Monday Morning, November 2, 1998

Vacuum Metallurgy Division
Room 328 - Session VM+TF-MoM

Ionized-PVD: Processes, Properties, and Applications
Moderator: S.L. Rohde, University of Nebraska, Lincoln

8:20am **VM+TF-MoM1 Ionised PVD and Filtered Arc Deposition; Processes, Properties and Applications**, ***P.J. Martin***, *A. Bendavid,* CSIRO, Australia; *H. Takikawa,* Toyohashi University, Japan **INVITED**

Recent innovations in vacuum arc deposition have resulted in the development of the filtered arc source as a deposition tool for a range of technologically important materials. The vacuum arc was recognised early on as a potentially useful source of energetic, ionised material and a practical high rate method for depositing thin films with bulk properties and the deposition of new materials. The inherent problem of microdroplet contamination was overcome by several approaches, the toroidal magnetic duct being the most prevalent. The present state of the art of filtered arc deposition (FAD) is discussed in terms of the current understanding of the emitted fluxes, the properties of the materials deposited by these devices and new applications.

9:00am **VM+TF-MoM3 Transport of a Cathodic-Arc Plasma Through a Linear-Solenoid Macroparticle Filter**, ***B.P. Cluggish***, *B.P. Wood,* Los Alamos National Laboratory

A long standing problem in the use of cathodic arcs for deposition of coatings is the production of micron sized droplets, or "macroparticles," of the cathode material. These macroparticles hit and stick to the substrate, causing defects in the coating. One widely used method for "filtering out" the macroparticles is to guide the arc plasma through a solenoidal "magnetic duct" (a metal tube with an axial magnetic field.) The macroparticles travel in straight lines and thus hit and stick to the walls of the duct, rather than reaching the substrate. Unfortunately, most of the plasma ions are lost as well. For this reason, we are performing measurements to understand the transport of the plasma through a duct. The ion flux is found to decay exponentially along the length of the duct, and the magnetic field is crucial for reducing the ion losses. However, increasing the field strength above 50 G has no effect on the ion losses. Furthermore, unlike previous researchers @footnote 1@, we find that applying a positive voltage to the duct has little effect on the ion losses. We have developed a computer simulation which reproduces our results, and predicts that the injection conditions at the entrance to the duct are crucial in determining the ion losses. This work supported by the U.S. D.O.E. @FootnoteText@ @footnote 1@ A. Anders, S. Anders, and I. G. Brown, J. Appl. Phys., vol. 75, pp. 4900-4905, 1994

9:20am **VM+TF-MoM4 Characterization of Magnetron-Sputtered Partially Ionized Deposition as a Function of Metal and Gas Species**, ***M.M.C. Allain***, *D.B. Hayden, D.R. Juliano, D.N. Ruzic,* University of Illinois, Urbana-Champaign

A dc planar magnetron with a 33-cm diameter target is coupled with a secondary plasma source to ionize the sputtered metal neutral flux to control the angular distribution of the flux arriving at the surface of the substrate. The secondary radio-frequency (rf) plasma is created between the sputtering target and the substrate by a multi-turn coil located in the vacuum chamber. The rf plasma increases the electron density, which results in significant ionization of the neutral metal flux from the sputtering target. By applying a small negative bias to the substrate, metal ions are drawn to the substrate at normal incidence. A gridded energy analyzer and a quartz crystal microbalance (QCM) are attached to a pulley system that allows the ion and neutral deposition rates to be determined along the substrate plane. The ionization fraction of the flux incident onto the QCM can then be determined as a function of position. The ionization rate is a sensitive function of the metal's ionization potential (IP). The electron energy distribution in the plasma is affected by the metal being sputtered and the working gases' ionization and excitation potentials (EP). While keeping the magnetron power, rf coil power, target to substrate distance and pressure constant, the ionization fraction, as a function of position, has been measured. The electron temperature and density are measured using a Langmuir probe. The target metals analyzed in design of this experiment are aluminum(IP=5.98eV), copper(IP=7.72eV), and titanium(IP=6.82eV). The working gases will be krypton(IP=13.99eV, EP=1.702eV), argon(IP=15.76eV, EP=2.55eV), neon(IP=21.56eV, EP=3.52eV), and helium(IP=24.58eV, EP=5.36eV). An analytic model is compared to the experimental results.

9:40am **VM+TF-MoM5 Effects of Coil dc Potential on Ion Energy Distribution Measured by an Energy-resolved Mass Spectrometer in Ionized Physical Vapor Deposition**, ***E. Kusano***, *T. Kobayashi, N. Kikuchi, K. Fukushima, T. Saitoh, S. Saiki, H. Nanto, A. Kinbara,* Kanazawa Institute of Technology, Japan

In ionized physical vapor deposition, ion energy distribution is crucial to obtain films with desired properties. The energy distribution is supposed to be affected by the plasma potential that relates to the coil dc potential induced by an applied rf power. In this study, ion energy distribution of ionized Ti particles and Ar discharge gas has been measured by an energy-resolved mass spectrometer for various coil dc potential. The sputtering cathode used in the experiment was a conventional magnetron sputtering source with a Ti target (55mm@phi@). The cathode was coupled with an rf coil (60mm@phi@, made of Cu) generating an additional plasma in the region between the target and the substrate. The mass spectrometer was a Balzers PPM421 plasma monitor. The orifice to the ion optics was 0.1mm@phi@ and electrically grounded. The coil dc potential was controlled by changing the resistance of the resistor in the LCR circuit connecting the coil to the ground. The results showed that the energy of Ti@super +@ and Ar@super +@ was enhanced from a few eV to more than 100eV as a coil rf power increased from 0 to 200W for a constant cathode dc current. By changing the resistance of the LCR circuit, the peak of the energy spectra shifted from about 160eV for the resistance of 0@OMEGA@(the coil was grounded) to about 100eV for the resistance of 1k@OMEGA@. In addition, it was found that the total energy of Ti@super +@ or Ar@super +@ arriving to the spectrometer increased as the resistance decreased. The results suggest that the coil potential to the ground affect the plasma potential and thus the energy distribution of ions arriving to the electrically grounded substrate through the plasma sheath.

