Surface Engineering
Room Exhibit Hall C & D - Session SE-TuP
Poster Session

SE-TuP1 General Rule to Predict Under-layer Segregation on Film Surface, *M. Yoshitake, **Y.-R. Aparna**, K. Yoshihara,* National Research Institute for Metals, Japan

Film deposition with multi-layer structure is widely utilized in many industrial fields such as electronic device and magnetic film. Diffusion and reaction of under-layer metal sometimes cause troubles and considerable efforts are made to prevent diffusion and reaction. In catalysis field, on the other hand, surface segregation of one component in alloys or bi-layer thin film is decisive factor for its catalytic ability. We studied surface segregation of under-layer metal on the top of a film in a vacuum with Auger electron spectroscopy (AES) and/or X-ray photoelectron spectroscopy (XPS). When surface segregation of under-layer metal was observed, no significant interfacial reaction between under-layer and top layer was detected. Metallic films of sub-micron or micron order thickness were deposited on polished metallic substrates. Al, Ti, Cr, Ni, Cu, Nb and Fe were used as a substrate material, and Al, Ti, Cr, Cu, Zr, Nb and Fe were used as a film material. More than 25 combinations of film-substrate materials have been investigated. From the viewpoint of phase diagram, three types of combinations are included in those combinations, i.e., two elements in solid solution, two elements in separation, and two elements in an intermetallic compound. General rule to predict under-layer segregation on film surface is discussed based on adsorption energy. This rule is quite different from that for segregation in bulk alloy.

SE-TuP3 Role of Surface Condition in Diamond Nucleation during Bias-enhanced Nucleation, ***N. Ali**, W. Ahmed,* Manchester Metropolitan University, UK; *Q.H. Fan,* University of Aveiro, Portugal; *C.A. Rego,* Manchester Metropolitan University, UK

Thin polycrystalline films of diamond have been deposited on copper substrates using hot-filament chemical vapour deposition (HFCVD) system. It is known that substrate surfaces require some form of pre-treatment prior to diamond CVD. Substrate biasing has been extensively used to enhance diamond nucleation density. Majority of the work published, to date, relating to diamond nucleation by means of bias-enhanced nucleation (BEN) looks at either negatively or positively biasing substrates such as silicon where the surface biased is smooth. However, there is very little work been carried out which investigates the effect of surface roughness and surface impurities on diamond nucleation during the BEN process. We negatively bias polished copper substrates, where the polishing materials used were diamond paste, diamond powder and silicon carbide. Our preliminary results have shown that by amalgamating surface polishing with biasing there is a definite enhancement in the overall nucleation density with all the commonly used polishing materials. We observed that both surface roughness and polishing material residues seeded into the copper substrates play a critical role in diamond nucleation during the BEN process. The nucleation densities were calculated from SEM images and the surface roughness values were obtained from AFM analysis. Furthermore, the quality of the diamond grains was gauged using Raman spectroscopy.

SE-TuP4 High Rate Sputtering for Ni Films by r.f.-d.c. Coupled Magnetron Sputtering System with Multipolar Magnetic Plasma Confinement, ***K. Kawabata**, T. Tanaka,* Hiroshima Institute of Technology, Japan; *A. Kitabatake, K. Yamada, Y. Mikami,* Hiroshima Sanyo Vacuum Industries Co., LTD., Japan; *H. Kajioka, K. Toiyama,* Western Hiroshima Prefecture Industrial Institute of Technology, Japan

It is difficult to prepare ferromagnetic films such as Ni with the conventional magnetron sputtering at a low pressure and at a long substrate-target distance. Ni films were prepared by an r.f.-d.c. coupled magnetron sputtering with a multipolar magnetic plasma confinement (MMPC) at the low pressure of 6.7x10@super -2@ Pa and at the long distance of 120 mm, where the permanent magnets were placed around a Ni target (200mm, 5mm thick) outside the chamber. R.f. power and d.c. bias were applied simultaneously to the target where an r.f. power of 60W was utilized to stabilize the plasma discharge. The deposition rate of Ni films significantly increased with the increasing target d.c. bias voltage (V@sub T@) because the target current increased with the V@sub T@. The highest value of the deposition rate was about 250 nm/min at V@sub T@=-850V. The increase in the deposition rate with V@sub T@ might be attribute to enhanced gas ionization due to a strong magnetic confinement of the plasma. It was found that the high rate sputtering for Ni films is possible at the Ar gas pressure of 6.7x10@super -2@Pa. The resistivity for all the films deposited at different d.c. bias voltages was 7.1-8.2µm@ohm@cm whose values were close to the bulk value of 6.9µm@ohm@cm. The intensity of the Ni (111) plane observed from X-ray diffraction patterns markedly increased with the V@super T@ and the value of the grain size estimated from the plane was 32-75nm. Therefore, it is shown that the sputtering system with MMPC has some advantages, in comparison with conventional magnetron sputtering, such as high deposition rate, plasma discharge stability, and the preparation of high quality magnetic thin films.

