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MATERIALS RESEARCH SOCIETY

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E-MRS Spring Meeting 2003
June 10 - 13, 2003

# SYMPOSIUM G

## Protective coatings and thin films - 03

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# E-MRS 2003 SPRING MEETING

# SYMPOSIUM G

## Tuesday, June 10, 2003 — Morning
## Mardi 10 juin 2003 — Matin

08:45 SYMPOSIUM OPENING

### Session I PVD synthesized films and coatings
### Session chair: Y. Pauleau, O. Zywitzki

**G-I.1** 9:00 -Invited- ENERGY AND MASS SPECTROSCOPY STUDIES DURING ION PLATING OF HARD COATINGS

**M. Macek**, University of Ljubljana, SloveniaM. Maèek(a,b), M. Èekada(b), (a)University of Ljubljana, Faculty of Electrical Engineering, Trž aška 25, 1000 Ljubljana, Slovenia, (b)"Jož ef Stefan" Institute, Jamova 39, 1000 Ljubljana, Slovenia

The mechanical properties, microstructure and average chemical composition of metal (M=Ti, Cr) carbonitride hard coating M(C,N), deposited by means of the triode ion plating, strongly depends on many plasma parameters, but the most relevant are reactive gas partial pressures and the related concentration of plasma constituents (ions, radicals,...). To quantify these effects, we have thoroughly investigated the plasma during ion plating of M(C,N) coatings by energy-resolved mass spectrometry. Studies were performed for mixtures of Ar + $C_2H_2$, Ar + $N_2$, as well as different ternary mixtures of Ar + $C_2H_2$ + $N_2$, in the pressure range from 0.12 Pa to 0.30 Pa, with a constant Ar pressure 0.12 Pa. We have found that there is a significant difference in mass spectra of Ar + $N_2$ and Ar + $C_2H_2$ plasma. The latter ones are characterized by a high degree of dissociation. The main ionized species in Ar + $C_2H_2$ plasma during discharge is $H_{1,2,3}$, while the most abundant carbon-containing species is $^{12}C^+$. Overall intensity of carbon containing ionized species ( $C_xH_y$) drops with increasing arc current. This is in opposition to the intensities of other species (M, Ar) whose intensity follow the arc current. At high partial pressures of acetylene, in excess of 0.10 Pa, the ion flux is reduced and the evaporation of metal even stops. The Ar + $N_2$ plasma does not show such strong dissociation, due to the much lower ionization cross section of nitrogen molecule. The most abundant nitrogen containing ionized species is $N^+$ whose intensity is proportional to the plasma intensity, i.e. arc current. On the basis of present understanding we believe that the metal ionization occurs within the arc, close to the crucible, while the ionization of reactive gases takes place within the whole volume of the plasma.

**G-I.2** 9:30 MICROSTRUCTURE AND OXIDATION RESISTANCE OF TiAlN FILM DEPOSITED BY DC MAGNETRON SPUTTERING TECHNIQUE

B.Y. Man(a,b), L. Guzman(a), A. Miotello(a) and M. Adami(a), (a)INFM and Department of Physics, University of Trento, 38050 Povo (Trento), Italy, (b)Department of Physics, Shandong Normal University, Jinan, 250014, P.R.China

The ternary compound TiAlN coating has been known to be superior to binary compound TiN in protecting tools which may be damaged by high thermal load. In the present study, TiAlN coatings are deposited on stainless (AISI 316L) and other steel substrates by using DC sputtering technique. The structure of TiAlN coatings with different Al content is studied using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results reveal that the structure evolves from the fcc structure of TiN to the hexagonal phase of AlN when the Al content increases from 0 to 70 at. %. The oxidation behavior of deposited TiAlN coatings with different Al concentrations are investigated at oxidation temperatures ranging from 300 *C to 800 *C by an evaluation of energy-dispersive X-ray (EDX) spectra and XRD analysis. It is concluded that the oxidation resistance is enhanced at first and then decreases with increasing Al content, the addition of 40 at. % Al leading to the best anti-oxidation effect.

**G-I.3** 9:50

DEPOSITION MECHANISM AND CHARACTERISATION OF TIO2 FILMS PRODUCED USING ESAVD METHOD

X.H. Hou and K.L. Choy, School of Mechanical, Materials, Manufacturing Engineering and Management, The University of Nottingham, University Park, Nottingham NG7 2RD, U.K.

As a promising simple and cost-effective deposition technique, Electrostatic Spray Assisted Vapor Deposition (ESAVD) involves the generation and charging of droplets which are then delivered into a heated zone where they undergo the decomposition and/or chemical reactions in the vapor phase. However, the fundamental of the deposition is yet to be established. Based on the experimental results of deposition of Titanium Dioxide film, we discussed the ESAVD deposition mechanisms using a simple charged droplet model and found that in some cases the ESAVD process with multi-jet spray can also produce uniform film with controlled crystalline phase.

**G-I.4** 10:10

NEW DEVELOPMENTS IN GALLIUM DOPED ZINC OXIDE DEPOSITED ON POLYMERIC SUBSTRATES BY RF MAGNETRON SPUTTERING

Elvira Fortunato, Alexandra Gonçalves, Vitor Assunção, António Marques, Hugo Águas, Luís Pereira, Isabel Ferreira, Rodrigo Martins, Department of Materials Science/CENIMAT, FCT-UNL and CEMOP-UNINOVA, Campus da Caparica, 2829-516 Caparica, Portugal

Zinc oxide doped thin films have generated much attention in recent years, because of their material low cost, relatively low deposition temperature, non-toxicity and stability in hydrogen plasma, compared with indium tin oxide (ITO) and tin oxide (SnO2). It has been recently obtained by the present authors the best optoelectronic result on zinc oxide gallium (GZO) doped thin films at room temperature by rf magnetron sputtering on glass substrates. However, when flexible optoelectronic devices are required, a polymeric substrate must be used. Nevertheless these substrates present certain challenges such as considerably lower working temperature and rougher surfaces as compared to glass substrates. In order to overcame these limitations, we have optimised the rf magnetron sputtering process in order to be able to produce transparent high conductive, low resistivity, low film stress and with a smooth surface GZO films.

The films were grown by rf magnetron sputtering at room temperature on two kinds of commercially available polymeric substrates (Melynex and PEN from DuPont) in order to investigate the relationship between the polymeric substrate and the surface morphology presented by the films. The GZO films deposited on Melynex substrates, at room temperature and without any post treatment, presents a very low sheet resistance of 8 ohm/sqr and an average transmittance in the visible region of 80% (including the substrate). In this paper a detailed description on the preparation as well as on the electrical (Hall effect and resistivity as a function of temperature), optical (transmittance/reflectance and spectroscopic ellipsometry), structural (X-ray diffraction) and morphological (FE SEM and AFM) characterization will be presented.

**G-I.5** 10:30

INFLUENCE OF ZIGZAG MICROSTRUCTURE ON MECHANICAL AND ELECTRICAL PROPERTIES OF CHROMIUM MULTILAYERED THIN FILMS

J. Lintymer, N. Martin, J.-M. Chappé, P Delobelle, J. Takadoum, LMS – ENSMM, 26 chemin de l'Epitaphe, 25030 Besancon cedex, France

Chromium thin films exhibiting a columnar microstructure have been prepared by dc magnetron sputtering. The glancing angle deposition (GLAD) technique and the substrate motion have been implemented to sculpt this typical columnar microstructure into desired zigzag shapes. By changing the direction of the incident flux of the species impinging on the substrate surface, the deposited films led to columns that are tilted with respect to the substrate normal. A systematic and periodic variation of the angle of incidence “alpha” and “-alpha” (“alpha” ranging from 0 to 50°) was applied to deposit chromium multilayered thin films with a controlled zigzag microstructure. The growth mechanisms and the morphology of such films were studied by scanning electron microscopy and X-ray diffraction. The influence of the flux angle, as like as the size of one period of multilayered coating “lambda” (100 < lambda < 1000 nm), on the film’s Young modulus and nanohardness was investigated by nanoindentation. Electrical properties of these coatings were also measured and discussed taking into account period and microstructure.

10:50 **BREAK**

## Session II Tribological properties

## Session chair: J. Nowacki, T. Pieczonka

**G-II.1** 11:10 -Invited-

MECHANISMS AND BASIC ASPECTS IN ADVANCED SOLID LUBRICANT COATINGS

**Christophe Donnet**, Laboratoire Traitement du Signal et Instrumentation, UMR 5516, Université Jean Monnet, France, Ali Erdemir, Argonne National Laboratory, Argonne IL, USA

In recent years, several new solid lubricant and modern lubrication concepts have been developed to achieve better lubricity and longer wear life in demanding tribological applications. Most of the traditional solid lubricants were prepared in the forms of metal, ceramic and polymer-matrix composites. They have been used successfully in a variety of engineering applications. Recent progresses in thin film deposition technologies have led to the synthesis of new generations of adaptative, self-lubricating coatings with composite or multilayered architectures, by using duplex/multiplex surface treatments. These modern self-lubricating capabilities make progressively their way into the commercial marketplace and meet the ever-increasing performance demands of more severe applications. The present paper proposes a review on the recent understanding of the lubrication mechanisms of both traditional and new solid lubricants, with particular emphasis on solid-lubricant methods and practices.

