

SYMPOSIUM S

Fundamental Studies of Corrosion and Oxidation

April 17 – 19, 2001

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* Invited paper

8:30 AM *S1.1

OXYGEN VACANCY GENERATION IN AMORPHOUS ALUMINUM OXIDE FILMS AND THEIR IMPACT ON LOCALIZED CORROSION. K.R. Zavadil, J.C. Barbour, J.P. Sullivan and F.D. Wall, Sandia National Laboratories, Albuquerque, NM.

Defects in passive oxides on active metal surfaces are invoked in several models to explain susceptibility for localized corrosion. For example, the role of oxygen vacancies is considered to be stabilizing in the point defect model and de-stabilizing in a general electrode kinetic model. One approach to defining the role of vacancies is to generate a tailored oxide that mimics the native oxide, incorporate an O vacancy population, and explore the resulting electrochemical impact.

Amorphous aluminum oxide thin films are generated by exposure of Al to an O₂ plasma either during or after Al deposition. Oxygen vacancies are generated using electron stimulated desorption of oxygen in an ultrahigh vacuum environment. The resulting film properties are tracked using a combination of core level and valence band photoelectron spectroscopies and DC conductivity. We find that electron fluences of up to 10²² mC/cm² are sufficient for defect generation avoiding vacancy coalescence and metal Al cluster formation. Immersion of defective films in de-aerated water or 50 mM NaCl, in the time frame of our electrochemical measurements, show that the primary film composition change is a reversible uptake of hydroxide originally lost from the surface and bulk of the film during electron irradiation. Photoelectron emission shows that the original electronic state (Fermi level) of the surface is also restored with immersion. Voltammetry shows a decrease in the stable pitting potential in 50 mM NaCl with vacancy incorporation. Our results indicate that O vacancies distributed through the bulk of the oxide film destabilize the film toward pitting, in contrast to their anticipated role in the point defect model. The fate of vacancies in solution and alternate anion occupation of these defects will be discussed. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. Department of Energy under contract DE-AC04-94AL85000.

9:00 AM S1.2

CORROSION FAILURE OF COLUMNAR TIN LAYER BY ENHANCED ANODIC OXIDATION. Sergei Rudenja, University of Illinois, Materials Research Laboratory, Urbana, IL; Priit Kulu, Tallinn Technical University, Department of Materials Technology, Tallinn, ESTONIA; Valdek Mikli, Tallinn Technical University, Centre for Materials Research, Tallinn, ESTONIA.

The passivity and anodic oxidation of TiN layers have been studied by potentiodynamic polarization, cyclic voltammetry and capacitance measurements. TiN layers were deposited by arc ion plating on AISI304 stainless steel and glass substrates. The morphology and structure of the layers were studied with XRD and SEM. The chemical composition of the TiN layer surface was analyzed by XPS, whereas the occurrence of weak grain boundaries in the structure was verified with TEM. The TiN layers were a highly textured along [111] direction with a close-packed lamellar columnar structure. An exposure of TiN to aqueous electrolyte produces passive films on the surface already at potentials close to equilibrium. The passivity of titanium nitride is extending up to 1.3 V/SHE of anodic potential, however above this potential the stability of titanium nitride is undermined by higher oxidation rate. Loose columnar structure of the layer, weak grain boundaries and structural defects may enhance the oxidation towards the substrate. Although TiN layer possesses a relatively high barrier properties, associated with high polarization resistance and low passivity current, a rapid oxidation and/or breakdown of passivity occurs at anodic potential above 1.2 V/SHE. A direct evidence of the enhanced oxidation is also provided by capacitance measurements. The oxidation rate of TiN was found to be 2.4 nm/V at anodic potentials below 1.3 V/SHE and 17.7 nm/V at the higher potentials. A similar pattern of the oxidation behaviour was assessed from the XPS studies. In spite of the apparent close-packed structure of the layer, the chemical etching of the layer revealed a selective dissolution of TiN taking place at the grain boundaries, which may imply a prospective breakdown of the barrier properties of the layer during anodic oxidation. The TiN oxidation behavior and its influence on barrier properties of the layer will be discussed.

9:15 AM S1.3

Abstract Withdrawn.

9:30 AM *S1.4

COMPUTER MODELLING OF CORROSION. R.I. Eglitis^{1,2}, M.R. Philpott^{2,3}, S.V. Izvekov^{2,4}. ¹University of Osnabrueck, Fachbereich

Physik, Osnabrueck, GERMANY. ²Institute of Materials Research and Engineering (IMRE), SINGAPORE. ³Dept. of Materials Science, NUS, SINGAPORE. ⁴Dept. of Chemistry, University of Utah, UT.

In order to inhibit corrosion, it is extremely important to understand the fundamental mechanisms involved in it. The dissolution of metals is an important step in corrosion. Taking into account an increase of the predictive power of first-principles quantum electronic structure calculations due to increased abilities of computers and recent developments of a new and powerful computational methods that allow one to model basic aspects of corrosion processes, we have explored features of the potential energy surface (PES) of a metal atom (ion) leaving a hydrated metal surface using a model that retains the key physics of the dissolution process. In a separate calculations aspects of dissolution/deposition dynamics are followed using *ab initio* molecular dynamics. Scenarios for dissolution include adatom detaching from kink, step or terrace site of light metals. Comparison of processes on the pure (001) and (111) surfaces is presented, as well as for additional atom in the (001) surface plane.

10:30 AM *S1.5

INTERACTIONS AMONG LOCALIZED CORROSION SITES: EXPERIMENTS AND MODELING. J.R. Scully, N.D. Budiansky, Department of MS&E, University of Virginia, Charlottesville, VA; T.T. Lunt, J.L. Hudson, Chemical Engineering Department, University of Virginia, Charlottesville, VA; A.S. Mikhailov, Fritz-Haber-Institut, Berlin, GERMANY.

The possibility of spatial and temporal interactions between localized corrosion sites has been recognized for many years, but not often quantified. Moreover, the development of spatial patterns of corrosion damage remains poorly explained. Interactions among local pit sites were investigated using both 5x5 arrays of 25 electrodes and 5x20 arrays of 100 electrodes. Each consisted of closely spaced, flush-mounted 316 stainless steel wires exposed in dilute NaCl solutions. Experiments were performed under both open circuit and potential controlled conditions. Three types of interactions occurred when actively corroding pits existed while the remaining electrodes were initially passive in dilute NaCl solution. Inhibition of pitting occurred on electrodes near pre-existing pits due to either ohmic potential drop (at applied anodic potentials), or cathodic polarization (at open circuit). Enhancement of pitting at initially passive electrodes was observed due to both alternations in the local solution composition and the damaging effect(s) of solution composition on nearby, initially passive surfaces. Each of these effects exhibited different periods of persistency after pit deactivation and could operate over different length scales. The 5x20 array of 100 electrodes enhanced experimental examination of pitting behavior at distances over which such interactions occurred. A phenomenological model was developed which incorporated these features and helped explained at least one type of pitting damage pattern.

11:00 AM S1.6

EVALUATION OF MECHANISMS FOR ATMOSPHERIC SULFIDATION OF Cu. J.C. Barbour, J.W. Braithwaite, J.P. Sullivan, N. Missert, A.F. Wright and K.R. Zavadil; Sandia National Laboratories, Albuquerque, NM.

An important aspect to determine the reliability of electronic components is a physics-based understanding of Cu corrosion mechanisms. The approaches being examined in this work are: 1) parallel microscopic experimentation to test rates for copper sulfidation in varying relative-humidity air environments, and 2) *ab initio* modeling to calculate activation energies for diffusion in Cu oxides and sulfides. Low energy ions from an oxygen plasma are used to grow metal oxide passivation layers. Ion implantation is used to create elevated point defect concentrations and for local modification of the composition in order to evaluate these effects on product layer growth. During accelerated aging, copper was exposed to sulfidizing environments (100-600 ppb H₂S in 0-85% RH air) in a matrix experiment to determine independent and synergistic effects of initial Cu oxide thickness and point defect density. This combination revealed the importance of oxide quality in passivating Cu. A Cu₂O layer reacts to form Cu₂S, while different thicknesses of CuO stop the reaction. For the native copper oxide (Cu₂O), *ab-initio* density-functional modeling of Cu vacancy and divacancy binding energies suggests that alloying with In or Al causes vacancy trapping and possibly slows copper sulfidation. Experimental verification of the effect of In and Al alloying was done with near surface implantation followed by sulfidation. The sulfidation rate of alloyed samples was decreased relative to that of control samples. A marker experiment for unalloyed Cu identifies Cu from the substrate as the dominant "moving" species during sulfidation rather than sulfur from the atmosphere.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

11:15 AM S1.7

EFFECT OF INHIBITOR IONS ON THE DISSOLUTION OF SURFACE INTERMETALLICS ON Al 2024-T3 ALLOY. Artur Kolics, Amy S. Besing, Andrzej Wiecekowi, University of Illinois, Dept of Chemistry, Urbana, IL.