10:00am **VM+TF-MoM6 Modeling of Large Cluster Synthesis**, ***A. Hosseini-Tehrani***, *F.K. Urban III,* Florida International University

The original idea of the ionized cluster beam (ICB) thin film deposition technique was based upon producing, ionizing and accelerating beams of atoms clusters from vaporized material onto a substrate in a vacuum environment, using a supersonic jet source. Simulation of this process using classical nucleation theory and one dimensional gas flow equations will be presented. This approach is an extension of previous methods used for simulation of condensation of water vapor during supersonic expansion in nozzles and simulation mechanism of large clusters from vaporized solid materials. Zinc cluster sizes predicted by the model are in qualitative and quantitative agreement with our experimental results. Simulation results will be presented for different materials as well. Recently, other methods of synthesizing clusters and nanoparticles, using different types of cluster source, like magnetron sputtering mounted in a cooled chamber, have come under development. We are in the process of extending the model for the magnetron sputtering gas aggregation cluster source and will present new results for this process.

10:20am **VM+TF-MoM7 Combined Monte Carlo and Fluid Sputter Transport Model in an Ionized PVD System with Experimental Plasma Characterization**, ***D.R. Juliano***, *D.B. Hayden, M.M.C. Allain, D.N. Ruzic,* University of Illinois, Urbana

A code has been developed to model the transport of sputtered material in a modified industrial-scale magnetron. The device has a target diameter of 355 mm and was designed for 200 mm substrates. The chamber has been retrofitted with an auxilliary RF inductive plasma source located between the target and substrate. The source consists of a water-cooled copper coil immersed in the plasma, but with a diameter large enough to prevent shadowing of the substrate. The RF plasma, target sputter flux distribution, background gas conditions, and geometry are all inputs to the code. The plasma is characterized via a combination of a Langmuir probe apparatus and the results of a simple analytic model of the ICP system. A Monte Carlo routine in the code then tracks high energy atoms emerging from the target as they move through the chamber and undergo collisions with the electrons and background gas. The sputtered atoms are tracked by this routine whatever their electronic state (neutral, ion, excited). If the energy of a sputtered atom decreases to near-thermal levels, then it exits the Monte Carlo routine as is tracked with a simple diffusion model. In this way, all sputtered atoms are followed until they hit and stick to a surface, and the velocity distribution of the sputtered atom population (including state information) at each surface is calculated, especially the substrate. Through the use of this simulation the coil parameters and geometry can be tailored to maximize deposition rate and sputter flux uniformity.

10:40am **VM+TF-MoM8 Plasma Diagnostics of Magnetic Field Assisted Ionized Magnetron Sputtering**, ***J.H. Joo,*** Kunsan National University, Korea, South Korea

The effects of axial magnetic field generated by solenoid coil has been studied for controlling the capacitive coupling between RFI antenna and metallic chamber wall, which causes severe coil sputtering at high RFI power levels. From OES results, at small magnetic flux density of 8G, RFI plasma showed sharp drop of plasma potential and reduced emission from Cu coil. Also visually the RFI plasma was confined within the RFI coil area. We compared two types of coil materials, metallic and ceramic coated. The plasma potential varied very much with materials and RFI power, which will affect the incomming ion's energy distribution. Also pulsing the sputtering power was studied to control average electron temperature of the RFI plasma, where electrons are easily quenched by heavily sputtered metals. As time dependent measuring of the plasma parameters is not readily available, some metallic films were deposited with different duties and the resulting film properties were measured. There was a big difference in preferred orientations of the grown Ag films. And the effects of ceramic coating on the RFI antenna will be addressed in the view point of plasma diagnostics, electron temperatures, electron densities, plasma potentials, contaminations and the change when it is coated by sputtered metals. Also the impedance characteristics of the RFI plasma were measured by RFZ-60 impedance analyser to study the type of coupling in mixed plasmas of DC magnetron and RFI plasma.

11:00am **VM+TF-MoM9 Study of Thin Films Deposited from a Copper Beam Formed in an Argon Atmosphere Capable of Condensing Nanoparticles**, ***F.K. Urban,*** *A. Khabari, A. Housseini-Tehrani, P. Griffiths, G. Fernandez,* Florida International University

Although thin films formed from beams of nanoparticles or clusters have been discussed since the early 1970s, the question of the usefulness of this method has remained open as few films of any significant thickness have been formed to date. Early attempts did not condense, could only condense a few "high vapor pressure" solids, or were so low rate as to make growth too slow to be of use. A new deposition system has been designed and built here along the lines of those of Averback and Haberland, as they appear to have the most promise. The new system was specifically designed for high rate with a high throughput intermediate pressure pump and 2 kW capable sputter source. Preliminary films of copper deposited onto single crystal silicon substrates show a small beam divergence of less than 1 degree total. The beam is highly non-uniform with maximum intensity on-axis, which drops rapidly to zero within less than 10 mm off axis. Deposits have been made using a 1 Torr Argon + Helium sputtering and condensation atmosphere followed by nozzle aperture extraction. Films are affected by the amount of He and by cooling of the sputter chamber walls using liquid nitrogen. Nothing appears (detectable optically) on the substrate using Ar and no cooling and increases in both factors result in films of generally increased thickness. Optically transparent films of copper have been deposited but are not yet understood. SEM, TEM, and AFM results of Cu and other films will be presented.