SE-TuP5 The Properties of the Wettability and Corrosion Resistance of Surface Preparation and PVD Coatings on Mold Steel, ***S.-M. Chiu**, C.-H. Lin, W.-C. Lo, Y.-C. Chen,* Metal Industries Research & Development Centre, Taiwan

During the production of IC components, packaging process is used for protection IC chips from harmful environments.Molding,trimming,and forming stages are three sequential works of packaging process.There are many factors affect moldability including molding die,mold condition,EMC,package design,and operator status.The function of molding die is to capsulate IC chips with thermosetting epoxy molding compound(EMC).The EMC is composed of many additives will abrade and corrode the molding die.It is important to extend the duty life of molding die for upgrading the production rate. In this study we compare several mold steels such as high-speed steel,stainless steel,tungsten carbide,and ceramics.Electrical discharging machining(EDM) and shot peening processes prepare the different surface roughness of mold steels. Some commercial surface treatment are preformed for comparing the surface characteristics of treated mold steels. There are including electroplated hard chromium,plasma nitriding,PVD coatings,and PCVD coatings.The contribution of these factors and their interactions to the contact angle,salt spray test,and wear test are determined.In the research of wettability shows,the influence of surface roughness on contact angle is to effect an increase in the contact angle from 77° to 110° as the roughness increases from an Ra value of 0.05µm to 2.0µm.The surface treatment can obviously reduce the influence of surface roughness on the contact angle.PVD Cr-based coatings show the highest contact angle value,above 120° ,even better than PTFE polymer material.PVD Cr-based coatings and plasma nitriding can effectively improve corrosion resistance of molding steels.To optimize the surface charactristics of PVD Cr-based coatings on molding die and be used in the IC packaging production lines.It shows that about 50% of production shots,comparing with electroplated hard chromium coating,before needing to clean the molding die.

SE-TuP6 On the Shielding Influence of Charged Particles on the Kinetics of the Oxide Film Growth, ***D.G. Mukhambetov**, O.V. Chalay,* Karaganda Metallurgical Institute, Kazakhstan

The object of this work was to investigate kinetics of the two phase oxide film growth on the @alpha@-Fe surface at the temperatures of 650 - 750 K. It is experimentally attained that film thickness h - time oxida- tion @tau@ relationship in the range denoted above is logarithmic function, whereas Kabrera and Mott's theory gives square law of the film growth. In our work analytical treatment of obtained data was made on the basis of this theory, but we suppose that self-deceleration of the film growth is caused not by attenuation of the electric intensity in the film because of increase of h but by shielding influence of the space charge of diffusing ions and elec- trons in that oxide film. With that aim in view the Debye shielding distance for plasma substance state in the oxide film was taken into consideration. Logarithmic law of the oxide film growth was derived. Estimating calcula- tions of this law parameters quantitatively corresponding with the literature data were made . The obtained results were used in the development of the surface oxidation technology of the electric steel.

SE-TuP8 Characterization of Plasma-nitrided Iron by SEM, XRD and XPS, *L.C. Gontijo,* Centro Federal de Educacao Tecnologica do Espirito Santo, Brazil; ***P.A.P. Nascente**, R. Machado,* Universidade Federal de Sao Carlos, Brazil; *E.J. Miola, L.C. Casteletti,* Universidade de Sao Paulo, Brazil

Plasma nitriding technique has been used to improve the tribological and mechanical properties of materials, specially iron-based alloys. In this work, the Pulsed Glow Discharge (PGD) technique was used for nitriding pure iron. Four samples were nitrided in a gas mixture of 80 % H@sub 2@ and 20 % N@sub 2@ under a pressure of 400 Pa, discharge frequency of 9 kHz, and temperature of 853 K. Samples 1, 2 and 3 were nitrided for 30, 60 and

90 minutes, and then quenched in situ. The fourth sample was nitrided for 90 minutes and then quenched in air. The nitrided iron samples were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). SEM micrographs showed differences in the surface morphologies for the samples which were quenched inside the chamber. However, when the results for samples 3 and 4 were compared, it was noticed an even more significant change in the surface morphology, which demonstrates the importance of the cooling rate on the formed layer. XRD identified the Fe@sub 4@N phase in all samples. Besides this phase, also the Fe@sub 3@N, Fe@sub 2@O@sub 3@ and Fe@sub 3@O@sub 4@ phases were detected in the sample quenched in air. XPS was employed to obtain chemical-state and quantitative information of the plasma-nitrided iron surfaces.