The presence of surface heterogeneities on the Al 2024 surface induces a strong susceptibility toward local corrosion. To inhibit the corrosion of these alloys, an inhibitor is required that will prevent local dissolution and cathodic reactions at the intermetallics as well as contribute an inhibitive action on the bulk matrix. So far chromate is the best inhibitor, but a replacement is needed because of its health hazards and environmentally unfriendly characteristics. Cerium has been considered to be the best candidate for chromate replacement. Using Auger electron, X-ray photoelectron, and energy dispersive X-ray spectroscopic, as well as scanning electron microscopic techniques, we have studied the interaction of inhibitor ions with surface intermetallics on Al 2024-T3 in NaCl media under open circuit conditions at pH = 3 and 6. To provide a comparative analysis, the dealloying of the surface intermetallics was studied in inhibitor-free sodium chloride solutions under the same conditions. In acidic NaCl solution S-phase particles undergo bulk dealloying through preferential dissolution of magnesium and aluminum, which leaves the particles enriched in copper. Copper enrichment is also observed on the bulk matrix. In both acidic and near neutral solutions, we found that chromate deposited on the entire surface with the extent of deposition increasing in the following order: bulk matrix < (Cu,Fe,Mn)Al₆ intermetallics < S-phase particles. Chromate developed a smooth surface layer on the both intermetallics and inhibited the matrix dissolution as well as the copper redeposition. In contrast, cerium deposition in pH = 3.0 NaCl solution was found to be a more site-dependent process. After 45 minutes of solution exposure, cerium deposition was the highest on the anodic intermetallics, significantly lower on the cathodic ones, and almost non-existent on the bulk matrix.

11:30 AM S1.8

CORROSION PROTECTION OF STEEL USING CONDUCTING POLYMER. Chan Sup Park*, Jung Il Lee**, Lei Yu**, Kwon Woo Shin**, Chan Eon Park**. *Surface Treatment Research, Technical Research Laboratories, Pohang Iron & Steel Co., Pohang, KOREA; **Polymer Research Institute, Dept of Chemical Engineering, Div of Electrical & Computer Engineering, Pohang Univ of Science & Technology, Pohang, KOREA.

Zinc or chromium compounds have been used for corrosion protection of steel. However, zinc or chromium compounds is needed to be replaced with alternative materials because of environmental and health concerns. Polyaniline is a most suitable conductive polymer due to its stability in air, easy of preparing and special chemical and electrochemical properties. Polyaniline has been chemically synthesized using ammonium persulfate oxidant. Chemically synthesized undoped polyaniline in NMP and camphor sulfonic acid doped polyaniline in m-Cresol has been coated on steel, and then commercial paint has been topcoated to avoid pinhole effect. Then corrosion has been tested in 0.1M HCl and 3.5wt% NaCl with a 0.6mm hole. Corrosion behavior has been studied using potentiodynamic method and Tafel method. Undoped polyaniline has been effective in 0.1M HCl solution for 20 days since undoped polyaniline can be doped in 0.1M HCl solution, and more effective in 3.5wt% NaCl solution and salt spray test. Doped polyaniline and polyaniline synthesized electrochemically have been effective more than 20 days in 0.1M HCl solution. But it has not been effective in 3.5wt% NaCl solution. The exposed hole in corrosion environment has been examined to analyze the formation of passive oxide layer (Fe₂O₃) using ESCA. Water-dispersed polyaniline has been prepared to apply the polyaniline to steel substrate in aqueous solution. Water-dispersed polyaniline has been synthesized using ammonium persulfate oxidant and sodium dodecylsulfate as a surfactant and mixed with various binders such as water-soluble polyacrylates to improve coating characteristics. The polymerization of water-dispersed polyaniline has been monitored by UV-VIS spectroscopy and open-circuit-potential measurement. The size and shape of water-dispersed polyaniline have been investigated by TEM.

11:45 AM S1.9

LOCALIZED CORROSION RESISTANCE OF HIGH NITROGEN AND HIGH CHROMIUM BEARING STAINLESS STEELS. Youngsik Kim, Andong National University, School of MS&E, Andong, KOREA; Hyunyoung Chang, Gon Hwangbo, Sungho Hong, Power Engineering Research Institute, KOPEC, Yongin, KOREA.

This paper focused the effect of Cr content on the corrosion resistance of high nitrogen bearing austenitic stainless steels. Chromium is one of beneficial elements for improving corrosion resistance. This was proven in the PRE equation of %Cr 3.3%Mo 30%N. However, high

chromium in Fe-base alloys can make the hazardous phase as like sigma phase to deteriorate mechanical properties and corrosion resistance. 3 stainless steels - 25%Cr, 31%Cr, 36%Cr - were used. Microstructure, pitting resistance (chemical and electrochemical tests), anodic polarization test were performed. High chromium improved the resistance to localized corrosion, but extremely high chromium reduced the corrosion resistance inversely. This behavior was related to the formation of sigma phase which it decreased the effective chromium content in matrix. Also, corrosion resistance of high nitrogen stainless steel was due to the stability of passive film. Passive film was composed of high chromium and high nitrogen. Nitrogen existed as atomic nitrogen, nitric oxide, nitro-oxyanions (NO_x-) and N-H species, not nitride in the passive film. The enriched atomic nitrogen acts as a reservoir, and N-H species buffer the pH of the film and facilitate the formation of oxyanions in the film. Oxyanions improve the cation selectivity of the film in chloride solutions. NO_x- acts as a strong inhibitor in both film and active sites and facilitates the formation of chromium oxide.

SESSION S2: CORROSION STUDIES USING NOVEL TECHNIQUES AND SYSTEMS

Chairs: Frederick Doug Wall and John Robert Scully
Tuesday Afternoon, April 17, 2001
Salon 12 (Marriott)

1:30 PM *S2.1

CORROSION STUDIES USING XPS/AES WITH ELECTROCHEMICAL SIDE-CELL. Charles F. Windisch, Jr., Donald R. Baer, Mark H. Engelhard, Russell H. Jones, Pacific Northwest National Laboratory, Richland, WA.

Electrochemical corrosion studies are often limited by the difficulty in spectroscopically analyzing corrosion products prior to exposure to atmospheric conditions. One way to minimize this exposure is to connect the spectrometer to an electrochemical "side-cell" via a UHV transfer system. An XPS/AES system at the Pacific Northwest National Laboratory (PNNL) equipped with such a side-cell has facilitated the characterization of corrosion mechanisms in several important systems including IGSCC of Ni, Fe, steel, and, most recently, Al. The XPS data on samples treated in the side-cell have helped explain the role of impurities such as S and P (in Ni and Fe) and alloying agents such as Mg and Cu (in Al) on corrosion in various aqueous electrolytes. Depth profiles, including information on oxidation states as a function of depth, have helped quantify corrosion film thickness (without the ambiguity of how exposure to atmospheric oxygen influences the thickness) and composition as a function of thickness. Ion-implanted samples, which contain an impurity selectively introduced within the surface region of the metal, have been especially useful in studies of synergistic effects (e.g. involving the metal and the impurity) when used in conjunction with the electrochemical side-cell. The instrumental setup at PNNL will be described and several examples of experiments that used this system to determine corrosion mechanisms will be discussed. Advantages and limitations of UHV transfer of samples will be explored in detail. This work was sponsored by the Materials Science Division of the Office of Basic Energy Science, USDOE. Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the USDOE under Contract No. DE-AC06-76RLO1830.

2:00 PM S2.2

ELECTROCHEMICAL CORROSION STUDY OF HIGH COERCIVITY Co-Sm THIN FILMS WITH SILICON NITRIDE PROTECTIVE LAYER. Iulica Zana and Giovanni Zangari, The University of Alabama, Dept of Metallurgical and Material Engineering, Tuscaloosa, AL.