11:20am **VM+TF-MoM10 Novel (111)-Textured AlCu Growth by Ionized Metal Plasma (IMP) Ti Underlayer**, ***J.-B. Lai,*** *L.-J. Chen,* National Tsing-Hua University, Republic of China*; C.-S. Liu,* Taiwan Semiconductor Manufacturing Company, Republic of China

(111)-textured AlCu is well known to possess better electromigration resistance than those of (200) and random orientations. In general, stronger (111)-textured AlCu can be obtained with the deposition of Ti underlayer compared with AlCu deposited directly on oxide or TiN underlayer. The improved texture is attributed to the small lattice mismatch between (0002)Ti and (111)AlCu. In this paper, (111)-textured AlCu (0.5 at. %) enhanced by Ti had been investigated using Auger electron spectroscopy, x-ray diffraction, transmission electron microscope, high-resolution transmission electron microscope, four-point-probe and EM test. Using thicker ion metal plasma (IMP) sputtered titanium underlayer was found to enhance the stronger growth of (111)-textured AlCu compared to conventional and collimated Ti films because of stronger (0002) textured-Ti was formed and hence the growth of (111)-textured AlCu was facilitated. However, TiAl@sub 3@, about 50 µm@OMEGA@-cm in resistivity, was found in the samples annealed at 400 °C. As the samples were annealed at 450 °C, a continuous but not smooth TiAl@sub 3@ precipitate layer was observed. If the precipitates of TiAl@sub 3@ were discontinuous and restricted to grain boundaries, the (111)-textured Al was destroyed and local joule heating caused the early failure of AlCu line. TiN, as a barrier layer, can retard the growth of TiAl@sub 3@. In our study, TiN/IMP-Ti was also found to enhance the stronger tendency of the growth of (111)-textured AlCu than TiN/collimated-Ti and TiN/conventional-Ti. The growth of (111)-textured TiN was enhanced by (0002)Ti. AlCu/TiN/IMP-Ti samples were observed to possess longer EM lifetime compared with those of AlCu/TiN/collimated-Ti (or conventional-Ti).

11:40am **VM+TF-MoM11 Plasma Polymerization of Fluorine Alloyed Amorphous Carbon Coatings**, ***A. Vanhulsel,*** *J.-P. Celis,* KU Leuven, Belgium*; E. Dekempeneer, J. Smeets,* VITO, Belgium

This paper reports on the deposition conditions and characterization of plasma polymerized fluorocarbon coatings grown by an inductively coupled r.f. plasma (ICP) source, using CH@sub 4@ and CF@sub 4@ as precursor gases. SiH@sub 4@, H@sub 2@or Ar were further added to the plasma to investigate their influence on the coating properties. The coatings were characterized by XPS to determine the surface and bulk composition and combined with FTIR-spectroscopy to reveal the structure of the coatings. The mechanical properties (hardness and Young's modulus) were measured by nano-indentation. The surface energy was obtained by contact angle measurements with 2 different liquids. By varying the deposition conditions, we were able to deposit coatings with surface energies as low as 14 mN/m. With the appropriate feed gases and process parameters it is possible to adjust separately the polar and dispersive part of the surface energy. A low polar component of the surface energy corresponds to a high fluorine ,CF@sub 3@and CF@sub 2@ content at the surface of the coatings. The wetting behaviour of the coatings against water is mainly dependent on the polar component. The maximum contact angle achieved was 113°. By adding H@sub 2@ to the plasma, it is possible to minimize the polar component and maximize the dispersive component of the surface energy to obtain a relatively hard (3 GPa) coating with a hydrophobic nature (contact angle (H@sub 2@O) = 90°). The fluorocarbon coatings deposited in this system are not sensitive to atmospheric aging.

Vacuum Metallurgy Division
Room 328 - Session VM-MoA

Plasma Assisted Surface Treatments and Coatings

Moderator: I. Petrov, University of Illinois, Urbana

2:00pm **VM-MoA1 Low Temperature Growth of Protective Coatings in an ECR Plasma**, *C.-T. Lin, F. Li,* ***T.D. Mantei,*** University of Cincinnati

A high density microwave electron cyclotron resonance (ECR) discharge has been used to grow hard, colorless, and transparent silicon dioxide barrier coatings at deposition rates up to 0.7 µm/min and substrate temperatures from 80 to 120°C. The deposition precursors tested were tetraethoxysilane (TEOS), hexamethyldisiloxane (HMDSO), and hexamethylcyclotrisiloxane (HMCTSO). Metal substrates were introduced into the process chamber through a vacuum loadlock and subjected to an in situ three minute argon plasma cleaning cycle. Oxygen was then metered into the chamber through ports located upstream just below the input microwave window, while the precursor reactant gas was introduced downstream. The total gas pressure prior to plasma ignition was 1 to 10 mTorr and the O@sub 2@/precursor flow ratios were varied from 2:1 to 8:1. The substrate temperature, measured with a clamped thermocouple, rose to 80-100°C within a few minutes and then rose slowly during the remainder of the deposition cycle to a final temperature less than 120°C. Final film thicknesses were 3 to 10 µm. Maximum deposition growth rates were 0.25 µm/min for TEOS, 0.65 µm/min for HMDSO, and 0.68 µm/min for HMCTSO, increasing with increasing precursor gas flow, increasing input power, and decreasing O@sub 2@/precursor flow ratio. Fourier transform infrared spectroscopy analysis showed mainly Si-O elemental bonding for all films, with small Si-CH@sub 3@ and SiOH components. Coating compositional analyses performed with X-ray photoelectron spectroscopy showed oxygen-to-silicon ratios of approximately 2:1, but with significant carbon percentages; e.g. the carbon fraction for TEOS films ranged from 29% with an O@sub 2@/precursor flow ratio of 2.5, down to 14% for an 8:1 flow ratio.