**G-II.2** 11:40

CHARACTERISATION OF NANOSTRUCTURED COATINGS BASED ON OXIDES FOR TRIBOLOGICAL APPLICATIONS

S. Lang(a), T. Beck(a), A. Schattke(a), A. Dinia(b), C. Uhlaq(b), (a)Robert Bosch GmbH, PO Box 106050, 70049 Stuttgart, Germany, (b)IPCMS, 23 rue Loess, BP 43, 67034 Strasbourg, France

The aim of the project is to develop single layer nanostructured coatings combining oxidation resistance, temperature stability, and chemical inertia with wear endurance in various environments. In order to reduce the brittleness of ceramic materials, we embedded ZrO2 nanoparticles in a metallic matrix.

Coatings were produced using a reactive magnetron sputtering. The deposition parameters (substrate Bias, pressure) were correlated to the structure and the composition of the coating (phase, topography). The structure was studied by TEM and SEM, the topography by AFM, and the composition by XPS. In order to investigate the homogeneity of the plasma, we determined the ion current and the ion energy by Langmuir probe. The formation of nanoparticles in the plasma was studied by capturing particles in-situ with TEM-grids. Mechanical properties like hardness and brittleness were determined by nanoindentation. Wear resistance in dry and humid environment is presented.

**G-II.3** 12:00

CHARACTARIZATION OF TRANSFER LAYERS ON LOW-FRICTION PACVD TIN COATINGS

E. Badisch(a), K. Gammer(b), H. Hutter(b), H. Störi(c), C. Mitterer(d), (a)Materials Center Leoben, 8700 Leoben, Austria, (b)Institute for Chemical Technology and Analytics, Vienna University of Technology, Austria (c)Institut für Allgemeine Physik, Vienna University of Technology, Austria, (d)Department of Physical Metallurgy and Materials Testing, University of Leoben, Austria

Recently, a low-friction effect with friction coefficients of 0.15 … 0.20 against steel has been reported for chlorine-containing TiN coatings grown by plasma-assisted chemical vapor deposition (PACVD). These low friction coefficients are attributed to the formation of an interfacial lubricant film on the coating surface formed during ball-on-disc testing in humid air.

The aim of this study was to characterize these transfer layers to shed light on the low-friction effect. In pursuit of this goal, dry sliding experiments were performed for coatings with different chlorine contents against ball-bearing steel in ambient air and dry nitrogen. Wear tracks on the coatings were investigated using both scanning electron microscopy (SEM) and an optical profiler. The transfer layers obtained on the wear tracks were characterized using auger electron spectroscopy (AES) and secondary ion mass spectroscopy (SIMS). The low-friction effect was obtained for chlorine concentrations exceeding 3.2 at.-% and suitable humidity in the testing atmosphere. For these conditions, chlorine is released from the coating by mild abrasion and subsequently incorporated in the transfer layer. AES results showed that thin oxide layers with a thickness of about 30 nm were formed on the wear tracks. SIMS indicated the formation of coating oxides (TiO and TiO2) and oxides of the transferred material (CrO and CrO2).

**G-II.4** 12:20

SURFACE PERFORMANCE OF THERMOCHEMICALLY TREATED LOW ALLOYED PM STEEL

J. Kazior(a), T. Pieczonka(b), J. Ploszczak(a), M. Nykiel(a), (a)Cracow University of Technology, (b)Academy of Mining and Metallurgy, Poland

Thermochemical treatment can be used to modify surface performance of sintered low alloyed steels. A Cr and Mo low alloyed steel based on the prealloyed Astaloy CrM powder has a very good nitridability and for this reason was thermochemically treated in industrial furnace in different atmospheres containing nitrogen, sulphur and oxygen. The base materials were manufactured with different carbon and manganese addition. All the treatments investigated improve surface performance of the study materials but the results show that sulfonitriding has a better effect in reducing the friction coefficient and improving wear behaviour that other ones.

**G-II.5** 12:40

INFLUENCE OF SOLID LUBRICANTS ADDITION TO THE Fe-Cr AND Fe-Cr-B BASED CORED WIRES ON THE STRUCTURE AND TRIBOLOGICAL PROPERTIES OF ARC SPRAYED COATINGS

V. Pokhmurskii(a), M. Student(a), V. Dovhunyk(a), I. Sydorak(a), I.I. Rjabtsev(b), Ju.M. Kuskov(b), W. Wielage(c), A. Wank(c), H. Pokhmurska(c), (a)G.V. Karpenko Physico-Mechanical Institute of National Academy of Sciences of Ukraine, Lviv, Ukraine, (b)Paton Electric Welding Institute National Academy of Sciences of Ukraine, Kiev, Ukraine, (c)Chemnitz University of Technology, Institute of Composite Materials, Chemnitz, Germany

The technology of wear resistant coatings and new powder wire composites were developed. Coatings with low porosity and small grains were obtained by arc spraying of Fe-Cr-B and Fe-Cr based cored wires in steel cover. A modified arc spraying torch was used. Cored wires design was aimed on the suiting of filling powder composition to the further coating application. The addition of solid lubrication components into the filling powder allows to wider an application of this technological process and enlarge the restored components resources. The initial phase contents of coatings and their changes in subsurface region during friction processes were studied by X-ray diffractometry (XRD). Wear tests with the block-on-ring configuration at boundary lubrication and friction in abrasive-oil mixture under normal pressure 5 MPa have been performed. The best tribological behavior of arc sprayed coating was observed in the case of ferro-phosphorous and graphite additions. The mechanisms of structure adaptation and phase transformations during friction process is discussed.

13:00 **LUNCH**

## Session III: Protective nitrides and carbides
## Session chair: I. Bertoti, L.A. Guzman

**G-III.1** 14:30 -Invited- HARD TRANSITION METAL NITRIDES AS PROTECTIVE COATINGS

**F. Lévy**, P.E. Schmid, R. Sanjinés, E. Martinez, Institute of physics of complex matter, EPFL Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

Transition metal nitrides are known as hard, resistant and protective coatings. Both film composition and film morphology have an influence on the functional properties. Physical vapor deposition techniques allow a control of the chemical and structural characteristics. Sputter deposited titanium nitride thin films have been optimized, for example, as hard, wear and oxidation resistant coatings for cutting and forming tools and for decorative applications. New developments consider composite and compound ternary thin films like nano-composites (TiNx ? SiNy, or Cr2N ? CrN), multi-layers (TiN/NbNx or TiN/CrN) or composition gradient coatings.

A broad investigation of several ternary systems of transition metal nitrides deposited by reactive magnetron sputtering confirms the complexity of the influence of the composition variations, including the stoichiometric ratio of nitrogen to the metals, on the phases, morphologies and properties in general. The strain state, the crystallite size and the preferential orientation are quite typical of the morphology. The mechanical properties (indicated by the hardness) and the physical properties (optical reflectance, electrical conductivity) are significantly influenced by the composition directly or through the morphology. The mixing of metal atoms can be interpreted in terms of ionic/covalent trends in the bonding, related with specific population of the valence states. Measured by photoelectron spectroscopy, the evolution of the density of states of core and valence band states correlate with the coating properties.

**G-III.2** 15:00 THE COMBINED EFFECT OF LASER FLUENCE AND TARGET DETERIORATION IN DETERMINING THE CHEMICAL COMPOSITION OF PULSED LASER DEPOSITED BORON CARBIDE FILMS

T. Szörényi(a,b), J-P. Stoquert(a), F. Antoni(a) and E. Fogarassy(a), (a)CNRS-PHASE, BP 20, 67037 Strasbourg Cedex 2, France, (b)Research Group on Laser Physics, PO Box 406, 6701 Szeged, Hungary

Boron carbide is a material possessing attractive properties, and pulsed laser deposition, PLD is a well established technique of thin film growth. Fabrication of boron carbide thin films by PLD is therefore a challenging approach. The few results, however, are inconsistent (eg. F. Kokai et al., Diamond Relat. Mater. 10 (2001) 1412-1416 and Appl. Phys. A 74 (2002) 533-536; Shin-ichi Aoqui et al., Thin Solid Films 407 (2002) 126-131): the two critical issues are particulate deposition and stoichiometry.