Due to their high anisotropy and high coercivity, CoSm alloys are potential candidates for ultra-high density recording media. The presence of Sm in the alloy however rises concerns over its corrosion resistance and environmental stability. A set of samples with different Cr underlayer thicknesses (20 to 100 nm) but with fixed CoSm thickness (16 nm) was intentionally left unprotected in laboratory condition. Saturation magnetization was periodically measured by AGM and the increase in its decay rates for films on thinner underlayer were related to a larger surface area of the film, as determined by topography measurements carried out by AFM. In order to evaluate the reliability of disk structures comprising a CoSm alloy, we used electrochemical methods to investigate the corrosion resistance of glass/Cr(60nm)/CoSm(16nm)/Si₃N₄(x nm) with x=2-8 nm multilayer films and compare it to that of conventional thin film media (CoPt). The samples were subjected to anodic polarization and corrosion tests in (a) 0.25M NaCl and (b) 0.25M Na₂SO₄ electrolytes at various pHs. As the thickness of Si₃N₄ increases, the corrosion potential is shifting to higher values accompanied by a decrease in the corrosion current density. This suggests an

improvement in the corrosion resistance with increasing Si₃N₄ thickness. SEM investigations showed pits on the sample surface (Si₃N₄ = 2 nm) formed during anodic polarization. Pitting corrosion potentials are much higher than the values usually observed for Co and its alloys. XPS was employed to characterize the surface before and after various experiments. The evolution of Co 2p and Sm 3d peaks were monitored in order to evaluate the protective quality of Si₃N₄ overcoat. We conclude that Si₃N₄ protective layers down to 6 nm thickness are able to avoid interactions between the environment and the magnetic layer, thus increasing reliability.

2:15 PM S2.3

HOW THICK IS MY OXIDE? David Allred, Matthew B. Squires, Joseph Choi, Cort Johnson, Douglas Markos, Yenny Martinez, and Michael Newey, Brigham Young University, Dept of Physics and Astronomy, Provo, UT.

After a thin film is deposited it is frequently removed from the deposition system exposing it to air. It is then subject to oxidation on its top surface. How thick is the oxide on this sample? This is a question that the technologist who prepared the film is frequently asked, sooner or later after she has taken the film out, particularly when it is to be used in an application for which the presence of an oxide layer even an ultrathin one is important. Our EUV optics deposition group labors in an area where the thickness of ultrathin post deposition films is extremely important. The reflectance, transmittance and absorbance of most materials changes noticeably with the addition of each 0.1 nm of oxide. This has dramatic effects on the properties of optical films for EUV applications. We have looked for a single or set of papers which would help us answer such questions for materials of interest for the extreme ultraviolet (EUV or XUV) community. Since they couldn't be found, although exist we undertook to study the oxidation and oxyhydration of a variety of ultrathin films including Al, Cr, Ru, Sc, Si, U, and W using visible-near UV ellipsometry, low angle x-ray diffraction and EUV reflectance measurements. This paper will discuss our results and make the case for incorporating laboratory EUV measurements in studies of the initial stages of oxidation of many materials.

2:30 PM S2.4

CORROSION MAPPING UNDER PROTECTIVE COATINGS. A. Mahan, J.P. Hoffmann, M. Khobaib, S. Satish., University of Dayton Research Inst., Dayton, OH; M.S. Donley, Air Force Research Laboratories, Wright Patterson Air Force Base, OH.

The scanning vibrating probe method allows in-situ examination of the minute d.c. current associated with localized corrosion activity. The scanning vibrating electrode technique (SVET) offers high resolution in current measurements of the order of 0.5 A/cm² and is able to detect and quantify the early stages of corrosion damage. In the current study, this technique was used to investigate the early stages of corrosion activity under a protective coating. SVET testing of panels with intact high-resistance barrier coatings could not reveal corrosion damage under normal testing conditions because of little or no corrosion activity within the limited time of exposure. Chemical, mechanical, and electrochemical means of accelerating the corrosion damage were utilized to obtain results in a reasonable time frame. Corrosion initiation and its progress under the coating were studied in detail and the results are discussed here. Imposing an external potential proved to be the most promising way of artificially creating corrosion damage. Complimentary high resolution nondestructive evaluation (NDE) techniques, such as pulse/echo scanning acoustic microscopy and continuous acoustic wave measurements were used to identify the corrosion sites. The overall objective of this investigation is to establish a correlation between the electrochemical and NDE techniques.

2:45 PM S2.5

CORROSION OF ELECTROPLATED NANOCRYSTALLINE NICKEL. Fengli Wang, Jiechao Jiang, Efsthios I. Meletis, LSU, Mechanical Eng. Dept., Baton Rouge, LA; Kun Lian, LSU, Center for Advanced Microstructures and Devices, Baton Rouge, LA.

Electroplated Ni is used extensively in numerous engineering components, ranging from conventional thin film applications to microfabricated MEMS devices. There is considerable interest at present in improving its properties through understanding of the processing-structure-property relationship. In the present work, a sulfamate bath was used to produce Ni electrodeposits. Electroplating temperature and current density were varied between 37°C-50°C and 5 mA/cm²-30 mA/cm², respectively to produce 50 nm thick Ni layers with a grain size ranging from 70 nm to 100s nm. The structures of the layers produced at the various processing conditions were studied by cross sectional TEM. The corrosion behavior was investigated as a function of the grain size by conducting anodic polarization experiments in a 3.5% NaCl aqueous solution. A special corrosion cell was also constructed by microfabrication to allow study of the

corrosion behavior in occluded areas as these pertain in high-aspect-ratio MEMS devices. Results obtained from high-aspect-ratio Ni MEMS components are discussed.

3:30 PM *S2.6

CHLORIDE UPTAKE BY THE OXIDE FILMS ON SINGLE CRYSTAL ALUMINUM: AN INVESTIGATION BY X-RAY ABSORPTION NEAR EDGE STRUCTURE. Steven Y. Yu, 3M Company, Austin, TX; Paul M. Natishan, William E. O'Grady, Heather E. Canavan, U.S. Naval Research Laboratory, Washington, DC.

Two distinct chloride (Cl⁻) species were detected on and in the passive oxides of aluminum (Al) single crystals with a <110> orientation, which were anodically polarized below the stable pitting potential in Cl⁻ containing solutions. Chloride was found to be present as an adsorbed species at the surface of the oxide, as well as an incorporated species within the oxide. The two species of Cl⁻ were recorded by X-ray absorption near edge structure (XANES) using an electron yield detector. Electron yield XANES results indicate that adsorbed Cl⁻ migrates from the solution/Al oxide interface into the passive Al oxide film, prior to stable pit initiation. Also, anodic polarization of aluminum single crystals show that the critical potentials for the onset of stable pitting (E_{pit}) of Al were dependent on the crystallographic orientation of the electrode surface, where $E_{pit<111>} < E_{pit<100>} < E_{pit<110>}$.

4:00 PM S2.7

CHARACTERIZATION OF OXIDE SURFACE LAYERS ON AL NEEDLES WITH EFTEM. D.S. Elswick, J.J. Hren, North Carolina State University, Raleigh, NC; P.G. Kotula, F.D. Wall, N.A. Missert, Sandia National Laboratories, Albuquerque, NM.

High purity (99.99%) Al wire, electropolished to produce sharp needles ranging in radii of 50-100 nm, was used to study localized corrosion. A uniform oxide layer approximately 3-5 nm thick was formed on the Al needles with a 50% nitric acid treatment. The needles were exposed to several electrochemical conditions to initiate pitting corrosion. Energy-filtered transmission electron microscopy was then utilized to characterize the needles. In particular jump-ratio images were taken at the aluminum, oxygen and chlorine core-loss edges. The experiments utilized a specially designed TEM holder which allowed the needles to be removed, processed ex situ and then replaced in the holder for further characterization.

This work was performed at Sandia National Laboratories, a Lockheed Martin Company, for the U.S. Department of Energy under contract number DE-AC04-94AL85000.

4:15 PM S2.8

IN-SITU FLUORESCENCE MICROSCOPY OF AL THIN FILM CORROSION AT ENGINEERED Cu ISLANDS. N. Missert, R.G. Copeland, J.C. Barbour, J.E. Mikkalson, F.D. Wall, and M.A. Martinez, Sandia National Laboratories, Albuquerque, NM; H. Isaacs, Brookhaven National Laboratory, Upton, NY.