2:20pm **VM-MoA2 Low Temperature Polycrystalline Silicon Resistors on Glass Substrates**, ***A.T. Krishnan,*** *S.H. Bae, S.J. Fonash,* Pennsylvania State University

Polycrystalline silicon (poly-Si) thin film resistors have been processed on glass substrates at low temperatures (<300@degree@C) using a novel approach. This approach involves direct deposition of n+ polycrystalline silicon thin films using an electron cyclotron resonance (ECR) high density plasma (HDP) tool, with phosphine as the dopant source. These n+ poly-Si films have been deposited on both Corning 1737 glass and soda-lime glass substrates at 300@degree@C. The dependence of film quality on film thickness has been exploited to obtain devices with resistivities over a range of 1-10 ohm-cm. The range of resistivities that can be obtained can be further increased by altering the phosphine flow rate. The deposition rates are of the order of 100 Å per minute. The temperature coefficient of resistivity of these devices is less than 2000 ppm/@degree@C. Preliminary studies indicate that it is possible to obtain n+ poly-Si films at temperatures lower than 200@degree@C, which would allow the use of clear flexible plastic substrates. Thin film resistors processed at low temperatures find a wide range of applications, such as flat panel displays, multi-chip modules,@footnote 1@ anolog circuits, @footnote 2@ and high frequency applications.@footnote 3@ In CMOS technology, low temperature resistor fabrication would enable integration of resistors on fully processed Si chips. Conventional non silicon based resistor technology requires more than one material, such as a cermet for high resistivities and a metal for low resistivities, to achieve a wide resistivity range. Currently existing Si based resistor technologies, like LPCVD cannot be used for low temperature applications, because of the high deposition temperatures (600@degree@C, which is close to aluminum melting point) or higher temperatures needed for dopant activation (700-800@degree@C). The HDP technique allows the use of a single material (n doped poly-Si) to obtain a wide range of resistivities. Because it is Si based, it is compatible with current ULSI processing techniques. Its low deposition temperature and the fact that no annealing is required to activate dopants makes it ideally suited for low temperature applications listed above. @FootnoteText@ @footnote 1@Integration of passive components for microwave filters in MCM-D, Pieters, Philip; Brebels, Steven; Beyne, Eric, Proceedings of the 1997 6th International Conference and Exhibition on Multichip Modules 1997 Denver, CO, USA p 357-362. @footnote 2@BiCMOS analog front-end circuit for an FDM-based ADSL system Langford, D. Scott; Tesch, Bruce J.; Williams, Brian E.; Nelson, G. Rodney; Ross, Robert B.; Bechtel, Gerry R.; Lewis, Mike G, Proceedings of the 1997 Bipolar/BiCMOS Circuits and Technology p 180-182. @footnote 3@110 GHz slow-wave electrodes for velocity-matched distributed MSM photodetectors with integrated bias load, Pfitzenmaier, H.; Boettcher, E.H.; Droege, E.; Bimberg, D, Proceedings of the 1997 IEEE Lasers and Electro-Optics Society Annual Meeting, USA p 218-219

2:40pm **VM-MoA3 Closed Loop Control of Reactive Sputtering of Oxide Thin Films**, ***L. Lou,*** *M. Mai, G.W. McDonough, H.V. Walde, R. Scholl, G.A. Roche,* Advanced Energy

Rapid closed loop control of oxygen flow was used to prevent target poisoning and facilitate high growth rate during reactive sputtering. Low frequency AC reactive sputtering of Al@sub 2@ O@sub 3@ and SiO@sub 2@ was performed achieving stable film formation with high deposition rates. Thin film properties of rate, refractive index and stress are reported as a function of pressure and power. Results are compared to reactive sputtering of these films by other techniques.

3:00pm **VM-MoA4 Unbalanced Magnetron Sputtered Composite Metal-DLC Coatings**, ***X.T. Zeng,*** Gintic Institute of Manufacturing Technology, Singapore

Composite metal-diamond like carbon (DLC) coating is an approach to achieve a combination of high hardness and toughness, good adhesion, a low friction coefficient, and a low wear rate, which is ideal for various tribological applications. Previous studies often used hydrocarbon gases to produce amorphous a:C-H coating doped with metal (Ti, W, Cr) and/or their nitrides by magnetron sputtering from metallic targets. Relatively high hardness (15 ~ 20 GPa) could be obtained in these coatings by increasing the doping level at the expense of an increasing friction coefficient which results in high wear rates. This paper reports the preparations of composite metal-DLC coatings on high speed steel substrates using unbalanced magnetron sputtering of both metallic and graphite targets. W and Ti/Cr targets were used to deposit both the bond layer and transition ceramic layer to support the surface composite DLC coating. For comparison, amorphous CN@sub x@ surface coating was also prepared for sliding wear testing. Nanoindentation and scratch tests were used to characterize the mechanical properties and pin-on-disk wear tests, using @phi@9 mm alumina as the pin and 10 N normal load, were carried out to evaluate the tribological properties of the coatings. Friction coefficient of about 0.06 ~ 0.1, at an air humidity of 40% RH, hardness of 15 ~ 18 GPa, critical load of about 65 N in scratch tests, and normalized wear rate of about 5 x 10@super -8@ mm@super 3@.N@super -1@.m@super -1@ for wearing for 38000 to 76000 cycles (3400 m to 6800 m) were measured. This wear rate is substantially lower than those of the nitride coatings. The superior wear resistance coupled with good adhesion implies that composite metal-DLC coatings could be good candidates for sliding wear applications.

3:20pm **VM-MoA5 Overview of Plasma Source Ion Implantation**, ***J.R. Conrad,*** University of Wisconsin, Madison **INVITED**

Plasma Source Ion Implantation (PSII) represents a radical departure from conventional ion implantation technology. PSII circumvents the line of sight restriction inherent in conventional ion implantation. In PSII, targets to be implanted are placed directly in a plasma source and then pulse-biased to a high negative potential. A plasma ion matrix sheath forms around the target and ions bombard the entire target. Compared with conventional ion implantation, PSII minimizes the problems of shadowing and excessive sputtering of the target material, which can severely limit the retained dose of the implanted ion species. This talk will present: a historical overview of the development of PSII; a brief review of PSII physics and technology; a summary of world-wide PSII activities; a discussion of laboratory and industrial field test results in PSII; recent activities leading to scale-up and commercialization of PSII; recent extensions of PSII technology to semiconductor processing.