A series of boron carbide films of 180+-30 nm thickness has been deposited by KrF excimer laser ablation of a sintered B4C target in high vacuum. Rutherford Backscattering Spectroscopy revealed that the chemical composition of the films grown on Si substrates, at room temperature, at laser fluences tuned between 2 and 14 Jcm-2 varied depending not only on the actual laser fluence but also on the past record of the B4C target. Parallel SEM mapping of both film and target surfaces pointed to a correlation between changes in film composition, particulate density and target surface deterioration. This correlation is discussed in detail.

**G-III.3** 15:20 Cancelled

**G-III.4** 15:40 SYNTHESIS AND DEPOSITION OF COATINGS IN THE ELECTRON BEAM PLASMA

M.N. Vasiliev and A.H. Mahir, Moscow Institute of Physics and Technology, Dolgoprudny, Moscow Region, 141700 Russia

Non-equilibrium Electron Beam Plasma (EBP) proved to be promising for surface modification of materials, synthesis of protective coatings and film deposition. The EBP was produced by an Electron Beam (EB) injected into a plasmagenerating medium. Atomic and molecular gases, vapors and gas-vapor mixtures were used as plasmagenerating media. Large solid bodies of irregular shapes and dispersed powders were treated, the treatment being carried out in both still EBP and plasma flows. The processes of synthesis and deposition appeared to be very effective due to chemical activity of the EBP at sufficiently high plasma pressures (up to 50 Torr). The optimal combinations of the EB parameters and gas pressure were selected to produce active plasma particles in desired concentrations and to heat the surface to the required temperature.

The following processes were studied: ·

-synthesis of nitride, carbide oxide and boride layers on the surface of metallic bodies, synthesis of combined compounds and multylayers; ·

-carbon deposition on substrates of various types: glass, natural and artificial polymers, fibers and clothes (the basalt cloth, for example); ·

-ceramics deposition on polymers at low temperature of the substrate; ·

-powder treatment both in the dusty EBP and in dusty-plasma crystals.

The multifunction Electron Beam Plasmachemical Reactor equipped with a set of interchangeable reaction chambers and diagnostic complex was developed to realize and study the processes considered.

**G-III.5** 16:00

TiN COATINGS ON WC CARBIDE AND THEIR RESIDUAL STRESSES

Stanislaw J. Skrzypek, Andrzej Baczmanski, Tadeusz Pieczonka, Andrzej Ciak, University of Mining and Metallurgy, al. Mickiewicza 30, 30-059 Krakow, Poland

Residual stress is important property of the surface because of its superposition with loading stresses and their influence on physical, chemical, structural and microstructural phenomena e.g. stress-induced phase transformation and stress-induced self-disintegration, piezoelectricity, linear relation of electrical resistance etc.

Most methods of measurements of residual stresses are still under development. The non-destructive diffraction methods of measurement of various kind of residual stresses are suitable for surface examinations. The most known sin2y diffraction method elaborated for Bragg-Brentano geometry has one important fault i.e. penetration depth changes vs. tilt angle y. This is particularly important for RS of coatings and surface layers with big gradients of RS. The new version of sin2y method, designated as g-sin2y due to grazing angle scattering geometry was applied to study residual macrostresses of TiN coatings deposited on sintered WC carbides. Result of measurements were compared with calculated macrostresses.

16:20 **BREAK**

## Session IV: Carbon based films and coatings

## Session chair: F. Rossi, G. Radnoczi

**G-IV.1** 16:40 -Invited-

DIAMOND-LIKE CARBON FOR MAGNETIC STORAGE DISKS

**Andrea Carlo Ferrari**, Department of Engineering, University of Cambridge, Cambridge CB2 1PZ, U.K.

The areal density of magnetic recording on disk drives has been advancing at a pace in excess of 100% a year in present years. Diamond-like carbon films form a critical protective layer on magnetic hard disks and their reading heads. The ultimate limit to storage density is the super-paramagnetic limit, where the thermal energy is able to overcome the coercive energy of the magnetic bit. For longitudinal recording this limit is ~100 Gbit/in2, whilst vertical recording should allow storage densities up to ~1Tbit/in2. This requires the read head to approach closer to the magnetic layer and ever-thinner layers of carbon 1-2 nm thick. The main role of such ultrathin films is to provide a corrosion barrier to the recording medium. They must be atomically smooth, dense, continuous and pin-hole free. It is unclear if the carbon can give continuous coverage under 2 nm thick. A critical review of the properties of the main classes of carbon films used for magnetic storage disks is presented. It is shown how tetrahedral amorphous carbon can provide the atomic smoothness, continuity and density required for magnetic storage applications down to a few atomic layer thickness. For such thin layers, finding reliable characterization tools is one of the most decisive factors for technology development and production. The main approaches to assess the structural and morphological properties of ultrathin carbon layers are reviewed. Raman spectroscopy, X-ray Reflectivity, Atomic Force Microscopy and Surface Acoustic Waves based methods allow a full non-destructive characterization of ultrathin carbon layers. In particular, Resonant Raman spectroscopy emerges as a most reliable tool readily applicable in a production line.

**G-IV.2** 17:10

THERMAL-INDUCED DELAMINATION OF AMORPHOUS CARBON COATINGS MONITORED BY POSITRON BEAM ANALYSIS

R. Escobar Galindo, A. van Veen and H. Schut, Interfaculty Reactor Institute, Delft University of Technology, Mekelweg 15, 2629 JB Delft, The Netherlands, F. Rabbani and G.C.A.M. Janssen, Department of Materials Science and Technology, Delft University of Technology, Rotterdamseweg 137, 2628 AL Delft, The Netherlands and J.Th.M. De Hosson, Materials Science Centre, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

In this work we have studied the adhesion of PVD amorphous carbon (a:C-H) thin coatings (<200 nm) on crystalline silicon by means of Positron Beam Analysis (PBA). PBA allows the study of the a:C-H layer and the interface by monitoring changes in the Doppler Broadening parameters S and W. Depending on the deposition conditions some samples already delaminate after deposition. Further annealing experiments were performed on samples that did not delaminate after deposition. During the deposition of these samples the only difference was the presence of nitrogen in the gas mixture. Samples were annealed for 30 minutes in vacuum up to 600°C. PBA experiments were performed after each annealing step. For the samples without N2 there are no S-W changes either in the coating or at the interface until 600°C.On the other hand, for the samples containing N2, there is a gradual change with temperature. After 500°C annealing the increase of W of the coating is related to a release of N2 and H2 and consequent restructuring of the layer. The decrease of S between 500 and 600°C indicates the formation of graphitic crystallites. At the interface there is porosity since the S parameter gradually increases while W remains constant until 400°C is reached. This is related to the removal of physisorbed hydrogen. At around 400°C also the H bonded to C at tetrahedral sites is released. This leads to an internal restructuring of the 'lattice', hence a decrease in the value of S is observed. Finally at 600°C, both coatings delaminate as the Doppler parameters for the interface become equal to those of the samples which showed delamination already after deposition. These observations will be explained in detail and compared to other techniques such as Raman and Thermal Desorption Spectrometry.

**G-IV.3** 17:30

APPLICATION OF DIAMOND-LIKE CARBON COATINGS ON STEEL TOOLS IN THE PRODUCTION OF PRECISION GLASS COMPONENTS

J. Brand, R. Gadow, A. Killinger, Institute for Manufacturing Technologies of Ceramic Components and Composites, Surface Technologies and Composites, Allmandring 7b, 70569 Stuttgart, Germany

The application of highly wear resistant DLC-coatings with an extremely low friction coefficient and a low wettability with regard to glass melt has been performed on steel substrates.

These coatings are of high interest for the glass industry to improve the performance of high precision glass forming tools for various products like high precision glass tubes for laboratory equipment or in the fabrication of wine glasses. Me-DLC coatings are a special type of DLC coatings and consist of a metal rich carbon phase near the metal substrate interface which is graded into a carbon rich diamondlike phase towards the interacting surface. The metal rich phase optimizes the adhesion to the ground substrate and the metal type can be varied (Ti, Cr, Si etc.). However the metal mainly determines the chemical behaviour of the coating system, i. e. its wettability. For the glass producing industry there are mainly two advantages: Environmentally hazardous release agents can be abandoned and the purity and surface quality of the produced glass products can be drastically improved. The presentation describes related vacuum deposition techniques and gives examples for industrial applications.

**G-IV.4** 17:50

DENSITY, STRESS AND MECHANICAL PROPERTIES OF ULTRA-THIN TETRAHEDRAL AMORPHOUS CARBON FILMS PREPARED BY FCVA TECHNIQUE

Gamal A. Abbas, J.P. Quinn, P. Lemoine and J.A. Mc Laughlin, NIBEC, University of Ulster, Newtownabbey, North Ireland, U.K.