Corrosion of Al thin films in the vicinity of engineered Cu islands was investigated in-situ, using confocal laser scanning microscopy combined with fluorescein indicator, in order to determine the spatial distribution of alkalinity in solution at the sample surface. The samples were fabricated by electron beam deposition of ultra high purity Al and Cu, where photolithography was used to define the Cu island size and spacing. During the early stages of exposure to 0.05 M NaCl and 0.1 mM fluorescein at pH ~ 6.5, we observe an alkaline solution environment above the Cu islands, while Al corrodes in an acidic environment beneath. Although all Cu islands participate equally in the cathodic reaction, the overall cathodic rate fluctuates with time, and appears to be governed by the anodic dissolution rate of Al beneath the islands. The corrosion product from this Al dissolution precipitates at the perimeter of the high pH region in a halo surrounding the islands. When the spacing between islands is $\geq 50 \mu\text{m}$, individual halos are observed around each Cu island, showing that they behave as individual cathodes, with the alkaline environment confined to their vicinity. However, when the spacing between islands is reduced to 10 μm , we observe a crossover from isolated cathodes at large spacing to an array of islands acting as a single cathode. The implications of these findings will be discussed.

4:30 PM S2.9

Abstract Withdrawn.

SESSION S3: TEMPERATURE AND ENVIRONMENTAL EFFECTS
Chairs: Robert G. Kelly and J. Woods Halley
Wednesday Morning, April 18, 2001
Salon 12 (Marriott)

8:30 AM *S3.1

COMPARING SULFUR SEGREGATION AT DIFFERENT Al_2O_3 /ALLOY INTERFACES. Peggy Y. Hou, Lawrence Berkeley National Laboratory, Materials Sciences Division, Berkeley, CA.

The segregation of sulfur to oxide-scale/alloy interfaces that form as a result of high temperature oxidation has been recognized as detrimental to scale adherence. However, there is little fundamental understanding of this segregation behavior. This paper reports results of sulfur segregation to Al_2O_3 /alloy interfaces as a function of oxidation time on three different types of Al_2O_3 -forming alloys: FeCrAl, FeAl and Fe₃Al. The interface was studied using Scanning Auger Microscopy after removal of the oxide scales in ultra high vacuum. Sulfur was found to segregate to all interfaces, on regions where the scale was adherent or had detached at the growth temperature, and reached a saturation level with time. However, the time to achieve saturation and the final concentration at the interface differ depending on the type of alloys. Other than sulfur, co-segregation of chromium and carbon was found on FeCrAl, where the carbon segregated during cooling. The observed behaviors are compared to surface and grain boundary segregation, and related to the oxide growth process. Effects of the segregants on interface microstructure and scale adhesion are also discussed.

9:00 AM S3.2

OXIDATION RESISTANCE OF NiAl AND NiAl-AlN COATINGS DEPOSITED BY MAGNETRON SPUTTERING. Dalong Zhong, John J. Moore, Graham Mustoe, Colorado School of Mines, Advanced Coatings and Surface Engineering Laboratory, Golden, CO; Joachim Disam, Steffen Thiel, Schott Glas, Service Division, Mainz, GERMANY.

It is well known that NiAl exhibits excellent oxidation resistance and it shows improved cyclic oxidation resistance when NiAl-AlN composite is used. In this work, NiAl and NiAl-AlN coatings have been deposited from a NiAl compound target by using RF magnetron sputtering technique. Their structures and microstructures were characterized using x-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM). The film residual stresses were measured using XRD. The oxidation behaviors of NiAl and NiAl-AlN films were studied using a Netzsch Simultaneous Thermal Analyzer (STA409C) and Rutherford Backscattering Spectrometry (RBS). It was shown that they are excellent oxidation resistant coatings. In this paper, their oxidation rates and mechanisms will be reported and discussed together with their structure and stress observations as well.

9:15 AM S3.3

SCANDIUM OXIDE FORMING ON SCANDIUM THIN FILMS: A STUDY OF ITS GROWTH AND OPTICAL PROPERTIES. Guillermo Acosta, Dr. David Allred, Doug Marcos, Brigham Young University, Department of Physics & Astronomy, Provo, UT.

Thin films play an ever-increasing role in today's techno-flooded world, while managing to maintain a modest profile on the front of scientific discovery. With the scale of electronics continually shrinking, though, there is more and more attention being paid to the nano-behavior of deposited films: preferred orientations of growth, diffusion between materials at film interfaces, and formation of oxides. Also, these physical phenomena also have an impact on the optical properties of a thin film in the extreme ultraviolet. We have thermally evaporated scandium of several thicknesses, ranging from 7-50 nanometers, and have monitored them closely throughout extended annealing periods. Characterization includes roughness and thickness measurements via atomic force microscopy; transmission and polarization data at multiple wavelengths and multiple angles taken with an ellipsometer; and reflectivity tests made using a scanning monochromator. By employing several characterization techniques in our study, we are able to speak more confidently of scandium oxide in scandium thin films, including the mechanics behind its growth and the influence it has over scandium's optical performance.

9:30 AM S3.4

OXIDATION PERFORMANCE OF Ni-BASED SUPERALLOYS TMS-75 AND RENÉ N5. Karin Prüssner*, Hans-Jürgen Christ*, and Hiroshi Harada#. *Institut für Werkstofftechnik, University of Siegen, GERMANY. #National Research Institute for Metals (NRIM), Tsukuba, Ibaraki, JAPAN.

The composition of single-crystal Ni-based superalloys, which are state-of-the-art materials for high-temperature applications such as turbine blades, has to be carefully chosen in order to achieve a combination of excellent mechanical properties due to the gamma/gamma'-structure, and good oxidation performance resulting from the formation of a protective alumina scale. A number of different commercial alloys are currently in use, but the fundamental effects of different alloy compositions on the formation and adhesion

of the oxide scale are poorly understood. Therefore, we study the effects of alloy composition on the microstructure and micro-chemistry of oxide scales on Ni-based superalloys. The oxidation behavior of the alloy TMS-75 (nominal composition: Ni-3Cr-6Al-6Ta-6W-5Re-12Co-2Mo-0.1Hf), which was recently developed for balanced intermediate and high temperature creep strength, was studied and compared to that of commercial alloy René N5 (nominal composition: Ni-7Cr-6Al-6Ta-5W-3Re-7Co-1.5Mo-0.16Hf). In our experiments, we use thermo-gravimetry, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) to monitor the oxidation in-situ and to characterize the thermally grown oxide scales. Internal interfaces are analyzed using energy-dispersive x-ray spectroscopy (EDS) with a fine probe in a FEG-TEM. Results show that initially the oxide scale consists of transient oxides such as NiO and Ni-Al-spinel before the protective alumina scale forms. Reactive elements such as Y, Hf and Zr, which segregate at oxide grain boundaries and at the scale/metal interface, are necessary doping elements to achieve scale adhesion. Ta diffuses rapidly into the scale and can form precipitates in the scale, which act as stress concentration sites and promote spallation. Particularly detrimental for the adhesion of the oxide scale are large Ta-rich particles in the alloy, which allow internal oxidation of the alloy. Other elements such as Mo and Re are also found in the scale and their effect on the oxide scale formation will be discussed.

9:45 AM S3.5

HIGH-TEMPERATURE OXIDATION OF NANOSTRUCTURED AlN-BASED FILMS. Rostislav Andrievski, Inst of Problems of Chemical Physics, Chernogolovka, Moscow Region, RUSSIA; Vladimir Lavrenko, Inst of Problems of Materials Science, Kiev, UKRAINE; Jean Desmaison and Martine Desmaison-Brut, Faculty of Science, Limoges Univ, Limoges, FRANCE; Gennadiy Kalinnikov, Inst of Problems of Chemical Physics, Chernogolovka, Moscow Region, RUSSIA; Alla Panasyuk, Inst of Problems of Materials Science, Kiev, UKRAINE.

Nanostructured films of AlN-TiN, AlN-TiB₂, and AlN-SiC-TiB₂ were obtained by non-reactive magnetron sputtering. Interaction with oxygen up to 1500°C was studied under non-isothermal conditions (the heating rate being 15 degr/min) with DTA and TG methods. Films were characterized by XRD, EPMA, and SEM analyses before and after oxidation. Films of AlN-SiC-TiB₂ exhibited the highest oxidation resistance. Features of film interaction with oxygen are discussed in detail.

10:30 AM *S3.6

MECHANISMS OF ENVIRONMENTALLY ASSISTED-DEBONDING IN THIN-FILM STRUCTURES. Reinhold H. Dauskardt, Department of MS&E, Stanford University, Stanford, CA.