4:00pm **VM-MoA7 Improvement of Tribological Properties of Pure Aluminium by Isotropic ECR Ion Implantation**, ***D. Popovici,*** *B. Terreault, A. Sarkissian, B.L. Stansfield, R.W. Paynter, G.G. Ross,* INRS-Energie et Materiaux, Canada

There are serious limitations to using Al and its alloys for light-weight components: in the absence of lubrification they have relatively poor tribological properties such as high friction and wear rates in sliding contact. These characteristics are due to a low flow stress of the metal and the brittleness of the aluminum oxide. The improvement of the tribological characteristics of Al, by conventional and high energy(@>=@50keV)nitrogen and oxygen implantation has already been demonstrated. In the case of N@super +@ implantation the increase in

hardness is due to the formation of an AlN film. Because relatively high substrate temperatures(400-500°C)are necessary when conventional plasma nitriding is used, the difference in the thermal expansion coefficients of Al and AlN leads to microcracks in the AlN coatings. In the case of O@super +@ implantation, the formation of a maetstable phase is followed by a thermal annealing, inducing the synthesis of nanoprecipitates of Al@sub 2@O@sub 3@ which are dense enough to pin all dislocations. In this study, we used a low temperature, low energy (30keV)isotropic PBII whith an ECR plasma source, to investigate and compare near-surface N@super +@ and O@super +@ implantation into high purity (99,99%) Al. The surface chemical composition and chemical bond formation of the implanted Al layer were investigated by AES, XPS and RBS. The surface tribological properties, structure and cristallinity were analysed by lateral force microscopy (LFM), nanoindentation and XRD. Implantation depth profiles were determined for several implantation times and sample-plasma geometries. The profiles were found to agree with TRIM simulations that supposed a monoenergetic ion source. The implantation of monoenergetic ions by our PBII technique, using a high frequency pulsed plasma and a steady high voltage for ion acceleration, allows for a precise tailoring of the implantation depth profile.

4:20pm **VM-MoA8 Molecular Dynamics Study of Al PVD Processes**, ***U.P. Hansen***, *P. Vogl,* Technical University Munich, Germany*; A. Kersch,* Siemens Ag, Germany

We present a computationally efficient classical many body potential that has been designed to model the Al-Al interaction in a wide range of bonding geometries ranging from bulk AL to Al surfaces and to the Al@sub 2@ dimer. It is shown that this potential yields Al elastic constants, Al surface diffusion barriers, surface formation energies and Al@sub 2@ properties in excellent agreement with experiment and/or previous ab-initio results. Detailed molecular dynamics simulations are performed that elucidate the different surface reactions taking place during Al physical vapor deposition. We find a high sticking probability for Al atoms impinging normal on Al surfaces and the sticking coefficient is decreasing with increasing incident angle to the surface normal. Detailed explanation for this prediction including atomistic surface reactions is presented. The energy dependence of the sticking probability calculated by our model deviates clearly from predictions of a simple hard sphere picture.

4:40pm **VM-MoA9 An XPS Study of the Effects of Chemical Pre-Cleaning of Aluminum Alloys on the Anti-Corrosion Properties of Plasma Deposited Films**, ***C.E. Moffitt***, *D.M. Wieliczka,* University of Missouri, Kansas City*; H.K. Yasuda,* University of Missouri, Columbia

DC-plasma deposited films are showing great promise as an alternative to chromate conversion for enhanced coating adhesion and corrosion protection of the aircraft alloys AA2024 and AA7075. The oxide structure of these alloys is usually modified by chemical treatments prior to application of corrosion resistant coatings. The effects of cleaning with certain chemistries employed in industry were investigated with XPS sputter depth profiling. This study of the remaining oxide layer indicates that the cleaning process leaves some undesirable deposits on the surface, which affect the stability of the coating/alloy interface region during corrosive attack. The XPS depth profiles reveal the extent of the changes in alloy surface composition after cleaning. Depth profiles of plasma film coatings on alloy surfaces treated with specific chemistries are also presented. This work was supported under Air Force contract AF F33615-96-C-5055.

Vacuum Metallurgy Division
Room Hall A - Session VM-MoP

Vacuum Metallurgy Division Poster Session

VM-MoP1 Studies on Corrosion, Wear and Erosion-Corrosion of Aluminum Coated Steel before and after Nitrogen Ion Implantation, *M. Ghoranneviss,* ***M. Abyar Monfared Kashani****, S. Meery, H. Parcharmi, A. Shokohi,* Islamic Azad University, Iran

Aluminum base coatings have been used many years as a protective layer on steels, but application of this coating is limited due to its poor wear and corrosion resistance. The main goal of this work is increasing corrosion and consequently erosion-corrosion resistance of these coatings. Steel samples were coated with different aluminum alloy by means of ion beam sputtering and then implanted by different dose and energy nitrogen ion beam. We studied properties of this coating before and after ion implantation by potentiodynamic polarization, pin on disk and rotating coupon tests. Optical and electron microscopes were also used. The results of these tests are discussed in the paper.

VM-MoP2 Deposition of bcc Ta and beta-Ta Films using Different Underlayers, ***L.V. Kozlovsky****, A. Antinsh,* University of Daugavpils, Latvia

The formation of crystalline phases in sputtered Ta films can be attributed to the deposition conditions as well as to the nature of the substrate. We deposited 100 nm Me / X nm Ta (Me: Mo, W, Nb, Ti, Zr, Hf, Dy, Fe, Al; X = 40,100, 200 nm) bilayers on room-temperature glass substrates in a Xe discharge at a pressure of (5 - 8) x10@super -4@ Torr using Penning discharge sputtering devices @footnote 1@. The base pressure was nearly 5x10@super -9@ Torr. 10 nm C underlayers were deposited on substrates at the same vacuum conditions before bilayers deposition. The structure of the films was investigated by X-ray diffraction (XRD). XRD profiles revealed peaks corresponding to (110), (220), (211) reflections of bcc Ta, peaks at d = (0.2665 0.2672) nm and the second orders of these reflections. The peaks were attributed to the beta-Ta phase in the films. Ta films on Nb, W, Mo, Ti, Al had bcc structure. Ta/Dy, Ta/Fe films structure was characterized as beta-Ta and Ta/Zr and Ta/Hf films consisted of a mixture of bcc Ta and beta-Ta. The Me and Ta layers had preferred orientation of close-packed planes parallel to the substrate plane (the [111], [110], [001] planes for the fcc, bcc, hcp metals correspondingly). The shortest interatomic distances (SID) in the Me are the shortest distances between the atoms in these planes. The correlation between beta-Ta formation in Ta/Me bilayers and mismatching of the SID in bcc Ta and in Me was found. Results of Ta films crystal structure investigations will be presented and discussed. @FootnoteText@ @footnote 1@ 1. L.V. Kozlovsky. Istrum. Experim. Techniq., 38, iss. 3, pt. 2, 417, (1995).

