, Wandee Luesaiwong, Department of Chemistry, Clemson University, Clemson, SC; Patrick Chapon, Jobin-Yvon, Horiba Group, Longjumea, FRANCE; Tina Harville, Jobin-Yvon, 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 ($<1 \mu\text{m}$) barrier-type alumina coatings are commonly used as protective layers on aluminum surfaces and as dielectric layers in electronic devices. Much thicker (5 - 100s of μm) porous-type alumina is used as keying layers for organic coatings and separation membranes. In many applications, metal ions are doped within the layers to achieve specific chemical or esthetic properties. The combination of the fact that these alumina coatings are electrically insulating and range in depths 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 arenas. 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 $\mu\text{m}/\text{min}$), deep penetration depths ($>300 \mu\text{m}$), and high depth-resolving powers ($\sim 10 \text{ nm}$). The utility of the rf-GD-OES method is demonstrated in the analyses of both barrier and porous-type coatings. In the first case, the ability to distinguish very thin dopant layers is demonstrated as an $\sim 7 \text{ nm}$ thick Cr layer located $\sim 15 \text{ nm}$ beneath the surface of a barrier-type alumina coating that has a total thickness of 180 nm as shown at the oxide/metal interface. The second example is a depth profile of a 10 μm thick porous alumina 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 presented after the evolution of the Ni coating. It is believed that the rf-GD-OES technique offers a great deal 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. McGervey, G. Welsch, 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. 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 breakdown voltage than (ceramic) capacitors that are without any electrolyte. The titanium dioxide dielectric film of electrolytic titanium capacitors has dielectric strength of 0.75 V/nm and charge storage capacity of 10-200 $\mu\text{C}/\text{cm}^2$. The present study deals with modifying the dielectric by doping it with alkali earth elements to further enhance its dielectric constant. The aim is to incorporate certain amount of (alkali-earth) titanates into the titanium dioxide thin film, as they are known 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. Viorel Branzoi, Polytechnic Univ. of Bucharest, Dept. of Chemical Engineering, Bucharest, ROMANIA; Florina Branzoi, Romanian Academy, Inst. of Physical Chemistry; Florentina Golgovici, Luisa Pilan, Polytechnic Univ. of Bucharest, Dept. of Chemical Engineering, Bucharest, ROMANIA.

Using the potentiodynamic 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 electrode, within given potentials ranges (i.e. -1200mV to -800mV; 800mV to 1600mV and -1200mV to 1600mV), 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 has been investigated under the various conditions by changing the potential region, sweeping rate, and concentration of an electrolyte. The characteristics 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_n(1.2)/PbSO₄ 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_n(1.2)/PbSO₄ is discussed in detail. The behaviour of lead and lead alloys anodes during oxygen evolution in H₂SO₄ concentrated solutions 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 anodes have been shown that with increasing anodic polarization, first an insulating layer of PbSO₄, then a conductive layer of PbO₂, are successively formed on the electrode. In the PbO₂ potential domain, different crystalline phases (alpha and beta) can be formed, the alpha phase of PbO₂ being in fact a non-stoichiometric alpha-PbO₂ layer, with $n=1.4-2$). The impedance data were consistent with the Pavlov's model of Pb/PbO_n/PbSO₄ electrode, and the anode behaviour appeared to be essentially determined by the electrolysis time. It has been shown that the layer growth is first controlled by the solid state diffusion of sulphate ions, and then by a chemical step associated with a change in charge carriers taking place at the PbO_n/PbSO₄ interface.

4:45 PM M6.10

KINETICS OF PURE ALUMINIUM DISSOLUTION IN PHOSPHORIC ACID SOLUTIONS CONTAINING DIFFERENT AGGRESSIVE ANIONS AND ORGANIC INHIBITORS. Viorel Branzoi, Florentina Golgovici, Dept of Chemical Engineering, University Polytechnic of Bucharest, Bucharest, ROMANIA; Florina 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 as 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 an oxide film which changes its properties with current density of anodic dissolution, being the less resistive 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 hydrogen ion concentration) leads to the increase of the corrosion rate and favours the dissolution of the oxide film, in according to 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. Physical (electrostatic) adsorption and chemisorption are the principal types of interaction between the organic inhibitor and the metal surface. The best efficiencies appear to be obtained at concentrations around the critical micelle concentration (CMC). The adsorption of the organic inhibitor prevents the adsorption of aggressive anions and the destruction of the aluminium oxide layer.

SESSION M7: POSTER SESSION

Chairs: Dieter M. Kolb, Benjamin M. Ocko, Peter C. Searson and Karl Sieradzki
Wednesday Evening, November 28, 2001
8:00 PM
Exhibition Hall D (Hynes)

M7.1

ELECTRONICS STRUCTURES OF III-V SEMICONDUCTOR SURFACES. Junho Lee, Dept of Electrical Engineering, Univ of Arkansas, Fayetteville, AR; Sangchan Lee, Inho Sohn, Dept of Physics, Kyungham Univ, Masan, 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 and interfaces physics have especially been carefully studied for two decades. Most researches in these fields are focused on the electronic structure of Si and GaAs. In this paper, we drive and study ideal (111) surfaces for iii-v materials (GaAs, GaP, InP, and InAs) using the empirical tight binding method. Using this method, we have determined nine fitting parameters that describe the potential with "s*" in the first nearest neighbor sp³s* model fitting the band structure. We calculate the electronic structure of ideal (111) surfaces for these 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 references to investigate reconstruction, relaxation, or any defects of semiconductor surfaces for the iii-v materials.