In this work, we compared the density, internal stress and nano-mechanical properties of FCVA (ta-C) and PECVD (a-C:H) ultra-thin films grown on Si and $Al_2O_3$-TiC substrates. The ta-C films were prepared by (DBOP) cathodic arc technique. The a -C:H films were deposited using $C_2H_2$ gas by a 13.56-MHz RF PECVD system.

XRR results showed that the ta-C films are formed of a single homogeneous layer. The density values were 3.2 $g/cm^3$ and 2.3$g/cm^3$ for the ta-C and a-C:H films, respectively. This higher density value for the ta-C material also translates into better mechanical properties. The hardness and Young modulus of the 50nm thick ta-C films on $Al_2O_3$-TiC substrates were, respectively 51GPa and 603GPa whereas, for the a-C:H samples, these values are, respectively 23GPa and 224GPa. This correlation is not surprising as hydrogen acts as a network terminator, locally increasing the free-volume and lowering the strength and rigidity of the material. Nano-scratching experiments with a ramping compressive load indicates that there exists a well-defined critical load. Generally, the ta-C films have the highest critical loads; 3.4 mN and 2.13mN for 50nm thick ta-C and a-C:H films, respectively. This is a striking result, considering how highly stressed are the ta-C films (>7 GPa). This high ta-C adhesion is attributed, however, to the atomic intermixing at the coating-substrate interface due to the highly energetic arc plasma, which is not available in the PECVD process.

**G-IV.5** 18:10

IMPROVEMENT OF POLYMER COVERS STABILITY BY DEPOSITION OF DIAMOND-LIKE CARBON FILMS

N.I. Klyui, V.G. Litovchenko, O.B. Korneta, A.V. Makarov, V.P. Kostylyov and L.V. Neselevska, Institute of Semiconductor Physics, National Academy of Science of Ukraine, 45 prospect Nauki, 03028 Kiev, Ukraine

Polymer covers are very prospective for solar modules (SM) encapsulation to decrease the SM weight and cost. The problem is to ensure the polymer covers stability against action of mechanical and radiation degradation factors. For the polymer protection diamond-like carbon (DLC) films may be used. Optical and mechanical properties of the DLC films, polymer covers (acrylic plastic) and DLC film polymer structures were investigated. The SMs with DLC film - polymer front covers were also studied. The DLC films were deposited by PE CVD technique.

It has been shown that deposition of the DLC films allows us to improve the polymer based cover mechanical properties due to high wear resistance of the films. Besides, the structure becomes stable against action of ultraviolet (UV) irradiation. Moreover, after UV treatment optical band-gap of the DLC film increases. As a result, optical transmittance of the polymer-DLC film structures is rather high (up to 95%) that is quite enough for application for SM encapsulation. Mechanisms of the DLC film formation and modification of their properties under action of UV treatment are also discussed.

18:30-20:00 POSTER SESSION I

+ parallel special session for graduate student awards (max. 5 candidates)

**G/PI.01** THE PROSPECTS OF NANODISPERSIVE POWDERS APPLICATION IN SURFACE ENGINEERING TECHNOLOGIES

E.A. Levashov(a), A.E. Kudryashov(a), D.V. Shtansky(a), F. Gammel(b), R. Suchentrunk(c), J.J. Moore(d), (a)Moscow State Institute of Steel and Alloys, Technological University, Leninsky prospect 4, Moscow 119049, Russia, (b)European Aeronautic Defense and Space Company (EADS), Munich 81663, Germany, (c)Daimler Chrysler AG, Wilhelm-Runge-Strasse 11, 89081 Ulm, Germany, (d)Colorado School of Mines, Golden CO 80401-1887, USA

The paper describes the present-day state of the investigations in the field of producing the coatings dispersion-hardened by nanoparticles by thermal spraying, electrospark alloying, thermoreactive surface strengthening using metal and composite nanodispersive metals and composites powders. The main advantages of such coatings are following:

The present work also submits affecting generalities of the additives of refractory-compound nanodispersive powders on the composition, structure, and properties of electrode materials produced by SHS especially for electrospark alloying method. The positive modifying effects in the grain structure of the synthesis products and visible simultaneous raise in hardness, crack growth resistance, and bending strength is demonstrated. Such effect take place due to the nanopowder component in the most studied systems takes an active part in structuring of the synthesis products and coatings producing solid solutions and new chemical compounds. Wear resistant 10-60 microns in the thickness coatings in W-C-Co system on steel and nickel alloy substrates with a friction coefficient less then 0.15 were deposited by thermoreactive surface strengthening (TRESS) method using nanosized W, Co, C powders. Nano- or micro structural TRESS - coatings based on cemented carbide is formed on dependent of pulse discharge energy and frequency.

This work was carried out at the partial support of ISTC, project # 1852.

**G/PI.02** STRUCTURE AND PROPERTIES OF ZrO2 AND CaO-DOPED TiCN COATINGS FOR BIOMEDICAL APPLICATIONS

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In the present work multicomponent thin films based on the systems Ti-Zr-C-O-N and Ti-Ca-C-O-N have been deposited and evaluated. TiC0.5+10%ZrO2 and TiC0.5+10%CaO targets were manufactured by means of the self-propagating high-temperature synthesis (SHS) method. The synthesized targets were subjected to DC magnetron sputtering in an atmosphere of argon or in a gaseous mixture of argon and nitrogen. The films were characterized in terms of their structure, chemical composition, hardness, elastic modulus, elastic recovery and surface topography. The biocompatibility of the films was evaluated by both in vitro and in vivo experiments (in mice). In vitro studies involved the investigation of the proliferation of fibroblasts Rat-1 and epithelial cells IAR-2 at the tested films and morphometric analysis of the cells cultivated on the films. The films deposited under optimal conditions showed high hardness in the range of 35-37 GPa, low Young's modulus 240-300 GPa and high percentage of elastic recovery 70-74%. Fibroblasts and epithelial cells were seeded on the coverslips, coated with examined films and incubated at 37oC for 24, 48 and 72 hours. We did not detect statically significant differences in the attachment, spreading and proliferation of cultured cells on the coated and the uncoated substrata. The adhesion and proliferation of cells was good at all investigated films. We also did not observe any inflammatory reactions on the implants, inserted under the mouse skin.

**G/PI.03** DETERMINATION OF INTRINSIC STRESS IN TEXTURED AND EPITAXIAL TiN THIN FILMS DEPOSITED BY DUAL ION BEAM SPUTTERING

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TiN thin films have been deposited by a dual ion beam sputtering technique which consisted in sputtering a pure Ti target with primary Ar ions while an (Ar+N2) gas mixture was used as a secondary assistance beam during deposition. The films were grown on two different substrates : Si wafers covered with native oxide for which TiN films exhibit a (001) or (111) texture, depending on the film thickness, and MgO (001) single crystals for which a cube-on-cube epitaxial growth is observed.

The intrinsic stresses in the TiN films were measured by X-ray Diffraction after subtracting the thermal stress contribution at room temperature. The influence of the substrate, energy of primary and secondary ion beam on the strain/stress state of the films have been systematically studied. For the textured TiN films deposited on Si wafers at 25°C, large compressive stresses, ranging from -7 to -5 GPa are measured. When (111) and (001) texture coexist, the stress is found to be larger for the (111) texture. For the epitaxial TiN films grown on MgO at 500°C, the intrinsic stresses decrease to -2.4 GPa. The obtained results are discussed in terms of ion induced point defect formation and annihilation during growth and in regard with the microstructure. A stress analysis is developed using the basic model of Kamminga et al. for stress generation by misfitting particles in magnetron sputtered TiN films.

**G/PI.04** MECHANICAL PROPERTIES OF NANOSTRUCTURED COPPER-HYDROGENATED AMORPHOUS CARBON COMPOSITE FILMS STUDIED BY NANOINDENTATION

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Nanocomposite Cu/a-C:H thin films have been deposited on silicon substrates from argon-acetylene mixtures by combination of a microwave plasma-enhanced chemical vapor deposition (PECVD) process with a sputter-deposition process. The hydrogenated amorphous carbon phase acted as a tough matrix while reinforcing nanocrystallites of copper were imbedded in the amorphous matrix. The mechanical behavior of nanocomposite thin films under point loading conditions was studied by nanoindentation using Berkovich indenter with 130 nm tip radius. Low load tests were used to study the effect of the deposition parameters on the hardness and elastic modulus of films. High peak load tests were used to estimate the film adhesion to Si substrates. The transition from deposition of soft polymer-like to hard ion-hardened a-C:H films was observed with increasing concentration of acetylene in the gas mixture. The hardness of the nanocomposite Cu/a-C:H thin films is two times higher than that of a-C:H films deposited under similar conditions. The increase in hardness is probably related to the strengthening effect of copper nanocrystallites dispersed in the amorphous matrix.