SE-TuP9 Surface Charge Assisted Ion Deposition: A New Possibility of Film Structure Control*, **I.G. Levchenko**,* Kharkov State Aerospace University, Ukraine*; M. Keidar,* University of Michigan

The method proposed namely Surface Charge Assisted Ion Deposition consists in using the surface electrical charge as a tool for thin film micro-structure and characteristics control. It was shown that the substrate electrical charge provides the powerful and convenient possibilities of nuclei distribution function control resulting in thin film growth with the required characteristics. Using the specified surface charge - film thickness function it is possible to influence the nuclei distribution function. Criterions of electrical controllability were determined on the basis of nucleus electrical balance. It was shown that the method can provide realization of the time-divergent and time-convergent distribution functions. Interesting are the modes provides the equalization of distribution function following by the uniform growth. The possibility to create composite films consisting of bearing very hard matrix such as TiN or TiC filled with the solid-state lubricant such as Cu is shown. The Surface Charge Assisted Deposition provides formation of high-uniform bearing matrix characterized by the high hardness and tensile strength. Other filling matters can be used to provide the wide range of thin film characteristics such as high thermal conductance, temperature conductivity etc. Experimental data on comparative tests of films deposited by the Surface Charge Assisted Deposition and films deposited with the usual methods are given. The friction test shows the film wear resistance increase by factor of 1.25 due to high wear resistance and low friction coefficient of the films applied with the controlled surface charge. The experiment set-up and test conditions are shown.

SE-TuP10 Formation and Dynamic of Nuclei Distribution Function in Ion Deposition. Theoretical and Numerical Investigation*, **I.G. Levchenko,*** Kharkov State Aerospace University, Ukraine*; M. Keidar,* University of Michigan

The defining role of nuclei distribution function in thin film structure formation is now proved. The present paper is intended to develop the complete model of distribution function formation covering the whole set of the most important factors influencing the film growth. In particular, the following processes were taken into account: adsorbed particles diffusion about the substrate surface; nucleus diffusion causing the distribution function change; nuclei collisions; nuclei coalescence accompanied with the transitional quasi-liquid layer formation; etc. The study was carried out on the basis of the continuity equation for nucleus distribution function and equation for adatoms concentration in the nucleus area. Dynamic of distribution function formation was studied in the various conditions of deposition namely in high and low external flow intensity, high and low diffusion mobility, etc. The numerical simulation was performed using the above model in the most complex conditions: high rate of adsorbed particles and nuclei migration, high intensity of external flow, high substrate temperature, various ionization coefficients. The program developed provides both distribution function calculation and surface ensemble visualization in the form of series of the screen shots. The nuclei ensemble consisting 1000 particles was investigated, and surface concentration fields were calculated in the area of non-continuous film being formed. Comparisons with experimental data are shown justifying the accuracy of the model proposed.

SE-TuP11 Effect of Annealing on the Microstructure and Mechanical Property of TiN/AlN Multilayer Films Prepared by the Ion-beam Assisted Deposition*, **D.G. Kim,*** Kwangju Institute of Science and Technology, Korea*; Y.-J. Baik,* Korea Institute of Science and Technology, Korea*; T.Y. Seong,* Kwangju Institute of Science and Technology, Korea

Nano-scale nitride multilayers are considerable research interests because lattice and composition modulation induces outstanding mechanical properties. Since the microstructure of nanolayered films is metastable both mechanically and thermodynamically, the thermal effect can be an important issue. In this study, we investigated the mechanical property and the thermal stability of the TiN/AlN multilayer films. TiN/AlN multilayers were prepared on (100) Si wafer by ion-beam assisted deposition (IBAD), evaporating alternatively Ti and Al metals with nitrogen and Ar ions bombardment. The multilayers were designed to have layer sequences in different bilayer periods (l) from 3.6 to 50 nm. In addition, the samples, having 3.6 and 20 nm periods, were annealed at temperatures between 800 @super o@C and 1100 @super o@C. Nano indentation hardness was employed to acquire the mechanical property of the samples. X-ray diffraction and cross-sectional transmission electron microscopy were also used to investigate the microstructural changes of the TiN/AlN multilayers with bilayer periods. The hardness for the multilayer films with ¥ë @>=@ 6 nm was around 22 GPa, whilst the hardness for the samples with ¥ë@<=@ 4 nm showed higher than 30 GPa. For the sample with ¥ë@<=@ 4 nm, a strong and narrow superlattice (111) peak was observed. However, the peaks of the hexagonal AlN and TiN were absent in this diffraction pattern. This result showed that the (111) oriented multilayer film composed of the TiN and cubic AlN was formed and these coherently bonded superlattice made the hardness with ¥ë@<=@ 4 nm sharp increase. There was no observable change in the micro-structure of the samples annealed at lower than 900 @super o@C, which preserved the discrete layered structure. But the interdiffusion of the multilayer was perceived at the higher temperature and led to deterioration of the mechanical property.