VM-MoP3 Graded TiAlN Layers Deposited by ECR Assisted Reactive Sputtering, *A. Raveh,* ***M. Weiss****,* Nuclear Research Center-Negev, Israel

Graded layers have been reported to reduce property discontinuities at the interface. TiAlN layers were deposited by plasma reactive sputtering employing dual cathode radio-frequency sputtering targets, Ti and Al, assisted by electron cyclotron resonance (ECR). The layers were deposited using various combination of parameters such as power input, bias substrate voltage and gas feed composition. The deposition process was monitored by optical emission spectroscopy (OES). The OES results indicate that microwave excitation added to radio-frequency plasma has contrasting effects on Ti and Al concentration in the gas phase, enhancing titanium and quenching aluminium species reaching to the deposited substrate. Thus, by the regulation of the ECR power and the ratio of nitrogen flow to nitrogen plus argon flow, the formation of graded layers is allowed. Hence, this approach was found appropriate for controlling and tailoring the interface between a metallic substrate and hard coating. The layers formed in this way were characterized with regard to structure, composition, and mechanical properties using X-ray diffractometer, Auger electron spectroscopy microscope, and Vickers microhardness and scratch tester (adhesion). It was observed that layers deposited at a low ECR power (@<=@100 W) yielded oriented (111) crystalline structure with good adhesion (failure load >70 N). These layers displayed a higher microhardness (~25 GPa) at bias substrate voltage (-50 VDC) than that of grounded substrate (10-15 GPa). However, layers deposited at an ECR power higher than 100W showed a random or amorphous structure with an intermediate adhesion range (failure load 30-50 N). The relationship between the processing parameters, the structure, and the properties of the layers formed will be presented and discussed.

VM-MoP4 Microwave Plasma Nitriding of Pure Iron, ***E. Camps,*** Instituto Nacional de Investigaciones Nucleares, Mexico, México*; S. Muhl, O. Alvarez-Fregoso, J. Chavez-Carvayar,* IIM, UNAM, Mexico*; O. Olea-Cardoso,* UAEM, Mexico

This paper presents the results of a study in which the performance of an electron cyclotron resonance (ECR) plasma source has been evaluated in regard to it's use for the nitriding of pure Fe. Diagnostic measurements,using optical emission spectroscopy (OES), Langmuir probes and an ion analyzer, were recorded as functions of the working pressure (2 - 8 x 10@super -4@ Torr) and for two different configurations of the external magnetic field near the substrate (compressed and divergent plasma flux). It was observed that the plasma source is capable of producing high density discharges, about 5 x 10@super 11@ cm@super -3@ and ion energies about 15 25 eV. Although the average ion energy was higher for the case of a divergent plasma flux (~ 45 eV). The most abundant radicals produced in the N/H discharges were NH, N@sub 2@ and N@sub 2@ @super +@ species. Experiments for nitriding of Fe showed the formation of distinct material structures when using different plasma conditions. Under certain conditions it was possible to form almost single phases of Fe@sub 3@N and Fe@sub 16@N@sub 2@ in the sample surface.

Vacuum Metallurgy Division
Room 328 - Session VM+TF-TuM

Advances in Hard and Superhard Coatings

Moderator: A. Inspektor, Kennemetal, Inc.

8:20am **VM+TF-TuM1 Deposition, Structure, and Properties of Superlattice Thin Films**, ***S.A. Barnett***, *A. Madan, P. Yashar, I. Kim,* Northwestern University **INVITED**

In this talk, superlattice thin films with nitride/nitride, metal/nitride, and oxide/oxide layers are described. Processing issues for high-rate superlattice deposition using reactive magnetron sputtering are described, including reactive-gas partial pressure control for obtaining stoichiometric layers and use of substrate bias to achieve ion bombardment densification. The stability of the layered structures at elevated temperatures is described; it is found that nanometer thick layers can exhibit excellent stability in cases where the relevant phase diagram shows little miscibility. The key materials criteria for obtaining hardness enhancements are delineated by making comparisons between different superlattice systems. Hardness predictions based on dislocation glide mechanisms are discussed. For cases where both superlattice layers have the same structure, a substantial difference between the layer shear moduli is required to limit dislocation motion and thereby strengthen the material. Superlattices where the layers have different structures, such that there is no common dislocation glide system, can also exhibit large hardness enhancements.

9:00am **VM+TF-TuM3 In-situ and Ex-situ Ellipsometric Analysis of Cr, CrN, Cr@sub 2@N Thin Films**, *D.M. Mihut, S.R. Kirkpatrick,* ***S.L. Rohde***, University of Nebraska, Lincoln

Chromium nitride thin films have technological applications in the tool and decorative coating industries, as well as providing an "environmentally-friendly" alternative to hard chrome coatings due to their unique combination of properties such as: low cost, high hardness (1600 - 3000 HK), excellent wear, corrosion, and oxidation resistance (up to 800 °C). An array of chromium and chromium nitride film monolithic and multilayered films were deposited in a ultra-high vacuum chamber equipped with an unbalanced magnetron sputtering system that combines the advantages of high-rate magnetron sputtering with high-flux, low energy ion bombardment. Ellipsometric analysis of the films was carried out by modeling layers of both stoichiometric and off-stoichiometry Cr, CrN and Cr@sub2@N thin films deposited on silicon. The ex-situ ellipsometry measurements were compared with X-ray diffraction measurements, and in-situ obtained ellipsometric information. The optical constants for CrN and Cr@sub2@N obtained using optical ellipsometry are given and compared with the optical constants for CrN and Cr@sub2@N found in the literature, and the potential of using ellipsometry in the monitoring and/or control of ionized PVD processes explored.