**G/PI.05** PTFE NANO-DISPERSION ANTIFRICTION COATINGS

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The aqueous dispersions of PTFE have gained increasing room in highly demanding industrial applications, such as antistick and antifriction coatings.

Such dispersions or latexes are basically manufactured by emulsion polymerisation, typically leading to average particle size in the range 150-300 nm, while 100 nm particles can be achieved at reduced conversion degree only. Conversely, a proprietary Ausimont technology, based upon microemulsion polymerisation, leads to control particle size within 10 to 100nm. In the present paper recent developments of this technology for antifriction applications has been shown. A new formulation of PTFE nano-dispersion has been reported. This formulation can be applied on untreated metal surfaces in order to obtain high performance antifriction coating characterised by:

-good adhesion
-high scratch and wear resistance
-low coefficient of friction (lower than 0.12)
-high chemical and thermal resistance.

This nanodispersion formulation could be advantageously used in special coating applications expanding the application field of conventional PTFE dispersions.

**G/PI.06** CONTACT PROPERTY OF METAL AND TANTALUM NITRIDE FILM CHARACTERIZED BY USING TRANSMISSION LINE MODEL

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Contact property between metal and TaNx layer was characterized by using transmission line model (TLM). Tantalum nitride film has been used as a thin film resistor, because of its high stability, high reliability and proper value of resistivity. Many papers have reported about TaNx film, but few works dealt with the interface property between TaNx and metal electrode. Recent advances in micro module technology make it necessary to consider not only the resistivity of the film but also the contact resistance between film and electrode.

The TaNx film was deposited by reactive sputtering. The target was pure Ta disk. The Ar and N2 was used as sputtering gas and reactive gas, respectively. The electrode was made from Au film deposited by sputtering. An interfacial layer of Ta, Ti or Cr was inserted between electrode and TaNx layer to improve the contact performance. The specific contact resistivity was determined by using TLM method, and was the order of 10-8 ohm-m2. The value of specific contact resistivity depended on the interfacial material. The Ti layer was found to be useful as the interfacial material between TaNx and metal electrode.

**G/PI.07** WEAR RESISTANCE IMPROVEMENT OF SINTERED STRUCTURAL PARTS BY CnHn SURFACE CARBORIZING

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Höganäs NC 100.24 grade iron powder with 3wt.-% Mn and 0.8wt.-% C additions was used to produce the sintered gears. Those underwent the thermochemical cyclical treatment using hydrocarbons (CnHn), which resulted in carbides layer formation on the compacts. Three different thermochemical treatment conditions in terms of cycle number were chosen. The initial phase contents in the surface layer and its changes during the thermochemical cyclical treatment were studied by SEM analysis, metallography and microhardness measurements. The control of wear resistance was based on a set of two gears working together under specified rotation speed and load. The weight changes of those gears after 1 and 2 hours of dry friction were controlled. A particular increase of wear resistance of the CnHn carborized gears as compared with the untreated ones was observed.

**G/PI.08** STRUCTURE AND PHASE TRANSFORMATION OF IRON SURFACE LAYER TREATED BY COMPRESSION NITROGEN PLASMA FLOWS

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The present work reports the results of XRD, AES, and SEM studies of phase and element structure, as well as a microstructure of iron layer caused by compression plasma flow action. The samples were processed in a magnetoplasma compressor with the energy storage of ~ 12 kJ. The initial pressure of working gas (nitrogen) in the chamber is ~ 400 Pa. Plasma parameters in the compression flow are as follows: discharge duration ~100 μsec; plasma velocity 5-10e6 cm/sec; electron density (4-7)∙10e17 cm^-3; plasma temperature 2-3 eV. Value of power density absorbed by a sample surface is 15 J/cm^2 per pulse. As a result of such an action, the layer by thickness of some micrometers immediately adjacent to a sample surface is formed. As XRD data show, its phase structure represents a superposition of following phases: α, γ, γN and ε-Fe2+xN. The average size of a grain makes ~ 300 nm. According to AES findings, concentration of nitrogen in the surface layer reaches ~20 atomic percents. Exposition of a sample to a series of pulses causes a change in a ratio of phases (α, γ, γN and ε-Fe2+xN) and in the sizes of grains. The hardness of superficial layers of iron was found to increase by 1.5 times as compared to untreated samples. Processing by a series of 10 pulses causes the hardness to increase still further (up to 2.5 times).

**G/PI.09** AFM AND AUGER INVESTIGATIONS OF AS-DEPOSITED AND HEAT TREATED COPPER COATINGS ON GLASSY CARBON SURFACES WITH CHROMIUM AND MOLYBDENUM INTERMEDIATE LAYERS

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It is known that the wetting behavior of C by Cu is very poor. This is a major drawback in the fabrication of Copper Carbon Metal Matrix Composites (Cu-C-MMCs) if the material is made by using Cu coated carbon fibers as starting material. In order to improve the wetting and - by doing this - the adhesion between Cu and C, a systematic analysis of the influence of adhesion promoting intermediate layers was performed. Plane carbon substrates were used as a model system instead of carbon fibers. In order to improve the interface between Cu and the C substrate, different intermediate layers (Cr and Mo) were deposited onto the carbon surfaces. The AFM was used to determine surface morphology and the roughness of different intermediate layer thicknesses before and after a heat treatment. Due to the intrinsic stresses thicker Ti layers (>200 nm) did not adhere on the substrate when deposited at room temperature while Mo layers did not show such a behavior.Using the results of these investigations, a series of copper coatings on intermediate layers with different thickness was prepared by sputter deposition. Surface topography of as-deposited and samples after heat treatment were investigated and compared in terms of growth mode, grain size and roughness. Using Auger analysis the element distribution on the surface of as-deposited and heat treated samples was investigated. The knowledge of optimal intermediate layers allows to give recommendations for suitable coating thicknesses.

**G/PI.10** PREPARATION, CHARACTERISATION AND CORROSION BEHAVIOUR OF PROTECTIVE COATINGS ON STAINLESS STEEL SAMPLES DEPOSITED BY PLASMA DETONATION TECHNIQUES

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Plasma-detonation techniques have been used to modify the surface of austenitic stainless steel samples in order to improve their corrosion resistance. Deposition of Al2O3 coatings in combination with high current electron beam treatment and deposition of titanium nitride (TiN) were applied for this purpose. The characterisation of the samples was performed using Nuclear Reaction Analysis and Rutherford Backscattering Spectroscopy. The corrosion behaviour of the samples was investigated in 1N H2SO4 using electrochemical techniques (cyclovoltammetry and potentiodynamic polarisation). The values of the critical and passivation current density as well as of the corrosion, passivation and repassivation potentials, showed a considerable increase of the corrosion resistance of the coated steel samples. This improvement is connected with the properties of the modified region (thickness, adhesion). The surface morphology and microstructure of the specimens before and after the corrosion experiments were investigated by X-ray Diffraction, Scanning and Transmission Electron Microscopy.

**G/PI.11** STRUCTURE AND MECHANICAL PROPERTIES OF Si-BASED COATINGS

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The development of innovative coatings, which are efficient both in terms of properties and cost, attracts attention of researches. Coatings based on silicon and produced using electron beam evaporation technique from recycling product waste are considered in this paper. Nanocrystalline structure was revealed by examination of the Si-based coatings deposited on high-speed steel substrates. It was found that these coatings contained less than 2 wt.% of light elements (C, N, O) and are alloyed by some amount of metals. Si-based coatings exhibited extremely high hardness and Young's moduli as compared to the cubic diamond phase of silicon (Si -I). In particular, the maximal Vickers hardness, which was found to be dependent on the coating composition, was as high as 32 GPa. The indentation measurement results were interpreted taking into consideration both nanostructure of the coatings and their specific deformation when indented. No sings of pressure-induced phase transformation typical for cubic silicon (Si-I) were revealed in load-displacement curves obtained in cyclic nanoindentation experiments. The suggested coatings are highly efficient in tools for cutting Ti-alloys.

**G/PI.12** ION BEAM ASSISTED DEPOSITION OF Ag(Au) LUBRICANT FILMS ON STEEL SPHERICAL SUBSTRATES

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A novel technology has been developed in order to produce 50-100 nm thick films on small steel spheres by using Ion Beam Assisted Deposition (IBAD). The films were produced by simultaneous steps of deposition and implantation. Several parameters were investigated (ion energy, ion current, evaporation rate, samples moving rate...) and different analysis were performed in order to reach the best process conditions. Optical and electronic microscopy and Energy Dispersion X Rays Spectrometry were carried out to study the resulting morphology, thickness and homogeneity of the deposited films. By using mechanical methods, the adhesion properties were tested. Finally well working coatings with good morphology and high adhesion have been produced in a controlled process.

