INTERNATIONAL CONFERENCE ON METALLURGICAL COATINGS AND THIN FILMS

PROGRAM AND ABSTRACTS

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properties of low dimension systems (in one direction). In order to analyze the elastic behavior of nanostructured W layers, W/Cu multilayers with period thicknesses ranging from 24 down to 1.7 nm and different W/Cu thickness ratios have been prepared by ion beam sputtering and characterized using X-ray reflectometry, X-ray diffraction, instrumented indentation and energy dispersive analysis in a scanning electron microscope. W and Cu are non miscible elements, but EXAFS measurements indicated that interface alloying may occur in tungsten sub layers for the lowest periods and for equiatomic composition. The mechanical elastic behavior of the W layers was observed to depend on the period and the W/Cu thickness ratio of these multilayers as well. Elastic response is observed to be well below that expected from a simple rule of mixture. The interface alloying may induce the change in the elastic behavior. In order to understand more precisely the mechanical properties of these multilayers, the elastic behaviors of both tungsten and copper sub layers have been analyzed using a method combining X-ray diffraction and tensile testing. Indeed, X-ray diffraction is phase selective and allows measuring the elastic deformations both in W sub layers and Cu sub layers. The first results for a multilayer composed of 10 bilayers of 6 nm W and 18 nm Cu and the microstructural evolution, i.e. texture evolution, of WCu multilayers as a function of period will be presented and discussed.

EP-25 Nanoceramic Based Coatings of High Lubricity and Low Friction Formed by Plasma Spray Processes, ***X. Ma*** *(animesh.basak@mtm.kuleuven.be), D. Xiao*, Inframat Corporation

This work has investigated the behavior of friction and wear of a nanocomposite coating that was formed in a process of plasma spray. A solid-state lubricant phase iron sulfide (FeS) was chemically converted from iron disulfide (FeS_2), and incorporated in a wear-resistant nano-aluminia/titania matrix in the process of plasma spraying. The nanocomposites also have been fabricated into lubricant coatings with a functionally graded structure in plasma spray processes. The nanocomposite coating exhibited a low coefficient of friction and low wear rate. Tribological test results for the nanocomposite coatings demonstrated dramatic increases in both sliding wear resistance and abrasive wear resistance, potentially for the applications that require a solid lubricant surface.

EP-26 Didactically Optimized Training Tools for Mechanical Thin Film Design, ***P. Heuer-Schwarzer*** *(p.heuer@esae.de)*, ESAE, Germany, *N. Schwarzer*, Saxonian Institute of Surface Mechanics, Germany

When the properties of a layered material shall be improved, the following three steps must be taken: First of all, the material needs to be characterized carefully with a suitable measurement instrument and an appropriate analysis software. It is a well known fact, that the characterization of the mechanical parameters constitute the basis for a successful optimization. Nevertheless, many people do not pay enough attention to this matter and are often content with rather poor results. The very advanced measurement techniques and instruments that exist on the market need to be supported by didactically edited material such as training videos or audiovisual presentations to ensure an optimal application for the user.

In the second step, the exact use of the material must be analyzed. Is its surface exposed to small, sharp contacts or rather to large and blunt contact counterparts. The question about the mechanical loads needs to be answered as well as the kind of contact and damage that occurs. Those concrete contact conditions lay the foundations for a simplified model-contact-system that will, like an idealized experiment, illustrate possible solutions.

Finally, the optimization of the actual mechanical layer can be approached: The characteristics of the layer and surface can be designed in a way that the material is protected optimally against the mechanical stresses and contact loads that do occur during the normal use.

The full understanding of these three steps contributes crucially to a successful mechanical thin film design. Thus, this paper will present a specialized didactic strategy for training tools for thin film design models, which include associations, motivate the user and is optimized with respect to the later application.

EP-27 Automated Analysing of Thin Film Nanoindentation Data Using the Concept of the Effectively Shaped Indenter, *N. Schwarzer (n.schwarzer@esae.de)*, Saxonian Institute of Surface Mechanics, Germany, ***L. Geidel***, TU Chemnitz, Germany

Recently developed analysing techniques applying the concept of the effectively shaped indenter allow a much more comprehensive analysing of nanoindentation data of thin films[1]. The new analysing procedures have even been successfully applied in the case of very thin coatings well below 100nm thickness. Important physical mechanical parameters like Young's modulus, critical stresses for phase transition and Yield strength can be determined[2]. From the theoretical point of view, also fracture toughness (critical stresses for cracks of various fracture modes) and intrinsic stresses should in principle be determinable. However, as the mathematical apparatus for such analysing procedures is rather complex and the performance of the evaluation very cumbersome and difficult to learn, it seems reasonable to develop software tools providing features for a rather automated calculation process. The present study is about the principle feasibility of such analysing tools and the state of their realisation.