Resistance to subcritical debonding of interfaces profoundly influences the long-term reliability of a wide range of thin-film microelectronic and biomedical devices exposed to moist or corrosive environments. Such time or loading cycle dependent debonding leads to a loss of mechanical, thermal, and, in some cases, electrical integrity. In this presentation, the debonding properties of representative interfaces in thin-film structures involving glass, polymer and metal layers are examined. Interface fracture techniques are described to characterize both critical adhesion values and subcritical debonding behavior under cyclic fatigue and monotonic loading conditions in a range of environments. Debond-growth rates are shown to be sensitive to a range of salient mechanical, microstructural and environmental variables including the interface morphology and chemistry, polymer layer thickness, activity of the environmental species, and loading mode. The micromechanisms controlling interfacial debonding are rationalized in terms of the prevailing deformation mechanisms and related to interface chemical reactions. The order of the debond tip chemical reaction with respect to the environmental species is determined. Implications for device reliability and life-time prediction are discussed.

11:00 AM S3.7

STRESS AND HYDROGEN ASSISTED ANODIC DISSOLUTION OF METALLIC MATERIALS. Scott X. Mao, N.Q. Wu, L. Qiao, Dept. of Mechanical Engineering, University of Pittsburgh, Pittsburgh, PA.

When a stress is applied to the metal film or containing hydrogen in a aqueous solution, a reaction (anodic dissolution in the aqueous) of the film can be expressed as: $M(\sigma, H) + 2H^+ = M^{2+} + H_2\uparrow$. The electrochemical potential and the reaction rate can be promoted by the free-energy change $DGM(s, H)$ of the stressed and charged metal. A thermodynamic model considering both stress and hydrogen in the metal has been developed to predict anodic dissolution of the metallic materials in aqueous solution. It has been found that the anodic dissolution current i_A , with the effects of stress and hydrogen in reaction could be promoted by -3 times compared with the dissolution

of the same metal without stress and hydrogen. Related experiments (electrochemical polarization test) for iron based alloy with stress and hydrogen in dilute bicarbonate solution has been conducted to support the proposed mechanism. It has been found that the presence of stress as well as hydrogen makes the anodic dissolution reaction more thermodynamically favorable.

11:15 AM S3.8

SCANNING FORCE MICROSCOPY STUDIES ON FRACTURE MECHANICS AND EROSION WEAR AT THE NANOMETER SCALE. Bettina Baumeister, Thomas A. Jung, Paul Scherrer Institute, Villigen, SWITZERLAND; Ernst Meyer, Univ. of Basel, Institute of Physics, Condensed Matter Dept, Basel, SWITZERLAND.

The understanding of tribological mechanisms at the nanometer scale is of key importance for the fundamental comprehension of tribology and wear. "Nanosopic" behaviour of atoms and molecules often determines the macroscopic failure of mechanical parts. Here we use 2D-arrays of SiO₂-nanotowers on a Si substrate as templates for well defined mechanical experiments towards friction, fracture and wear mechanisms at the solid-liquid interface. Forces are applied to the towers using the scanning force microscope tip. Detailed studies reveal two different mechanisms in the fracture behaviour: fracture of the structure at the bottom and erosive wear of the nanotowers from the top. Perpendicular as well as lateral forces are analyzed and compared to models. Statistical analysis of such force measurements provide information about the probability for fracture of the towers depending on the shape, the interface quality and the geometry of the microfabricated towers. The lubricative and corrosive influence of liquids with different chemical and physical properties can be compared in regard to these abrasion and wear experiments. This new methodology opens up a new field of tribology and wear studies for materials science which is relevant for materials engineering on all scales. In particular the mechanical properties of interfaces, here: "SiO₂ - Si", can be studied in detail as it is of increasing importance for current micromechanical systems. In the conclusion the size dependence of these effects will be discussed as one of the origins for "new" behaviour on the atomic and molecular scale.

11:30 AM S3.9

HYDROGEN EFFECTS ON ATOMIC SCALE RELAXATION PROCESSES THAT DETERMINE DEFORMATION AND FRACTURE BEHAVIOR OF Zr-Ti-Ni-Cu-Be BULK METALLIC GLASSES. Daewoong Suh and Reinhold H. Dauskardt, Department of MS&E, Stanford University, Stanford, CA.

Hydrogen is a well-known embrittling species in a wide range of crystalline metals. A great deal of research has been undertaken leading to several viable mechanisms of hydrogen embrittlement in crystalline metals. Previous studies of metallic glasses in the form of thin ribbons suggest that they are susceptible to similar deleterious effects of hydrogen embrittlement. Understanding of hydrogen embrittlement in amorphous metals is, however, far from complete compared to the considerable progress that has been achieved in crystalline metals. The objective of the present work is, therefore, to investigate the effects of hydrogen on the deformation and fracture behavior of a Zr-Ti-Ni-Cu-Be bulk metallic glass, specifically flow and crack-propagation behavior. Microstructure and thermal behavior of the hydrogen-charged metallic glass were examined using positron annihilation, high-resolution electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy and differential scanning calorimetry to identify the microstructural origin of hydrogen effects in the amorphous microstructure. It was found that hydrogen retarded the fundamental molecular rearrangement process responsible for plastic flow in the amorphous microstructure. The sluggish molecular rearrangement process is believed to be responsible for increased flow stress and degraded toughness. Possible mechanisms are discussed in terms of free volume changes measured by positron annihilation.

11:45 AM S3.10

THEORETICAL AND EXPERIMENTAL STUDIES OF ZIRCONIUM OXIDATION: STRESS AND ANISOTROPY EFFECTS. Jerome Favergeon, Tony Montesin, Christophe Valot, Gilles Bertrand, Université de Bourgogne, Laboratoire de Recherches sur la Réactivité des Solides, Dijon, FRANCE.

The frequent observation of cracks during metal oxidation confirms the contribution of mechanical strains to reaction processes: oxygen transport through material and transformation of metal into oxide induce strong mechanical stresses near the metal/oxide interface. To model this complex behaviour, the main theoretical problems consist in the formulation of the coupling between diffusion and stresses in the specimen, and of metal/oxide interface properties. The diffusion equation is obtained by using the Larche and Cahn's approach where the chemical potential is modified by stresses. The total strain of the metal is expressed as a sum of elastic and chemical strains. In the oxide, the epitaxial strains are added. As the high temperature

oxidation of zirconium obeys an anionic mechanism, the rate of the metal/oxide interface is controlled by the mass conservation law proposed by Stefan. The simulations are performed with a finite element method and take into account the anisotropy and the property gradients of the specimen. In this talk, we will first present the theoretical model, and more particularly the diffusion equation and the method used to obtain the epitaxial strains. Then different simulations will be used to show the potential effects of both metal and oxide orientations on the oxidation kinetics of zirconium. These theoretical results will be discussed on the basis of different experimental investigations. Actually oxidation kinetics have been obtained for different zirconium textures. In situ XRD measurements have allowed to determine stress values and to make a phase analysis. The comparison of the experimental and theoretical results will allow to conclude on the role of stresses and anisotropy during the zirconium oxidation.

SESSION S4: CHARACTERIZATION METHODS OF OXIDATION

Chairs: Peggy Y. Hou and Andrew A. Gewirth
Wednesday Afternoon, April 18, 2001
Salon 12 (Marriott)

1:30 PM *S4.1

TRANSMISSION ELECTRON MICROSCOPY STUDIES OF ALUMINUM OXIDE STRUCTURES. Xidong Chen, J. Murray Gibson, Materials Science Division, Argonne National Laboratory, Argonne, IL.

Understanding oxidation of metals is very important in corrosion science. There are many open questions regarding fundamental processes of oxidation, partially because of the lack of understanding of oxide structures, many of which are amorphous. Previous oxidation models are inadequate in addressing atomistic mechanisms. Structure studies at nanometer scales are necessary to advance our knowledge of oxidation processes. In this talk, we report our transmission electron microscopy (TEM) studies of aluminum oxides grown under different conditions. Those different oxides do have quite different passivation behaviors. We will address those differences from a structure point of view. The radial distribution function has been measured for those oxides to understand their short-range order structures. Moreover, medium-range order structures have also been investigated through a pair-pair alignment correlation function obtained with fluctuation microscopy technique. We will present a comprehensive review of our results. Future directions will also be discussed.

2:00 PM S4.2

SYNTHESIS AND CHARACTERIZATION OF METAL OXIDE MULTILAYERS OBTAINED VIA MOCVD AS PROTECTIVE COATINGS OF GRAPHITE AGAINST OXIDATION. Simone Battaini, Giovanni Carta, Gilberto Rossetto, Sergio Sitran, Pierino Zanella, Istituto di Chimica e Tecnologie Inorganiche e dei Materiali Avanzati, CNR, Padova, ITALY; Lidia Armelao, Eugenio Tondello, Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Centro di Studio sulla Stabilità e Reattività dei Composti di Coordinazione, CNR, Padova, ITALY.