**G/PI.13** PROPERTIES AND GROWTH OF ALN FILMS-EFFECT OF FILM THICKNESS

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Recently, aluminum nitride (AlN) has atracted great interest due to its excellent electrical, optical and mechanical physical properties. They make it suitable to be used in a wide variety of aplications: optical devices, thermal conductors, insulating layers and protective coatings. Protective coatings require high hardness, chemical inertness, good wear resistance and oxidation resistivity. Since AlN physical properties fit these requirements, AlN films are a candidate to be used as protective or anti-wear coating. It was found that preferential orientation of polycrystalline AlN films affects and often improves their properties for practical use such as hardness. Hence, it is important to study the conditions under which highly oriented AlN thin film structures can be grown and to correlate them with their mechanical properties.

Aluminum nitride (AlN) films have been deposited on Si (100) substrates by DC reactive magnetron sputtering technique. A range of different film thicknesses have been grown and characterized by X-Ray diffraction and reflectometry, atomic force microscopy and nanoindentation techniques, in order to correlate the structure and the growth mechanism with the mechanical properties. XRD measurements reveal polycrystalline hexagonal structure for all thicknesses. For the thinnest films are detected the smallest grains and the largest microstrains whereas for the thicker samples a columnar structure with well aligned grains are observed.

**G/PI.14** EFFECTS OF THE SUBSTRATE TEMPERATURE AND THE NITROGEN FLOW RATE ON THE HATDNESS AND THE GROWTH MORPHOLOGY OF (Ti,Zr)N FILMS DEPOSITED BY RF-REACTIVE SPUTTERING

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Ternary (Ti,Zr)N thin films were deposited by rf-reactive sputtering in Ar–N2 plasma and their hardness and oxidation resistance were investigated. The effects of the substrate temperature and the gas flow ratio of N2 to Ar on the microstructural properties of (Ti,Zr)N thin films were also studied using SEM, AFM, AES and XRD techniques. It appears that the (Ti,Zr)N film deposited by sputtering under optimal process conditions has as high hardness and good oxidation resistance as the (Ti,Al)N film. A substrate temperature of 300˚C and an N2/Ar ratio of 40/30 are suggested for getting a densely packed film structure with the highest hardness and the highest oxidation resistance.

**G/PI.15** AMORPHOUS Fe-B-N FILMS DEPOSITED BY REACTIVE SPUTTERING OF A FeB TARGET

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Fe-B-N films are deposited on glass and steel substrates by DC magnetron sputtering of a FeB target in Ar-N2 reactive mixtures. The film nitrogen concentration is controlled through the flow rate of nitrogen introduced in the deposition chamber. The films are characterised by X-ray diffraction, X-ray photo-emission spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR) and conversion electron Mössbauer spectrometry (CEMS). All films obtained so far are amorphous, irrespective of the nitrogen flow rate. FTIR and XPS evidence boron-nitrogen bonds in Fe-B-N films. Furthermore, XPS analyses show that the number of these bonds increases with increasing nitrogen flow rate, going along with a decreasing number of boron-iron ones. Thus, the chemical environment of boron atoms appears to be strongly dependent upon the nitrogen flow rate. The same conclusion holds for the chemical environment of iron atoms, as revealed by CEMS. At low nitrogen concentration, room temperature CEMS spectra are characteristic of magnetic amorphous iron-boride films, whereas for high nitrogen concentrations, spectra exhibit paramagnetic character encountered in iron-nitride films.

**G/PI.16** CHROMIUM THIN FILMS DEPOSITED ON STEEL SUBSTRATES

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Contribution to the study of chromium carbides formed by annealing of:

-the interaction between chromium thin films and steel substrate 100C6, containing about 1% mass of carbon is studied by scanning electronic microscopy (SEM), X rays diffraction (DRX) and by Auger electrons spectroscopy (AES).

-Samples are constituted of substrates made of steel in the shape of a disk of 10 mms in diameter and 1 mm in thickness, on which we put, by cathodic pulverization, thin chromium films of ~0.68µm in thickness, samples are thermally treated under vacuum (~10-6mbar) within the interval of temperatures of 400-1000°C. it's established that in the considered temperature interval, several composed forms; chromium carbide Cr7C3 and Cr23C6, forms and grows until the total consumption of chromium layer accompanied by a meaningful increase of the hardness and a change of color of samples free surface. The hardness increases with annealing temperature, reaches a maximum then decreases progressively, the growth of Hv is due to the diffusion of the carbon, and to the formation of chromium carbide. However, the decrease of Hv is associated to the diffusion of iron and the formation of iron oxide (Fe2O3), in the higher temperatures, we note the formation of chromium oxide (Cr 2O3). The formation of chromium carbides improve the surface materials properties, such as the resistance against chemical, mechanical, thermal solicitations.

-The mechanism of formation and growth of chromium carbides is discussed on the thermodynamic consideration basis.

**G/PI.17** S-O-N COMPOSITE LAYERS IMPROVING THE WEAR RESISTANCE OF THE STEEL

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Wear resistance of the steels is one of the key parameters deciding about their applying in industrial practice. Therefore to improve this property the chemical-heat treatment of the surface is widely applied. One of such treatment is nitriding which increases significantly the hardness of the surface. In the presented investigation the ammonia atmosphere together with SO2 were used to obtain the nitrided layers. The addition of the sulphur to the reacting atmosphere together with oxygen has a positive effect on the wear characteristic of the nitrided layers, increasing the hardness from one side and decreasing the friction coefficient from the other side. In the paper the sulphur-oxygen-nitrigen composite layers obtained for various nitriding atmospheres are characterised. The fallowing investigated method were used: light and scanning microscopy, X-ray diffraction, electron microprobe. The microhardness and wear resistance of the layers were also evaluated.

**G/PI.18** SYNTHESIS OF ZRO2/Y2O3 BY COMBINED ARC-MAGNETRON TECHNIQUE

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Zirconium oxide films with heat resistance, low thermal conductivity, extreme chemical intentness, high laser damage threshold, high ions conductor, have been used in variety of applications. Zirconium films by electron beam evaporation, reactive sputtering, chemical vapor deposition, sol-gel processing is prepared.

In this work we have investigated at determining dependencies of the thin film speed on partial pressures of oxygen, currents of discharge and distances between the target and the sample. ZrO2/Y2O3 thin films have been deposited on Si, on the alloy 600 and on the glass substrate at 300-500C temperature by combined arc-magnetron reactive sputtering. The structure of coating films, their phase’s composition was estimated using the X-ray diffraction method (XRD) and the electron scanning microscopy (SEM) method. Micro-hardness and resistance to oxidation of surface were measured. After complete analysis of the arc-magnetron process for abstraction of ZrO2/Y films, physics of the process, it is possible to select and control parameters of reactive sputtering process together, thus producing thin films of the required qualities.

**G/PI.19** PROPERTIES OF ALUMINA COATINGS PRODUCED BY GAS-DETONATION METHOD

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One of the most promising method of obtaining wear erosive and corrosive resistant coatings is the gas-dethonation method. The coatings produced by this method permit widening the application range due to increasing of useful properties of low alloy steels. The paper deals with the influence of technological parameters on the properties of coatings produced from alumina powder on 1045 steel. It shows the possibilities of forming the material structure and the penetration of the coatings into the substrate depending on the spraying powder speeds. The role of modifying the substrate surface before process is discussed. The four method of changing the surface are presented: grinding, sand-blast cleaning, sanding by gas-detonation method and the obtaining the nickel electro less coating as the intermediate layer. The structure and chemical composition of the Al2O3 coatings are described by metallographical and scaning electron microscopy by EDS method and X-ray diffraction method. The corrosion resistance of the coatings is examined by the potentiodynamic method in a 0,5 M NaCl solution. The wear resistance is estimated by the "three rolles and taper" test. The erosive properties are also examined.

**G/PI.20** MECHANICAL PROPERTIES OF HARD Si-C-N AND Si-B-C-N FILMS

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The ternary and quaternary materials containing Si, B, C and N have been attracting great interest due to their new features which can be used in microelectronics and coating technologies. Si-C-N and Si-B-C-N films were deposited on Si substrates by dc magnetron co-sputtering of silicon and carbon (Si-C-N) and silicon, carbon and boron (Si-B-C-N) using composed C-Si and C-Si-B (a fixed 20% boron fraction in the erosion track area) target, respectively, with variable Si/C magnetron area ratios in nitrogen-argon mixtures. Film properties were controlled by the Si fraction in the magnetron erosion track area, the Ar concentration in the gas mixture, the substrate temperature and the substrate bias voltage. The films, typically 1.0 to 2.0 microns thick, were found to be amorphous with a very smooth surface and good adhesion to substrates. Increasing the silicon fraction in the target area leads to a significant rise in the friction coefficient at almost constant values of the hardness (around 25 GPa). The lowest wear rates were achieved for the Si-C-N films with the highest and the lowest carbon content. Increasing the argon concentration in the gas mixture results in a progressive increase in film hardness (up to 35 GPa for Si-C-N films and 50 GPa for Si-B-C-N films) at almost constant stabilized values of the friction coefficient (around 0.45 for Si-C-N films and 0.70-0.80 for Si-B-C-N films).