[1] N. Schwarzer, T. Chudoba, G. M. Pharr: "On the evaluation of stresses for coated materials during nanoindentation with sharp indenters", Surface and Coatings Technologies, in press, Corrected Proofs, doi:10.1016/j.surfcoat.2005.01.011

[2] N. Schwarzer, T. Chudoba, F. Richter: "Investigation of ultra thin coatings using Nanoindentation", Surface and Coatings Technology, in press, accepted July 2005.

EP-28 Fretting Wear of TiC_x and TiN_y PVD Coatings Under Variable Relative Humidity Conditions - Development of a 'Composite' Wear Law, *R. Rybiak, T. Liskiewicz, S. Fouvry (siegfried.fouvry@ec-lyon.fr)*, Ecole Centrale de Lyon, France, *B. Wendler*, Technical University of Lodz, Poland, ***P. Kudlacek***, University of West Bohemia, Czech Republic

Fretting wear is defined as a small oscillatory displacements between two contacting bodies. The interface is damaged by debris generation and its ejections from the contact area. It is well-known that the application of hard coatings is potentially a solution against fretting wear. For this study TiC and TiN hard coatings manufactured by a PVD method have been selected and tested against polycrystalline alumina smooth ball. A fretting test programme has been carried out at the frequency of 5Hz, 100N normal load, 100µm displacement amplitude and at five values of a relative humidity (RH): 10, 30, 50, 70 and 90% at 296K temperature. The intensity of a wear process is shown to be significantly dependent on the environmental conditions. A dissipated energy approach has been employed to quantify wear rates of hard coatings. This approach is stable to predict wear kinetics under constant medium relative humidity. However, an increase of the relative humidity promotes the formation of hydrate structures through the interface and modifies the third body rheology. This phenomenon has been characterised by the evolution of wear kinetics associated to a significant variation of the corresponding energy wear coefficient (α). In this work a 'composite' wear law integrating the wear energy coefficients as a function of the relative humidity is introduced. It permits to predict the wear responses under variable relative humidity varying from 10 to 90% within a single fretting test. The stability of this approach is demonstrated by comparing various variable relative humidity sequences.

Advanced Materials Characterization
Room: Town & Country - Session FP

FP Poster

FP-1 Vacuum Electron Field Emission from SnO_2 Nanowhiskers Annealed in Oxygen and Nitrogen, ***S.H. Luo***, Shanghai Institute of Microsystem and Information Technology/Chinese Academy of Sciences, PR China, *W. Liu, M. Zhang, Z. Di, C. Lin*, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, PR China, *P.K. Chu (paul.chu@cityu.edu.hk)*, City University of Hong Kong, PR China

Tin oxide is known for its application in gas sensors, transparent conducting electrodes and dye-based solar cells. Our previous work has shown SnO_2 nanowhiskers are good electron emitters. However, the effects of surface states on the field emission properties have not been investigated. In this study $OSnO_2$ nanowhiskers are intentionally subjected to O_2 and N_2 annealing and the field emission properties of the annealed SnO_2 nanowhiskers are investigated. The current generated by the emission of electrons is observed to drastically increase and the threshold field defined as the emission current density at 1 $\mu A/cm^2$ is reduced from 3.17 of the as-grown sample to 2.59 V/µm of the sample annealed in N_2. The threshold field is increased to 3.63 V/µm after annealing in O_2. Analysis of the slope and intercept of the Fowler Nordheim plot reveals that the dependence of the threshold field on the surface treatment is due to the different work functions. Four transfer infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) results show that the amount of Sn-O bonds is reduced as N is introduced into the materials during annealing in N_2. High-resolution XPS results indicate that the binding energy of Sn 3d and O1s shift towards higher binding energies. For the sample annealed in O_2, the Sn-O bond i enhanced and the surface crystalline quality is improved. The binding energies of Sn 3d and O1s shift slightly towards lower binding energies. Our study shows that annealing in N_2 yields a surface that is locally terminated by N-O bonds. This increases field emission by raising the bands towards the vacuum level and lowering the

emission barrier. Our results also show that annealing in O_2 can make the surface more chemically uniform and increase the emission barrier.