Graphite and carbon based materials are widely used for many applications in different areas of state-of-the-art technologies such as the production of high-temperature structural components in advanced gas-turbine engines for their high resistance to erosion and wear, in aerospace applications including vehicle and aircraft construction for their high strength and low-weight and in the manufacture of holders for the fusion of metallic alloys, particularly gold, for their chemical inertness with regard to melting bath. While in an inert atmosphere or in vacuum, carbon materials retain their mechanical properties to temperatures higher than 2000°C, problems arise when they are exposed to an oxidizing environment. In fact the use of such materials at temperatures above 500°C without a suitable protection causes permanent damages as the reaction with oxygen produces a rapid degradation. Such materials can be protected from oxidizing environments by the use of refractory material films. The coating materials mainly used to this aim are generally carbides nitrides and some oxides such as silica (SiO₂) alumina (Al₂O₃) titania (TiO₂) and zirconia (ZrO₂). Usually multilayer coating systems composed of different materials are used, where each layer plays a specific function as hardness, adherence, wear and oxidation resistance. In this work zirconia, titania and alumina thin films have been deposited on graphite substrates, as monolayers and as multilayer (binary and ternary) systems with zirconia always present as bond layer to the graphite, to test their ability as protective coatings against oxidation at high temperatures. Metal organic chemical vapor deposition (MOCVD) has been adopted as synthetic procedure. The depositions have been performed using a hot wall reactor at reduced pressure (0.6 torr) in the temperature range

350-500°C, using, as precursors, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{CH}_2\text{C}(\text{CH}_3)_3)_2$, $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$, $(\text{CH}_3\text{CH}_2)_2\text{Al}(\text{OCCCH}_3\text{CHC CH}_3\text{O})$ respectively. Surface and topographical analysis of all the deposits were performed using X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. ZrO_2 thin film reveals a good adhesion when grown in a flux of oxygen/water vapor mixture with a low carbon contamination. While the TiO_2 films are polycrystalline and always homogeneously deposited without cracks formation, Al_2O_3 deposits are amorphous, not uniformly distributed and highly carbon contaminated. Thermogravimetric measurements (TG and DTA) in oxygen flux of the mono and multilayer systems reveal that the binary system zirconia/titania shows the best protective effect evidenced by an increase in the graphite combustion temperature of 250°C. Further research is in progress to improve the prepared systems by using new protective materials and by studying the influence of the deposition parameters on the properties of the obtained coatings.

2:15 PM S4.3

SEM AND IN SITU RAMAN SPECTROSCOPY OF THE FILMS FORMED ON Fe-Ni-Cr ALLOYS IN 288°C WATER CONTAINING DILUTE ADDITIONS OF H_2SO_4 . Todd Mintz, Christopher S. Kumai, Thomas M. Devine, Department of MS&E, University of California, Berkeley, CA.

A combination of in situ Raman spectroscopy, in situ surface enhanced Raman spectroscopy and ex situ scanning electron microscopy were used to investigate the influence of dilute concentrations of H_2SO_4 on the films that form on 304 stainless steel, Fe-13Cr-10Ni, Fe-5Cr-10Ni and Fe in 288°C water. The results indicate that M_3O_4 type films form on all the alloys in high purity 288°C water with low dissolved oxygen concentrations. For each alloy there is a critical dissolved oxygen concentration of the water above which the outer surface of M_3O_4 is transformed to M_2O_3 . For 304 stainless steel the critical dissolved oxygen concentration is = 4 ppb and M_2O_3 exists predominantly in the "gamma" modification with some "alpha" M_2O_3 . For Fe samples the critical dissolved oxygen concentration is = 53 ppb and only alpha- Fe_2O_3 is formed. For the other Fe-Ni-Cr alloys, the amount of gamma- M_2O_3 in the surface film increases and the critical dissolved oxygen concentration decreases with increasing Cr concentration in the alloy. 10 ppb of H_2SO_4 has no effect on the films that form on the alloys. 100 ppb of H_2SO_4 dramatically increases the critical dissolved oxygen concentration required to transform the outer surface of the film of M_3O_4 to M_2O_3 for all four alloys investigated. The results suggest that alpha- M_2O_3 is required to form over the grain boundaries in order for IGSCC to occur in sensitized stainless steel and that gamma- M_2O_3 will prevent IGSCC. Collectively, the results can explain why IGSCC in 288°C water (1) requires chromium depletion along the grain boundaries, (2) requires a critical minimum concentration of dissolved oxygen in the water, and (3) is exacerbated by dilute additions of H_2SO_4 .

2:30 PM S4.4

OXIDATION OF PECVD SILICON NITRIDE AND UNDERLYING METALS. G.C. Han, P. Luo, K.B. Li, Data Storage Institute, National University of Singapore, SINGAPORE; Y.H. Wu, Data Storage Institute & Department of Electrical and Computer Engineering, National University of Singapore, SINGAPORE.

Plasma enhanced chemical vapor deposition (PECVD) was employed to grow silicon nitride at various temperatures to find its application in magnetic random access memory (MRAM). In order to avoid the interdiffusion between PECVD nitride ($\text{SiN}_x\text{:H}$) and underlying metals (Ta & Cu), as well as between adjacent metal layers, low temperature deposition is required for MRAM process. The oxidation of PECVD $\text{SiN}_x\text{:H}$ films and underlying metals has been studied through Auger Electron Spectroscopy (AES) measurements. Oxygen content on the $\text{SiN}_x\text{:H}$ surface and characteristic sputtering time (t_o) after which oxygen signal falls below measuring errors of the system were used to characterize the oxidation of $\text{SiN}_x\text{:H}$ films. It is found that both oxygen content and t_o increase significantly for decreasing deposition temperature below 250°C. Above 250°C, the oxygen content and t_o keeps almost independent of temperature. The oxygen content is larger for $\text{SiN}_x\text{:H}$ films with lower Si/N ratios. The oxidation mechanism of $\text{SiN}_x\text{:H}$ was discussed in combination with the hydrogen content obtained by Fourier transform infrared spectroscopy (FTIR) measurements and the etch rate in Buffered Hydrofluoric (BHF) acid. Ta & Cu oxidation was investigated through changing sample loading methods. Ta oxidation is mainly from the long time exposure to the air. But for Cu, the strong oxidation was observed for samples loaded at higher temperatures, while almost no oxidation was detected for samples loaded at room temperature and heated up to deposition temperature after pumping the chamber to high vacuum.

2:45 PM S4.5

POLYHEDRAL EPITAXY OF PASSIVE OXIDE FILMS ON

NANOPARTICLES OF IRON AND NICKEL. K.K. Fung, X.X. Zhang, Y.S. Kwok and Boxiong Qin, The Hong Kong University of Science and Technology, Department of Physics, Hong Kong SAR, CHINA.

Passivated metallic nanoparticles are usually enclosed by polycrystalline oxide films containing defective grain boundaries which provide channels for ionic diffusion leading to further oxidation and corrosion. Consequently, they have to be stored in vacuum or in an inert gas atmosphere. Nanoparticles of iron and nickel we have prepared by gas condensation of plasma evaporated target metals were found to be remarkably oxidation and corrosion resistant in air and water. We have found that these nanoparticles are enclosed by 3 or 4 nm thick single crystal-like epitaxial films. The epitaxial relationship between the iron oxide identified as $\gamma\text{-Fe}_2\text{O}_3$ is: $(001)_{\text{oxide}} // (001)_{\text{Fe}}$, $[110]_{\text{oxide}} // [100]_{\text{Fe}}$. The above epitaxial relationship applies to each of the six cubic faces of the truncated rhombic dodecahedral iron particles rather than just one surface as in ordinary epitaxy. There is a 45° rotation about a cubic axis between the oxide film and iron particle. In a [001] high resolution transmission electron microscopy (HRTEM) image, the epitaxial oxide films on the {100} surfaces of iron are in $\langle 110 \rangle$ orientation. The oxide films on the {100} surfaces extend laterally to adjacent {110} iron surfaces to form compressively bent films. The oxide shell formed by films on the {100} and {110} surfaces of iron is thus single crystal-like which provides effective protection against further oxidation and corrosion. Polyhedral epitaxy of NiO hillocks on the {111} and {001} surfaces of truncated octahedral nanoparticles of nickel has also been observed by HRTEM. The formation of hillocks is related to the relaxation of the compressive stress in NiO arising from the very large lattice mismatch between NiO and Ni.