**G/PI.21** FUNCTIONAL PROTECTIVE COATING

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Application of a magnetron method of sputtering simultaneously with implementation of diagnostics and control during deposition enables to receive coatings with the required characteristics. On the basis of theoretical researches is calculated and by magnetron method of sputtering the functional protective coating for Al-mirrors is obtained. Selection of an optical thickness of layers Al2O3 and TiO2, components the protective coating, has increased reflection of a mirror in spectral range 0,4 … 0,7 microns up to 95 %. The equipment designed and the process engineering of deposition of protective coatings of Al-mirrors, improving reflection is completed.

**G/PI.22** POSSIBILITY OF INTRODUCING LASER SURFACING INTO MAINTENANCE SERVICE OF DIE CASTING DIES

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The shape and technology of tools for die casting of aluminium and magnesium alloys are usually extremely exacting and therefore very expensive. In a die casting process, these tools are subjected to strong thermo-mechanical loads. From the economic point of view the operation life of die is of extreme importance to a price of a casting. It has been proved that by a regular maintenance of die parts the life of die can be successfully extended.

The aim of the investigation was to find a fast, efficient and cost-effective repair procedure for worn surfaces of vital parts of dies made of maraging steel. In this paper, results of CO2 laser repair surfacing of maraging steel with a Ni-Co-Mo alloy similar to the maraging steel, carried out on suitably adapted specimens with shallow notches, are reported. The surfaced specimens were also post-weld heat treated. The results are based on optical and SEM microstructural and X-ray phase analyses of the repaired regions on the specimens and are supported by analyses of the micro-hardness and the residual stresses, carried out after surfacing and after post-weld heat treatment.

**G/PI.23** IMPROVMENT OF DIE CASTING TOOLS WITH DUPLEX TREATMENT

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A comparative performance test of duplex treated tools was made in die casting of driving wheels for automobiles with 2 cores in one casting plate. One set of cores was improved with Tenifer(r), while the other was improved with duplex treatment (plasma nitriding + deposition of 4,5µm thick PVD CrN coating). After 2700 injections surface damages on both types of tools were analysed using optical and scanning electron microscopes. Results obtained on plasma nitrided cores protected with PVD CrN coating are compared with those protected by Tenifer procedure. We found that cores protected with CrN coatings exhibited a lower tendency to adherence of aluminium than those protected with Tenifer process. The wear of coated tools was also much smaller.

**G/PI.24** TRIBOLOGICAL PROPERTIES OF AMORPHOUS CARBON THIN FILMS GROWN BY R.F. MAGNETRON SPUTTERING METHOD

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Thin films of amorphous carbon(a-C) generally combine high wear resistance with low friction coefficients. In this study the amorphous carbon(a-C) films are deposited on silicon with a r.f. magnetron sputtering system. It is obtained parameters on the deposition rate and tribological properties of a-C films using a wide range of Ar gas pressure and r.f. power and compared with a-C films by PECVD method. The films were analyzed by Raman spectroscopy, FT-IR(Fourier Transform IR), AFM(Atomic Force Microscopy) and the tribological properties are investigated by hardness and friction coefficient measurements.

**G/PI.25** DEPOSITION 316 L AND HASTELLOY C OF PROTECTING COATINGS ON LOW-CARBON STEEL SS 400 USING A PULSED PLASMA SPRAY FOR CORROSION PROTECTION IN SEAWATER

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In this report we present the review of results obtained by these authors for recent years. We used the powder of stainless steel 316L of 3056μm dimension and Hastelloy C on Ni base as the coatings. The coatings of various thickness from 60 to 480μm were deposited using the high-rate pulsed plasma jets produced by the device Impulse 3;5. Different methods of analysis as RBS, ERDA, SEM, XRD, TEM, seawater corrosion tests were applied. In our experiments we applied two different regimes: after stainless steel and Hastelloy C on Ni base coating deposition on the surfaces of samples, these sample surfaces were treated by the electron beam until melting. Then we applied the third regime: we treated samples by the high-rate plasma jet with the eroding (evaporating) cathode of Mo also until surface melting.

We investigated the composition of coatings and that of transition layer (the substrate-the coating). The obtained results of investigation are compared with known results, for example, HVOE, etc. This work was supported by National Institute for Material Science, Tsukuba, Japan

**G/PI.26** TRIBOLOGICAL PROPERTIES OF COPPER-CARBON FILMS PREPARED BY MICROWAVE PLASMA-ASSISTED DEPOSITION TECHNIQUES

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Copper and copper-carbon composite films have been deposited on silicon substrates by sputtering of a copper target associated with microwave plasma-enhanced chemical vapor deposition process of carbon from argon-acetylene mixtures of various compositions. The chemical composition, copper crystallite size, structure of carbon clusters were correlated with the coefficient of friction and wear resistance of Cu, Cu-C and a-C:H (formed without a copper target) films. The films were characterized by grazing incidence angle x-ray diffraction (GXRD), Raman spectroscopy and tribological tests.

Analyses by Raman spectroscopy demonstrated a change from “polymer-like” carbon films to disordered amorphous carbon films. The increase in C2H2 concentration in the range 60-100% was found to lead to a decrease in the value of the sp3 /sp2 ratio of carbon bond types down to 0.7. For a-C:H films, the sp3 /sp2 ratio was equal to 1.7. The tribological behavior of Cu/a-C:H films was different for Cu, Cu-C and a-C:H films. The viscous friction and higher coefficient of friction were observed for Cu-C films. The lowest coefficient of friction (0.2) was obtained from a-C:H films. The wear resistance of Cu-C films was dependent on the copper crystallite size, magnitude of residual stresses, value of the sp3 /sp2 ratio of carbon bond types in the films.

**G/PI.27** SYNTHESIS AND PROPERTIES OF NANOSTRUCTURED CARBON FILMS IN RF PLASMA

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Nanostructured carbon coatings are perspective materials for an electronic nanolithography, anticorrosive protection of conducting coatings in microelectronic, sources of multi-charged ions in tandem-accelerators. In this paper the conditions of semitransparent carbon films synthesis in a RF capacitively coupled discharge and their properties are investigated. The discharge was produced on frequencies 5.28 and 81 MHz in a discharge chamber with planar metallic cooled electrodes. The distance between electrodes was 3 mm. The top electrode was powered. The bottom electrode was grounded to the vacuum chamber. As a working gas helium and argon were used at pressures 5-25 Torr. Carbon films were deposited on a quartz, silicon, and also other semiconductor materials. Products of electric arc synthesis of fullerenes (a small-dispersed carbon soot, fullerene mixture С60 + С70 and material of a cathode deposit of a vacuum electrical arc) were used as an initial substance for making carbon films. The processes in the discharge were studied by emission spectroscopy methods. Semitransparent carbon films from fullerene-containing soot are obtained on a quartz in plasma of RF capacitive discharge, that is evidenced of a considerable share of sp3-hybridization of carbon. It is observed that optical properties of deposited films change when the gas kinetic temperature of the discharge changes.

**G/PI.28** CHARACTERIZATION OF ORGANOSILICON FILMS SYNTHETIZED BY N2-PACVD. APPLICATION TO FIRE RETARDANCY PROPERTIES OF COATED POLYMERS

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A N2-PACVD is used to synthetize organosilicon films from the polymerization of tetramethyldisiloxane monomer doped with O2. The influences of the oxygen flow rate (F(O2)) on the deposition rate, the density and the nature of the films are studied. Films have a polysiloxane like structure and a density approximately equal to 1.8 mg/mm3 whatever F(O2) value. The study of fire retardancy properties of the coated polyamide-6 (PA-6) and the coated PA-6 clay nanocomposite (PA-6 nano) shows the high efficiency of the coating : heat and gas releases are reduced. The residues obtained after the fire tests have a polysiloxane like structure for the coated PA-6 whereas they have a silica like structure for the coated PA-6 nano. These results could be explained by the reaction occuring between the coating and the clay nanocomposite under heating effect which promotes the formation of more thermally stable coatings. For example, the flammability is strongly decreased from the coated PA-6 to the coated PA-6 nano.