FP-6 Raman Spectra and Structural Analysis in ZrN_xO_y Thin Films, *P. Carvalho, C. Moura,* ***L. Cunha*** *(lcunha@fisica.uminho.pt), F. Vaz, L. Rebouta,* Universidade do Minho, Portugal, *E. Alves*, Instituto Tecnológico Nuclear, Portugal

Raman spectroscopy has been used as a local probe to characterize the evolution of phases on the preparation and annealing of decorative zirconium oxynitride (ZrN_xO_y) thin films produced by dc reactive magnetron sputtering. The lines shapes, the frequency position and widths of the Raman bands show a systematic change as function of the reactive gas flow. The as-deposited zirconium nitride film presents a Raman spectrum with the typical broaden bands, due to the disordered induced by N vacancies. The recorded Raman spectrum of the zirconium oxide film is also typical of the monoclinic phase of ZrO_2. Raman spectra of zirconium oxyniride thin films present changes related with the oxygen content in films composition. These changes are confirmed by XPS analysis. XPS spectra reveal that the N 1s, O 1s and Zr 3d peaks evolution are well correlated with the structural changes of the coatings. The N1s peak is composed of two components, which are related with the two existing zirconium nitride phases (ZrN and Zr_3N_4). On the other hand, the Zr 3d peak shows a complex structure that can be ascribe as revealing the presence of nitride, oxynitride, and oxide phases.

FP-8 Asymmetric Synthesis of Terminal Epoxides and Diols in the Zeolite Membrane System using New Chiral Salen Catalyst, ***Y.-H Lee,*** *C.-K Shin, G.-J Kim (kimgj@inha.ac.kr)*, INHA University, Korea

The unsupported self-standing films of zeolite were obtained by in situ traditional wet hydrothermal synthesis.[1] The most zeolite crystals were grown in the form of aggregates. In order to obtain a high productivity, thin mesoporous layer was coated on zeolite membrane with a high catalyst volume fraction.[2] The enantioseletive hydrolytic resolution of racemic epoxides was performed in the ZSM-5/MCM-41 membrane system containing chiral salen complexes.[3] The chiral salen complexes immobilized on the membrane showed a very high enantioselectivity in the hydrolysis of terminal epoxides such as epichlorohydrine, epoxybutane, styrene oxide and 1,2-epoxyhexane. The catalyst in membrane could be recycled again by filling the reactants in the separated reactor. The catalytic activity and selectivity of Co(salen) complexes have not changed more or less after four times of reusing. The catalytic membrane system allows to separate the reagents with markedly different polarities without the need for a mutual solvent and to increase the conversion of reactant.

[1]T. Sano, Y. Kiyozumi, F. Mizukami, H. Takaya, T. Mouri and M. Watanabe, Zeolites, 12 (1992) 131

[2] H.S. Roh, J. S. Chang, and S. E. Park, Korean J. Chem. Eng., 16 (1999) 331.

[3] M.Tokunaga, J.F.Larrow, F. Kakiuchi and E. N. Jacobsen, SCIENCE, 277 (1997) 936. .

FP-9 Measurements and Modelling of the DC Temperature Dependence of Electrical Conductivity in Thin Films of Lead Phthalocyanine, ***T.S. Shafai,*** Staffordshire University, United Kingdom, *R.D. Gould (r.d.gould@keele.ac.uk)*, Keele University, United Kingdom

Many of the phthalocyanines exhibit p-type conductivity, and electrical conductivity through thin films of these materials having ohmic contacts show space-charge-limited conductivity (SCLC) dominated by trap levels located within the bandgap. In the present work evaporated thin films of lead phthalocyanine with ohmic gold electrodes were prepared, which showed two distinct regions in the dependence of current density J on applied voltage V. At low voltages sample conductivity was ohmic, changing at higher voltages to a square-law dependence of J on V, which is indicative of SCLC dominated by trap levels located at a single discrete energy level. The results of temperature measurements indicate three distinct regions, in each of which the hole concentrations are controlled by different activation energies. A simple model is proposed in which a single trap level is located at the same energy spacing E_t from the valence band edge as a single acceptor level. This predicts three different temperature ranges, two of which correspond to those covered by the experimental results. The experimental results indicate a trap level located at an energy E_t = 0.36 eV above the valence band edge and a thermal band gap E_g = 1.51 eV. Using the proposed model together with data from the experimental J-V characteristics, an acceptor concentration of 4.85×10^{19} m^{-3} and a trap concentration of 5.18×10^{25} m^{-3} are indicated. Measurements of mobility based on this model yield a value of 2.6×10^{-4} m^2 V^{-1} s^{-1}, which is in close agreement with previous work.