SE-TuP12 Impression of High Voltage Pulses on Substrate in Pulsed Laser Deposition*, **T. Ikegami,** T. Ohsima, M. Nakao,* Kumamoto University, Japan*; S. Aoqui,* Sojo University, Japan*; K. Ebihara,* Kumamoto University, Japan

DLC film coatings are of technological interest for enhancing wear resistance and corrosion resistance of metals. Pulsed laser deposition (PLD) can deposit hydrogen-free DLC films, those are expected superiority in hardness and adhesion to the substrate, by graphite ablation in vacuum ambient. In PLD, controllable parameters, laser fluence, pressure and kind of ambient gas and bias voltage to a substrate, are limited. In this research, negative high voltage (HV) pulses are applied to a substrate holder synchronously with the plasma plume to modify carbon plasma plume in the similar way to plasma immersion ion implantation. Here, a carbon plasma plume produced by laser ablation is used as a high-density plasma source. High energetic carbon ions and excited atoms can be expected to improve film properties and its adhesion to the substrate. Effect of HV pulses on the plasma plume was investigated by optical emission spectrometry, laser induced fluorescence meth od and their effect on DLC films was examined using FTIR, AFM and Raman analyses. By applying HV pulses emission from C@super +@ increased and modification was found in film properties.

SE-TuP13 Characterization of Chromium Nitride Coatings Deposited by A Hybrid PVD and Metal Plasma Ion Implantation Process*, D.-Y. Wang, **K.-W. Weng**,* National Chung-Hsing University, Taiwan

Chromium nitride coatings were deposited using a hybrid PVD and metal plasma ion implantation (MPII) process. MPII is a plasma-based ion implantation process, which supplies low energy (10-80 keV) metal ions with multiple charge states. At the initial coating stage, low dosage of MPII ion flux helps in effective surface activation and ion mixing. The interface adherence is significantly improved. A subsequent ion bombardment by MPII in conjunction with a conventional cathodic arc evaporation process provides apparent advantage of film densification and stress relaxation. The influence of ion energy of MPII source upon film properties will be conducted using mechanical and tribological tests.

SE-TuP14 Energy and Angular Distributions of Deposition Flux in Magnetron Sputtering Systems*, **R.I. Erickson**, J.R. Doyle,* Macalester College

The substrate energy and angular distribution of atoms sputtered in a magnetron glow discharge in argon is studied using Monte Carlo simulations and deposition profiles in cavity substrates. The simulation uses the TRIM code for the nascent sputter atom energy and angular distribution. The gas phase collisions are modelled using Thomas-Fermi-Dirac potentials for the higher energies and Lennard-Jones potentials for near thermal energies. Comparison of experimental deposition profiles on cavity substrates with the predicted angular distribution of arriving flux yields good agreement. The simulation results predict that the average energy of arriving atoms exhibit a dependence Bexp(-apd) down to thermal energies where p is the pressure, d is the target-substrate distance, B is the average energy of the nascent sputter atoms, and a is a constant independent of p and d. The constant a can be considered the inverse of a characteristic pd value for thermalization, and is parameterized by the atomic number of the target atom yielding a universal relation for arbitrary targets sputtered in argon.

SE-TuP15 The Corrosion Resistance of the Chromium Nitride on Carbon Steel by Cathodic Arc Deposition*, **S. Han**,* National Chung Hsing University, Taiwan, ROC*; J.H. Lin,* National Tsing Hua University, Taiwan, ROC*; S.C. Chung,* Industrial Technology Research Institute, Taiwan, ROC*; S.H. Tsai,* National Tsing Hua University, Taiwan, ROC*; F.H. Lu,* National Chung Hsing University, Taiwan, ROC*; H.C. Shih,* National Tsing Hua University, Taiwan, ROC, Taiwan,ROC

The electrochemical behavior of CrN coating on steel is investigated. The CrN coatings are deposited using a reactive cathodic arc plasma deposition technology in an industrial scale. The microstructure and crystalline of chromium nitride have been investigated using XRD, XTEM and SAD. The CrN coatings exhibit microcolumnar morphologies. The aqueous corrosion behavior of the coatings was studied in a saline (3% NaCl solution) environment by OCP and EIS measurements. The OCP measurements indicated that the CrN coatings are nobler than the uncoated substrate. The R @sub p@ of the CrN coatings is at least an order of magnitude larger than the uncoated alloy steel. Moreover, the R @sub p@ of the CrN coatings tends to decrease with immersion duration, showing that the corrosion changes from charge transfer to diffusion control process especially when the immersion time is long enough.

Author Index

Bold page numbers indicate presenter