9:20am **VM+TF-TuM4 AlN/cBN Magnetron Sputtering: Effects on Adhesion and Phase Stabilization**, ***W. Otaño***, *L.J. Pilione, R. Messier,* Pennsylvania State University; *J.J. Santiago-Avilés,* University of Pennsylvania; *G. Lamaze,* National Institute of Science and Technology

The deposition of cubic boron nitride (cBN) thin films is of interest from a technological and fundamental point of view. It has been well established that the cubic phase stabilization depends on the energetic bombardment of the growing film. As a result of this bombardment the films show high stress levels that eventually produce delamination from the substrate. It is therefore interesting to consider atomic additions and compliant interfaces as alternative pathways to reduce the cBN stress level and/or improve film adhesion. With this purpose cBN thin films were co-deposited with Al reactively sputtered. The effects of the addition of aluminum and/or the use of AlN interlayers in the stabilization and adhesion of cBN films will be presented. The BN films were deposited by rf unbalanced magnetron sputtering and the substrate was biased using a low frequency dc pulsed excitation signal. Films with over 70% of the cubic phase, as measured by FTIR, were deposited at low negative bias voltages. A second dc pulsed power supply was used to reactively sputter the aluminum. AlN was added as an interlayer between the substrate and the BN film as well as co-deposited at different sputtering powers. The films were analyzed by FTIR, RBS and neutron depth profiling. It was found that the addition of Al to the BN films leads to a destabilization of the cubic phase for AlxB1-xN compositions above x=0.04. AlN interlayers deposited at specific pressures were found to prevent the delamination of the cBN films. A 0.7 micron multilayer coating of AlN/cBN was prepared that did not delaminate from the substrate.

9:40am **VM+TF-TuM5 Energetics of Cubic Boron Nitride Deposition**, ***R. Clarke***, *D. Litvinov,* University of Michigan **INVITED**

As a structural analog of diamond, cubic boron nitride (c-BN)is attracting increasing interest as an ultrahard coating material. An ongoing challenge towards exploiting the favorable properties of c-BN, including its chemical intertness and high thermal conductivity, is its tendency to build up substantial levels of stress at practically useful thicknesses of a few microns. If this stress is not remediated, it can lead to loss of adhesion. In this talk we present recent results demonstrating our approach to characterizing and controlling the intrinsic stress in c-BN coatings. Through an improved understanding of the kinetics of c-BN growth, using dc-biased ECR-assisted sputtering, we have achieved highly adhesive coatings on Silicon with film thicknesses up to 2µm. A novel multibeam optical wafer curvature method allows us to track, in-situ, the stress build-up during growth, and to implement 'reduced-bias' conditions after the initial nucleation and coalescence of c-BN islands. Reducing the kinetic energy of arriving nitrogen ions in this way (to ~ 50eV), leads to fewer defects in the film, reduced levels of stress, and higher growth rates, compared to values obtained at bias conditions necessary to initiate c-BN growth. Work partly supported by ONR grant N00014-94-J-0763, and by k-Space Associates Inc.

10:20am **VM+TF-TuM7 Deposition and Characterization of Ultra Thin CNx Films as a Thin-Film Disk Overcoat**, ***X. Chu***, *Z.D. Yang, J.F. Ying, S. Wang, B. Zhang,* MMC Technology Inc.

The deposition of CNx films has received great attention recently because of the potential of this material to have mechanical properties similar to diamond. One practical application of magnetron sputtered CNx films is for use as a protective coating for thin film magnetic recording disks. Ever increasing magnetic recording density requires not only a robust head-media interface, but also minimum spacing loss due to fly height, carbon thickness and magnetic layer thickness. A functional overcoat with a thickness of 50 to 100 Å is needed for the next generation recording medium. In this paper, we investigate sputtering process parameter effects on CNx film structure and mechanical properties. Target power, N% in the sputter gas, substrate temperature, and substrate bias were varied and correlated to film properties. XPS and Raman spectrum were used to study the bonding structure of the film. Sputtered CHx and CHNx films with 80 Å thicknesses and ion beam deposited CHx films were also studied for comparison. Nano-scratch wear tests showed that the 80Å film had the best wear property with 10-15% N in the gas. CNx films appear to be more wear resistant than CHx and CHNx films based on the nano-scratch test. Tribology properties of lubricated disks were tested using Contact Start Stop (CSS) testers and CNx carbon wear results can be correlated to the AFM nano-wear test. CHx films also showed good CSS results, suggesting that lubricant - carbon interaction is another important factor in head - media tribology.

10:40am **VM+TF-TuM8 Carbon and Carbon Nitride Films Prepared by Low-Energy, Isotopically-Mass-Separated, Negative C@sub 2@@super -@ and CN@super -@ Ions**, ***N.T. Tsubouchi***, *A.C. Chayahara, A.K. Kinomura, C.H. Heck, Y.H. Horino,* Osaka National Research Institute, AIST, Japan

Amorphous carbon (a-C) and carbon nitride (a-CN@sub x@) films were prepared by ion beam deposition using isotopically mass-separated, hyperthermal (50-400 eV) negative ion species such as @super 12@C@sub 2@@super -@ and @super 12@C@super 14@N@super -@ under ultra high vacuum (UHV) condition. Variation of optical constants as a function of ion's kinetic energy was investigated in the infrared-visible light region (0.8-1.5 eV). Optical band gaps of the films were estimated from optical constants. For the amorphous carbon films, the gaps were about 1.0-2.3 eV depending on kinetic energy of negative carbon ions. For the CN films, the values which did not almost depend on kinetic energy were about 0.8 eV.