FP-10 Study of the Structure of $BaTiO_3$ Thin Films by Raman Spectroscopy, ***J. Xu*** *(jxu@ece.eng.wayne.edu), D.P. Durisin, G.W. Auner,* Wayne State University

Raman spectra of $BaTiO_3$ thin films grown on Si (100) substrate by pulsed laser deposition have been studied at room temperature. The films were deposited at different substrate temperature and oxygen pressure to investigate their influence on the film structure, and hence the Raman spectra. The Raman peaks attributed to the tetragonal ferroelectric phase of $BaTiO_3$ were identified. The peaks of impurity (non $BaTiO_3$) phases were observed. The films were also examined by several characterization methods. The polycrystalline structure of the films was determined by x-ray diffraction (XRD). The stoichiometric analysis was carried out by x-ray photoelectron spectroscopy (XPS). The variation of Raman spectra of the $BaTiO_3$ films grown at different deposition parameters was qualitatively consistent with XRD and XPS measurements performed on the same films. Results indicate that Raman spectroscopy has particular advantage for detecting low-concentration impurity phases of $BaTiO_3$ films.

FP-11 A Study of the Surface of Copper Phthalocyanine Thin Films Using Atomic Force Microscopy, ***R.D. Gould*** *(r.d.gould@keele.ac.uk), Q. Zhou, A. Milling,* Keele University, United Kingdom

Copper phthalocyanine is an organic semiconductor whose surface conductivity varies in the presence of adsorbed gases. As a toxic gas sensor it has been successful in detecting NO_2 at a level of less than 1 ppm. To further characterise this material the surface morphology was investigated using atomic force microscopy (AFM). Twice-purified material was deposited by thermal evaporation onto glass substrates maintained at room temperature. The films were of typical thickness 100 nm and were deposited at rates of 0.3 - 0.5 nm s^{-1}. The samples were annealed for a period of 1 hour in nitrogen at various temperatures in the range 373 - 558 K and were characterised by X-ray diffraction (XRD) and AFM. There was a transition from the α-phase to the β-phase when annealed at 523 K and above, and the mean grain size progressively increased from about 20 nm to over 50 nm for annealing at 558 K. AFM images showed that the as-deposited films were composed of fine granules. When annealed above 423 K there was a clear increase in granular size which reflects the growth of crystallites. The topography of the films annealed at 523 K, where the XRD results showed an α-to-β phase transition, differed drastically from the others and showed a fine needle-like structure. Granular size exceeded the corresponding XRD crystallite size and it was concluded that each granule is composed of several crystallites. Higher magnification surface lattice images were obtained from β-phase single crystals and compared with those from β-phase films. Both showed the characteristic "herring-bone" molecular structure, with a distance between parallel stacks of 1.93 nm on the (001) surface. The surface lattice of the films had a disordered structure, with a higher concentration of defects, which it was concluded may act as a suitable site for gaseous adsorption.

FP-13 Fabrication of $CoSi_2$ Nanocrystals Embedded in SiO_2 with Memory Effect, ***P.-H. Yeh,*** *L.J. Chen,* National Tsing Hua University, Taiwan, *P.-T. Liu,* National Chiao Tung University, Taiwan, *T.-C. Chang (tcchang@mail.phys.nsysu.edu.tw)*, National Sun Yat- Sen University, Taiwan

$CoSi_2$ nanocrystals embedded in the SiO_2 layer exhibiting memory effect have been formed by dry oxidation of amorphous Si/Co/SiO_2 structure at 800°C. A pronounced capacitance-voltage hysteresis was observed with a memory window of 1.1 V under the 3-V programming voltage. The programming voltages of $CoSi_2$ nanocrystals are lower than the semiconductor nanocrystals (~7V). The processing of the structure is compatible with the current manufacturing technology of semiconductor industry.

FP-14 Comparison of Microstructure and Surface Evolutions for Nanolayered CrN/AlN and TiN/AlN Coatings at Elevated Temperatures, ***S.-K. Tien,*** *J.G. Duh (jgd@mx.nthu.edu.tw)*, National Tsing Hua Univerisity, Taiwan

CrN/AlN and TiN/AlN multilayer coatings with modulation period of 4 nm and thickness ratio equal to 1.0 were manufactured by RF magnetron sputtering. Both films were annealed at temperatures of 800°C and 900°C in air and maintained for 1, 9, and 16 hrs. The microstructure evolutions of both coatings at as-deposited and heat treated conditions were identified by transmission electron microscope (TEM) and X-ray diffraction (XRD). The variation of surface roughness was measured by atomic force microscope (AFM). After heat treatment at 800°C for 1hr, the thick oxide layer around 200 nm was formed on the surface on TiN/AlN coating. The oxide layer of TiN/AlN coating was composed of two different regimes, including Al_2O_3 doped Ti on the top surface and crystalline TiO_2 layer between Al_2O_3 layer and nitride coating. On the other hand, an oxide layer smaller than 50 nm was revealed in CrN/AlN coating and was identified by EDX as the metal-