3:30 PM *S4.6

X-RAY DIFFRACTION COMPARISON OF WET AND DRY OXIDES ON COPPER CRYSTALS. Ian Robinson, Yong Chu, Physics Dept, University of Illinois, IL; Andrew Gewirth, Chemistry Dept, University of Illinois, IL.

Cuprous oxide was found to grow epitaxially on Cu(111), both under native (air) oxidation conditions and in a controlled electrochemical environment. Both orientations of the interface were observed, with and without a stacking fault. There was a pronounced asymmetry between aligned and reversed stacking sequence under the electrochemical conditions: one crystal remained a monolayer thick while the other thickened considerably. Significant contraction of the resulting unit cell volume as found in addition to the usual hexagonal strain associated with the epitaxy. This suggests a considerable departure from stoichiometry of the electrochemically grown oxide.

4:00 PM S4.7

Abstract Withdrawn.

4:15 PM S4.8

DIFFUSION OF OXYGEN IN AMORPHOUS CARBON NITRIDE A-CN_x FILMS, AND THE ETCHING AND THE OXIDATION OF A-CN_x BY OXYGEN PLASMA. Yohko Naruse and Shoji Nitta, Department of Electrical Engineering, Gifu University, Gifu, JAPAN.

Amorphous carbon nitride a-CN_x film prepared by a nitrogen radical sputter method shows low dielectric constant and high photosensitivity. a-CN_x is prepared by a nitrogen radical sputter of carbon target with a glow discharge nitrogen plasma. The effect of oxygen plasma treatment on a-CN_x is compared with that of hydrogen plasma treatment. With the oxygen plasma produced by a glow discharge of oxygen gas, the surface of a-CN_x is etched and also oxidized. Then oxygen diffuses into a-CN_x and changing the sample into amorphous carbon oxynitrides a-CN_xO_y films. The etching and oxidation of a-CN_x by the oxygen plasma depend on the substrate temperature so much. At higher substrate temperature like 400 °C, the etching speed becomes so high. The etching by oxygen plasma is mainly for carbon atoms in a-CN_x and not so much for nitrogen atoms. With oxidation, defects are terminated by oxygen atoms and a number of defects are decreased. And then the photoluminescence properties are refined by the oxygen plasma treatment especially at the ultraviolet region. This refinement is good for the application of a-CN_x as an electroluminescent material. There is a tendency of a-CN_x films to be more porous with the oxygen plasma treatment which result is good for the application of a-CN_x to low dielectric constant materials. By observing the oxygen contents in a-CN_xO_y, the diffusion of oxygen in a-CN_x is confirmed. The diffusion constant is about 3×10^{-16} cm²/sec at 300 °C and the activation energy of it is about 0.28 eV.

4:30 PM S4.9

EFFECTS OF PHOTOWASHING-GROWN OXIDE LAYER ON ELECTRICAL PROPERTIES OF GaAs MESFET OBSERVED I-V AND DLTS MEASUREMENTS. Kyoung Jin Choi, Jong-Lam Lee,

Pohang University of Science and Technology (POSTECH), Dept of MS&E, Pohang, Kyungbuk, SOUTH KOREA; Jae Kyoung Mun, Heacheon Kim, Electronics and Telecommunications Research Institute (ETRI), Teajon, SOUTH KOREA.

Exposure of GaAs surface to oxygen/air causes the creation of many surface states that pin the surface Fermi-level. Surface states are closely related to the undesirable characteristics in GaAs MESFETs such as transconductance dispersion, low breakdown voltage behavior, and low frequency noise. Recently, it was reported that the PL intensity was sharply increased by the photowashing treatment on GaAs surface, which was explained by the reduction of surface states and the unpinning of surface Fermi-level. No works, however, were conducted on the effects of photowashing-grown oxide layer on electrical properties of GaAs MESFET. In this work, we applied photowashing treatment on ungated surface region between gate and source/drain electrodes of GaAs MESFETs and observed its effects on electrical characteristics using I-V and DLTS. The 0.8-micron-gate GaAs MESFETs with single recessed structure were fabricated. The devices were placed on a photoresist spinner and were subjected to a stream of D.I. water under the intense light (photowashing). Photowashing time was varied from 1 to 30 minutes. Photowashing-grown oxide was characterized using synchrotron XPS and ellipsometry. It was found that the oxide was primarily composed of Ga₂O₃ with a small amount of As₂O₃, which is due to the washing away of soluble arsenic oxide in water during photowashing treatment. In DLTS spectra, hole-like signals whose origin is surface states at ungated region between gate and source/drain electrodes were decreased after the treatment. In I-V measurements, drain current was decreased, but two-terminal gate-to-drain reverse leakage current was increased. The decrease of channel current can be explained by the reduction of channel thickness due to the oxidation of GaAs at the surface and the increase of gate leakage current is directly related to the reduction of surface states. From these results, the mechanism on the reduction of surface states by photowashing-grown oxide will be discussed.

SESSION S5: INITIAL KINETICS AND THIN OXIDE FILM FORMATION ON METALS

Chairs: Judith C. Yang and Xidong Chen
Thursday Morning, April 19, 2001
Salon 12 (Marriott)

8:45 AM *S5.1

TIGHT BINDING DIRECT DYNAMICS STUDIES OF MODELS OF THE PASSIVATION LAYER ON TITANIUM. J.W. Halley, Min Zhuang, School of Physics and Astronomy, University of Minnesota, Minneapolis, MN; P. Schelling, Argonne National Laboratory, Argonne, IL.

We report studies of a self consistent tight binding molecular dynamics model of the titanium oxide-titanium interface. Such models, which are parametrized by fitting results of full DFT calculations on bulk material to a self consistent tight binding model, permit direct dynamics studies of large systems. Here we report results on the energy of oxygen vacancies in the passivation layer as a function of distance from the metal/oxide interface. Progress on efforts to similarly model dissociable water on the other side of the passivation layer will also be reported.

9:15 AM S5.2

INITIAL OXIDATION OF NiAl(110): WHAT CAN WE LEARN FROM *AB INITIO* CALCULATIONS? A.Y. Lozovoi^{1,2}, A. Alavi² and M.W. Finnis¹. ¹Atomistic Simulation Group, School of Mathematics and Physics, Queen's University of Belfast, Northern Ireland, UNITED KINGDOM. ²Chemistry Department, University of Cambridge, UNITED KINGDOM.

We have studied the oxygen adsorption on the (110) surface of B2 Ni_{1-x}Al_x, using a plane-wave pseudopotential method. The clean surface and several oxidised surfaces were investigated, with three different oxygen coverages. The obtained data were then used to generate the dependence of the surface energy on the macroscopic parameters: temperature, partial pressure of oxygen, and the stoichiometry of the substrate. The dependence allows us to identify the crossover pressures at which different oxidised surfaces become stable. It turns out that at ambient conditions runaway oxidation of the NiAl surface should take place, subject to kinematic restrictions. With decreasing oxygen pressure, homogeneous oxidation can only proceed by overcoming barriers, because e.g., two monolayer adsorption becomes favourable before single monolayer adsorption. The oxidised surface can stay in equilibrium with the substrate in a small range of lower pressures, below which the clean surface is the most stable. The bulk stoichiometry of NiAl has a relatively small impact on the boundaries of the described regions.

We thank the EPSRC for provision of computer time on the Cray T3E-1200E via the UKCP consortium (Grant M01753), and for other resources (Grant L08380), and we acknowledge the Centre for Supercomputing in Ireland for computer resources on the IBM SP2.

9:30 AM S5.3

AFM STUDY OF PATCH ELECTRIC CHARGE DUE TO ADSORBATES ON TiO_x THIN FILM. Lucel Sirghi, Yoshinori Hatanaka, Shizuoka University, Research Institute of Electronics, Hamamatsu, JAPAN.

Recently it was shown that UV irradiation induces modifications of both the electric conductivity and the hydrophilicity of TiO_x thin films. It was suggested that radical species adsorbed by the film surface during UV illumination improve the hydrophilicity and generate on the surface electric patch charges that act like recombination centers, which lead to a lower conductivity. In order to obtain evidence on this we performed AFM measurements of the long-range electric force due the patch charge on the film surface. The force curve data taken by an AFM (Seiko Instruments Inc. SPI 3800) were fitted with force versus distance dependence expected from a theoretical computation based on the approximation of the image charge induced on the AFM probe. The method allowed for estimation of the electric patch charge density. Measurements performed on TiO_x thin film obtained by PECVD and rf magnetron sputtering discharge showed an increase of the patch charge density after UV irradiation.