M7.2

XPS STUDY OF H-TERMINATED SILICON SURFACE ANNEALED IN NON-OXIDIZING ATMOSPHERE.

Kazumasa Kawase, Junji Tanimura, Hiroshi Kurokawa, Mitsubishi Electric Corporation, Advanced Technology R&D Center, Hyogo, JAPAN; Kazutoshi Wakao, Akinobu Teramoto, Hiroshi Umeda, Mitsubishi Electric Corporation, ULSI Development Center, Hyogo, JAPAN.

Silicon oxide layers grown at low temperature during temperature rising 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 rather 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 than 500°C and remains even after thermal oxidation of 2.2 nm 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 organic contamination-free Si surface and atmosphere to prevent both low temperature growth of silicon oxide and SiC formation.

M7.3

ROUGHNESS IMPROVEMENT OF THIN SiO₂/Si INTERFACES PREPARED BY RADICAL OXYGEN GROWTH TECHNIQUE.
Koji Usuda, Makoto Nagamine, Hitoshi Itoh, 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 radical oxidation method has several advantages compared with conventional thermally grown film, such as a lower process temperature, higher oxide growth rate, etc. (1). These advantages are thought to derive from the radical oxygen reaction (O*) on the Si surface. To investigate the advantage of the radical oxygen reaction on the Si surface, characterization of both radical 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 radical SiO₂/Si interface decreased monotonically with thicker oxidation, and was superior to that attainable with conventional dry oxides. Atomic order steps & terraces emerged on interfaces with bilayer steps of 0.3 nm in height for Si(111), and single steps of 1.4 nm in height for Si(001), after the radical oxidation. Furthermore, we investigated other SiO₂/Si interfaces that were grown directly on an atomically 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 radical 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 radical 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. Satake, and A. Toriumi, IEDM Tech. Dig. (1998) 593.

M7.4

Abstract Withdrawn.

M7.5

THEORETICAL STUDY ON THE ELECTRONIC STRUCTURE OF Pd MONOLAYER ON Au ELECTRODE. Minoru Miyakoshi, Tsukuru Ohwaki, Koichi Yamashita, The Univ of Tokyo, Graduate School of Engineering, Tokyo, JAPAN.

We have studied theoretically the electronic structure of a Pd monolayer on Au(111) and Pd(111) electrode surfaces by using 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 B3LYP, 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 Pd-Au clusters are more positive than that of the Pd-Pd cluster. 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 are also restrained. We will show whether the effect of the bond length difference 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 Izaki, Ryusuke Osada, Youichiro Asou, Toho University, Department of Chemistry, Funabashi, JAPAN; Takashi Mochizuki, Sanshin 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 sulfate solutions. Interference colors of the films were found to depend dominantly on applied voltage. Analysis of the oxidized niobium films by means of SEM, EPMA, 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. Kazuya Oguri, Yasunori Isogai, Rie Fujii, Akira Tonegawa, Yoshitake Nishi, Tokai Univ, Dept of Materials Science, Kanagawa, JAPAN.

Photo-catalytic reaction is well known on the TiO₂ film surface

irradiated by UV light. It was been applied for blur free mirror of car attachment and the toiletry application for sterilization. TiO₂ coating materials show self cleaning functions which are also "maintenance free" semipermanently. Namely, it generates effects of sterilization and blur free of TiO₂ film. Then, photo-catalytic reaction induced super-hydrophilic and super-oleophilic 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 misting-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 blur free property of anatase phase of TiO₂ thin film. The sheet electron beam irradiation was homogeneously applied by an electron curtain processor (Type: CBI175/15/180L, 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 anatase phase of TiO₂ thin film. Namely, sheet electron beam irradiation increased surface energy of anatase 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, Choongnam, 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) inward interstitial diffusion of oxidants 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 network defects near the external surface. As planar intergrated circuit dimensions have been reduced, the gate oxide thickness has also been reduced. It has been predicted that gate oxide thickness as thin as 3.4 nm or 3.0 nm will be recognized when horizontal dimensions reach 0.1 micro meter. 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 to be introduced by two wet cleaning procedures. Despite the important relevance in device fabrication, the wet oxidation process of silicon wafer 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 aqueous as well as non-aqueous solutions under inert and reactive atmospheres. In this work we would like to present the similarities and differences between the electrochemically and thermally grown silicon oxides and among the anodic oxides.

M7.12

GROWTH OF BARRIER ANODIC ALUMINIUM OXIDE FILMS. Ura N. Lednik, Vacuum Microelectronic 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 alumina grow with the rate depending on the anodization conditions. In this work we have made an attempt to investigate the structure and properties of anodic aluminium oxide in 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 constant also decreases with the electrolyte temperature increasing and reaches 1.3 nm/V. This confirms our assumption about decreasing of amount of interstitial impurities from electrolyte 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 unporous anodic aluminium oxide (barrier oxide).