11:00am **VM+TF-TuM9 Investigation on Multilayered Chemical Vapor Deposited Ti/TiN Films**, ***J.C. Hu***, National Tsing Hua Univ., Rep. of China, Republic of China; *T.C. Chang,* National Nano Device Lab, Rep. of China, Republic of China; *L.-J. Chen,* National Tsing Hua Univ., Rep. of China, Republic of China; *Y.L. Yang,* National Nano Device Lab, Rep. of China, Republic of China; *P.T. Liu,* National Chiao Tung Univ., Rep. of China, Republic of China; *S.Y. Chen,* National Tsing Hua Univ., Rep. of China, Republic of China; *C.Y. Chang,* National Chiao Tung Univ., Rep. of China, Taiwan, Republic of China

As the device dimensions scale down to deep submicron level, chemical vapor deposition (CVD) for TiN films provided excellent step coverage and

uniformity. Cu is likely to replace Al for interconnect metallization in future integrated circuits. On the other hand, the CVD-TiN films are usually of columnar structure. As a result, the fast diffusion of Al (or Cu) and Si atoms along TiN grain boundaries would degrade the device performance severely. In the present study, a novel multilayered CVD-Ti/TiN structure is formed to alleviate the grain boundary effects. To investigation the barrier property of the multilayered Ti/TiN films, junction leakage current was also measured. All the films were deposited by CVD processed in a MRC multichamber cluster tool, using TiCl@sub 4@, NH@sub 3@ and H@sub 2@ as reactants. The Ti and TiN films were deposited by plasma enhanced CVD and low pressure CVD, respectively. In order to reduce chlorine concentration of the films, NH@sub 3@ plasma post-treatment was applied to multilayered CVD-Ti/TiN films. In addition, electroless deposition of Cu was deposited on the multilayered CVD-Ti/TiN films. Transmission electron microscopy and X-ray diffractometry were utilized to investigate the microstructure and crystal orientation. Auger electron spectrocopy was applied to determine the stoichiometry and uniformity along the depth direction. The morphology was studied by a field emission scanning electron microscopy. Electrical measurement was used by HP-4145. The enhanced multilayered Ti/TiN stack found to be a robust barrier against Al/Si interdiffusion. It also improved the electrical property of the films. The resistivity of the film was found to reduce from 240 to 120 µm@OMEGA@-cm by multilayered Ti/TiN structure with the NH@sub 3@ plasma post-treatment. The leakage current can also be kept low enough for device application. In addition, the thermal stability of electroless Cu/mutilayered (CVD-Ti/TiN)/TiSi@sub 2@/Si structure was improved.

11:20am **VM+TF-TuM10 Chemical Vapor Deposition of Metal (Ti) and Ceramic (TiO@sub 2@, TiN) Thin Films via Gas-Phase Reaction of Titanium Tetrachloride and Sodium Metal Vapor***, **J.H. Hendricks**, M.I. Aquino, J.E. Maslar, M.R. Zachariah,* National Institute of Standards and Technology

A new route for Chemical Vapor Deposition (CVD) of metal and ceramic thin films has been demonstrated. This novel method involves the use of a low pressure coflow diffusion reactor to react sodium vapor with titanium tetrachloride in the presence of a non-reactive gas (Ar) or a reactive gas (N@sub 2@, O@sub 2@). This reaction chemistry is described by the following general equation: (mn)Na + nMX@sub n@ --@super Ar@--> (M)@sub n@ + (nm)NaX. Here, Na is an alkali metal (e.g. Na, K, Cs, or Rb), M is a metal (e.g. Ti, Ta, Pt, W, ...) or non-metal (e.g. B, C, Si, ...), X is a halogen (e.g. F, Cl, Br, or I), Ar is a non-reactive gas (e.g. Ar or He) and m and n are integers. In this reaction, the alkali metal strips halogen from the metal or non-metal halide. The metal or non-metal is then free to form a thin film on a substrate placed in the reaction zone. This chemistry should be generic for the deposition of a wide class of metallic and ceramic thin films, and it is suggested that this technique could be used to grow superhard BN and CN thin films at temperatures which are significantly lower than conventional CVD techniques. Guided by theoretical modeling, reactant concentrations and substrate temperatures were adjusted to prevent salt (NaCl) incorporation into the deposited thin films. Using the described techniques, we have now produced Ti and TiN thin films on Cu substrates at 610 °C, and TiO@sub 2@ thin films on Si substrates at 600 °C. These temperatures are considerably lower than the (1000 to 1200) °C required for conventional CVD of Ti (by decomposition of titanium tetraiodide). The quality and composition of the thin films were analyzed by scanning electron microscopy (SEM), energy dispersive x-ray spectrometry (EDS), x-ray diffraction (XRD), Raman spectroscopy, transmission electron spectrometry (TEM), and selected area electron diffraction (SAED). Future work will focus on the use of this novel technique to grow CN and BN thin films.

11:40am **VM+TF-TuM11 Low Energy Ion Beam Deposition of Oriented Diamond Microcrystallites***, **P.K. Tse**, R.W.M. Kwok, K.M. Lui, W.M. Lau,* The Chinese University of Hong Kong, China

Ion beam deposition provides an additional control of film properties over the chemical vapor deposition (CVD) via the change of ion beam energy. In this study, low energy ion beam deposition of carbon films on silicon in the ion energy range of 200 - 1050 eV was studied. The ion beam was characterized by a Faraday cup equipped with a retarding lens. The films were characterized using X-ray photoelectron spectroscopy, characteristic electron energy loss analysis, and atomic force microscopy. It was found that graphitic films, amorphous carbon films and oriented diamond microcrystallites could be obtained separately at different ion beam energies. Highly oriented diamond microcrystallites were deposited on Si (100) wafer at energy of 200eV and substrate temperature of 420°C. The ion beam deposition will be used as a diamond seeding process which will be followed by a typical hot filament CVD process, for the growth of oriented diamond films on Si (100).

Author Index

Bold page numbers indicate presenter