9:45 AM S5.4

OXIDATION AND DECOMPOSITION IN Pd METAL/OXIDE SYSTEMS. Heng Zhang, Harris Marcus, Matthew Augustine, Jack Gromek, Gayanath W. Fernando, University of Connecticut, Institute of Materials Science, Storrs, CT; R. Samuel Boorse, Precision Combustion Inc., North Haven, CT.

The increased requirement for environmental protection requires improvement in the performance of the current catalytic Pd/PdO materials for hydrocarbon combustion. Bimetallic systems show potential for this purpose and such an approach will be described in this presentation. The equilibrium phase diagram for Pd/PdO over a range of partial oxygen pressures will be presented. Binary systems have been prepared and the structure, decomposition, re-oxidation and segregation characteristics have been investigated with high temperature X-ray diffraction, SEM, AES, XPS and thermogravimetric analysis. The X-ray map image and energy-dispersive spectroscopy analysis indicate a significant surface segregation in the metal systems. This phenomenon varies with the added element composition and oxygen partial pressure.

10:30 AM *S5.5

OXYGEN-METAL INTERACTIONS ON ELECTRODE SURFACES. Andrew A. Gewirth, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL.

In this talk we discuss ways in which the reactivity of metal electrode surfaces is modified by oxide and inorganic complexes exhibiting oxygen functionality. First, we examine the initial stages of oxidation on Cu electrode surfaces in dilute acid solutions. The oxygen monolayer formed controls the initial nucleation of Cu deposits onto Cu surfaces. We found in addition that deposition could be preferentially enhanced on Cu by scanning the AFM tip over areas on the surface. The tip removes the oxide layer and forms nucleation sites on the Cu substrate. This mechanism will be contrasted with what we understand to be the mechanism of Cu deposition derived from scaling and spectral analyses. In the second part of this talk, we present results demonstrating that alpha-dodecatungstosilicate anions spontaneously form adherent, ordered monolayer arrays on Ag and other oxophilic surfaces. These 'inorganic self-assembled monolayers' exhibit interesting structural chemistry and in addition strongly passivate silver electrode surfaces.

11:00 AM S5.6

EFFECT OF TEMPERATURE ON THE MORPHOLOGY OF COPPER OXIDES DURING IN SITU OXIDATION OF Cu(001). Guang-wen Zhou, Mridula D. Bharadwaj and Judith C. Yang
Department of MS&E, University of Pittsburgh, Pittsburgh, PA.

In order to gain insights into the initial kinetics of oxidation, we are investigating the initial oxidation stage of a model metal system from nucleation to coalescence by primarily in-situ ultra high vacuum (UHV) transmission electron microscopy (TEM). Since the oxidation reactions for metallic systems are extremely sensitive to the oxidizing environment and impurities, nucleation and growth of Cu₂O due to oxidation of Cu (001) films were monitored at a wide range of temperature and oxygen partial pressures. The Cu (001) film was oxidized in situ between temperature ranging from room temperature to 700°C and oxygen pressure ranging from 5X10⁻⁴ torr to 760 torr. The oxidation temperature had a dramatic effect on the copper oxide

morphology. At lower temperature, i.e. $\leq 450^\circ\text{C}$, oxide islands showed triangular morphology and the shape of the Cu_2O islands did not change with time. On the other hand at elevated temperature, i.e. $\geq 600^\circ\text{C}$, two distinct island geometries were seen. The Cu_2O islands were initially triangular shaped and later changed to rectangular geometry. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were also used to investigate surface morphology of the oxide islands. The high resolution electron microscopy (HREM) experiments provided information on the interface between Cu and Cu_2O . Also, the coalescence of the nano-sized oxide islands, formed by in situ oxidation of the Cu film at room temperature and atmospheric pressure, was observed when the temperature was elevated in absence of further oxygen exposure. Quantification of these data should provide key insights into the surface kinetics of metal oxidation and the significant role of temperature in oxide formation.

11:15 AM S5.7

A STUDY OF ULTRATHIN OXIDES ON Si PREPARED BY CONVENTIONAL OXIDATION AND RAPID THERMAL OXIDATION. C.H Ng, J.B. Xu, J. Xu, W.Y. Cheung, S.P. Wong, I.H. Wilson, Dept of Electronic Engineering, Chinese University of Hong Kong, Shatin, the New Territories, HONG KONG.

Conventional furnace oxidation and rapid thermal oxidation (RTO) were used to grow ultrathin oxide ($\sim 10\text{nm}$) films on Si. Nitrogen was used to dilute the oxygen oxidation. AFM was used to measure the surface morphology and ellipsometry was used to measure its thickness. After Al dots were deposited as top electrodes, samples were also characterized by C-V, I-V measurement. The samples fabricated by conventional furnace and subsequently annealing at 450°C for 30min showed the lowest interface state density ($\sim 10^{11}\text{ cm}^{-2}\text{ eV}^{-1}$), whereas the samples prepared by RTO showed that only 950°C oxidation gave reasonable results. The ultrathin oxides grown by conventional furnace were irradiated by Si. Only the sample implanted with low dose (10^{12} cm^{-2}) could give C-V curve, which suggested that the ion implantation with dose above 10^{12} cm^{-2} strongly degraded the Si/SiO₂ interfaces and/or SiO₂ films which resulted in large leakage current. The as-implanted samples were annealed at 1000°C for 30min and then post-metallization annealed (PMA) at 400°C for 30min. It was found that annealing could recover electronic characteristics. It was also found that the flatband voltage was gradually shifted with the implanted dose which indicated the increase of the fix charge density in Si/SiO₂ interface. Electrical characterization of e-beam and H⁺ irradiated RTO oxides will be carried out.

11:30 AM S5.8

A STUDY OF COPPER OXIDATION AND SULFIDATION. Michael J. Campin¹, J. Charles Barbour², J.W. Braithwaite² and Jane G. Zhu¹. ¹Department of Physics, New Mexico State University, Las Cruces, NM. ²Sandia National Laboratories, Albuquerque, NM.

The corrosion of copper is an important area in materials science because of the widespread use of copper in a number of high-reliability electrical applications. In this study, copper layers were deposited onto SiO₂ coated Si wafers by electron-beam evaporation and then exposed to an electron-cyclotron-resonance (ECR) O₂ plasma, which is meant to simulate an aggressive oxidizing environment. The samples, with different layer thickness and varying degrees of oxidation, are studied by transmission electron microscopy (TEM) in both planar and cross-sectional views. Both Cu_2O and CuO exist in the oxide layer, and the average grain size increases as the oxide layer thickness increases. Different grain structures have also been observed in the copper layer. The composition and thickness of the oxide and copper layers have also been confirmed by Rutherford Backscattering Spectrometry and X-ray Photoelectron Spectroscopy. Identification and characterization of the type of oxide on the surface and its behavior in corrosive environments is important because the degradation of this barrier layer can influence the initiation and rate of corrosion. Specifically, sulfidizing environments are examined in this work. The microstructure of the copper sulfide and influence of the oxide layer on the sulfidation will also be reported.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

11:45 AM S5.9

CHARACTERIZATION OF COPPER OXIDES FORMED BY THERMAL AND PLASMA OXIDATION USING LINEAR SWEEP VOLTAMMETRY AND GALVANOSTATIC REDUCTION. D.L. Cocke, M.A. Hossain, R. Schennach, Gill Chair of Chemistry and Chemical Engineering, Lamar University, Beaumont, TX.

The growing importance of copper in the semiconductor industry has lead to a renewed interest in the properties and growth modes of copper oxides under a variety of conditions. While thermal oxidation of copper has been studied extensively over the last decades, recent

surface studies seem to ignore the possible formation of Cu_3O_2 . It has been shown that thermal oxidation of copper leads to multilayer structures, which consist of Cu_2O , Cu_2O , Cu_3O_2 and CuO, depending on the oxidation conditions. These oxides can be analyzed by electrochemical methods, which probe the interfaces in an electrical potential controlled order. Linear sweep voltammetry (LSV) and galvanostatic reduction (GR) have been used to characterize the oxides formed by thermal oxidation. LSV and GR show that plasma oxidation at room temperature leads to the formation of a pure CuO film, which cannot be formed using thermal oxidation.