**G/PI.29** CHARACTERISTIC OF THE NITRIDED LAYER ON THE STAINLESS STEEL

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Stainless steel are widely employed in many areas of industry like automotive, aircraft and chemical industry or in biotechnology. To improve its surface hardness and wear resistance the nitriding process is usually applied. Unfortunately the nitriding tends to affect the corrosion resistance of that type of steel adversely. It was stated that during low temperature nitriding the supersaturated with nitrogen phase is formed. This phase called expended austenite can improve the corrosion resistance of the nitrided steel. In the presented paper the nitrided layers obtained on the stainless steel at the temperatures lower than 773K were investigated. The layers were obtained for the following process parameters: voltage – 1350 V, current density – 0,7-1,7 mA/cm2 and time 10-120 min. The morphology of the layers were investigated using the following techniques: SEM, LMA, XRD, AFM, SIMS. Moreover such characteristic of the layers as microhardness and corrosion resistance were evaluated and related to their morphology.

**G/PI.30** CHARACTERIZATION OF AS-DEPOSITED AND EXPOSED TO AIR a-SiC:H FILMS PREPARED FROM METHYLTRICHLOROSILANE

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Amorphous hydrogenated thin films based on silicon carbide (a-SiC:H) were deposited at substrate temperatures ranging from 180 0C to 250 0C from methyltrichlorosilane (MTCS) in a 40.56 MHz PECVD reactor. An additional bias of -100 V was applied at the substrates of crystalline silicon and glass. The films having the average thicknesses of 380 nm, were grown with the average growth rate of 0.21 nm/s. Infrared spectra, film compositions, thicknesses, optoelectronic characteristics of the films have been measured immediately and in two months after the deposition. The as-deposited films have the content of silicon, carbon and oxygen equal to about 65%, 28 % and 7 %, respectively. An exposition of the as-deposited samples during two months at the ambient air causes an increase of the oxygen content (by about 20%). Oxygen incorporates mostly in the substrate-film interface. The film oxidation is reflected in strengthening the Si-O peaks in the infrared spectra. The films obtained from MTCS represent the Si-C network with additional Si-O, C-H and Si-CHn bonds and contain a definite number of micro-voids, which form from undestroyed CH3-radicals originated from the precursor. Their concentration increases towards the substrate. The high film porosity is expected to be the main cause of the comparatively high film oxidation.

**G/PI.31** THE GROWTH CHARACTERISTICS AND MICROSTRUCUTRE OF ALUMINA THICK FILMS PREPARED BY ELECTROSTATIC SPRAY ASSISTED VAPOUR DEPOSTION

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This paper presents an alternative cost-effective ESAVD method for depositing alumina films in an open atmosphere with high deposition efficiency and at low temperature. ESVAD is a variant of CVD. It involves spraying atomized precursor droplets across an electric field into a heated environment where the charged droplets undergo decomposition and chemical reaction near the heated substrate and produced a solid stable film. Dense alumina film was deposited at 450 oC using a sol solution containing aluminium alkoxide precursor at a growth rate of 2µm/hr. The microstructure of the films was characterized using a combination of X-ray diffraction and scanning electron microscopy methods. The dense and porous alumina films could be deposited by varying the processing conditions. The relationships between the growth behavior and microstructure of the films were discussed.

**G/PI.32** MULTIPLE SURFACE COATINGS Of REFRACTORY CERAMICS PREPARED BY COMBINED LASER AND FLAME SPRAYING

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Hybrid laser-flame spraying may provide a new opportunity to deposit multiple surface coatings with various degrees of density and microstructures. In the present study, multiple alumina and zirconia coatings with different densities and thickness were applied on an alumina-based refractory substrate by the hybrid laser-flame spraying system using several sets of process parameters. The microstructures and porosity data of the coatings were characterized with scanning electron microscopy, optical microscopy and image analysis method. Results showed that the combined laser and flame spraying was a practicable approach to prepare multiple coatings. The relationships between the coating microstructure and process parameters as well as the powder materials were discussed.

**G/PI.33** STRUCTURE AND PROPERTIES OF THIN IRON PHOSPHIDES FILMS ON CARBURISED LAYERS

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Relations of the thin iron phosphates layers on the carburised layers base growth parameters; their structure and properties have been considered. The layers were generated as a result of a gas phosphorcarburising of Armco iron and 0.4%C, 1.1%Cr steels in an atmosphere achieved from the suspension of red phosphorus particles in isopropyl alcohol and water mixture instilled directly into the carburising chamber. The process of the diffusive phosphorcarburising was carried on in the process parameters: temperature T = 700 ÷ 1170 K, phosphorus partial pressure p = 100 – 3000 Pa, process duration t = 6 - 10 hours. There have been done calculations of the Gibbs free energy and the equilibrium constant of phosphates Fe3P, Fe2P, Fop and FeP2 synthesis reaction. Fe3P synthesis of iron and atomic phosphorus P1 has the greatest value of the Gibbs free energy. Phosphorus dissociation value in the phosphorcarburising process was sufficient to achieve iron phosphates synthesis in the reactions of iron and atomic phosphorus P1. Mechanism and kinetics of growth of iron phosphides layers was described. Investigations of the phosphocarburised layers by means of the methods: metallografic one, X - Ray structural analysis, microanalysis, measurement of Vickers hardness, and resistance to wear by pin on disk method have been done. Possibility of Fe3P and Fe2P phosphides layer and a solid solution of phosphorus in iron on the carburised layers generation have been proved. Thin iron phosphides layer increases hardness and friction wear resistance of carburised layers on iron and steels.

**G/PI.34** CANCELLED

**G/PI.35** INFLUENCE OF THE NITROGEN PRESSURE ON THE STRUCTURE AND PROPERTIES OF (Ti,Al)N COATINGS DEPOSITED BY CATHODIC VACUUM ARC PVD PROCESS

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The aim of the research was to define the dependence of the properties of vacuum arc deposited (Ti,Al)N coatings on the nitrogen pressure and resulting composition of generated plasma. The investigated (Ti,Al)N coatings were deposited by the cathodic arc-vacuum method using AlxTi1-x alloy cathodes with a composition of 66,3 at.% Al and 33,7 at.% Ti. Experiments were carried out on the industrial multi-source arc-vacuum device MZ-383 at four values of the nitrogen pressure (0.3 Pa, 0.8 Pa, 1.3 Pa and 3.0 Pa), constant substrate bias voltage (-100 V) and constant arc current (50 A). Emission spectra of plasma were recorded in the range from 300 to 500 nm using medium-resolution monochromator with the optical grating of 1800 lines/mm and the focal distance of 250 mm. Scanning electron microscopy (SEM) and X-ray energy dispersive spectroscopy (EDS) were used to investigate structure and chemical composition of the coatings. Hardness, Young's modulus and adhesion strength of the coatings were determined using nano-indentation method and scratch test, respectively. The relation between nitrogen pressure, plasma composition, surface morphology and chemical composition of (Ti,Al)N coatings as well as their mechanical properties was assigned.

**G/PI.36** STRUCTURE-PHASE TRANSFORMATION OF HIGH SPEED STEEL BY VARIOUS HIGH INTENSITY ION-PLASMA TREATMENTS

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The samples of AISI M2 high speed steel were subjected to various types of high intensity nitrogen ion-plasma treatments. These are high current density ion implantation (HCII) 1 kV, 3.5 mA/cm^2, 7*10e19 ions/cm^2, 500 C, plasma immersion ion implantation (PIII) 40 kV, 8*10e18 ions/cm^2, 380C and compression plasma flow (CPF) irradiation with energy density of 15 J/cm^2 per pulse of ~80 μs. The Mossbauer spectroscopy measurements as well as cross-sectional scanning electron microscopy studies were carried out. The main results obtained are as follows. The thickest modified layer in steel of about 20 μm is formed by HCII and contains precipitates of carbonitrides and more uniform martensite comparing with initial steel. CPF irradiation leads to modification more than 10 μm thick surface layer. This layer consists of austenite and martensite doped by nitrogen and by elements of almost completely attenuated special carbides of high speed steel (M6C, MC, M7C3). The PIII forms thinnest modified layer of about 2 μm consisting of austenite doped by nitrogen and other elements of steel. The regularities of formation of structure-phase state of steel during above treatments are discussed.

**G/PI.37** INFLUENCE OF THE MORPHOLOGY ON THE MECHANICAL PROPERTIES OF CR1-XSIXN THIN FILMS

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We have investigated the structure and mechanical properties of polycrystalline Cr1-xSixN thin films (0<x<0.10) as a function of the Si content. These films were deposited by reactive magnetron sputtering at 400 K using two confocal targets of Cr and Si. The films crystallize in the fcc structure with grain size of 40 nm. Addition of Si as low as 2% at. completely changes the preferential orientation from (200), typical for CrN, to (111). Transmission electron microscopy studies have shown that films have a columnar-needle structure and the Si segregation at grain boundaries for films containing more than 4% at. Si. Hardness values obtained by nanoindentation increase from 18.5 GPa (value for CrN films) to 22 GPa for the films with 3% of Si. On the contrary, the hardness values significantly decrease in films with higher Si content. Cr1-xSixN films have also been prepared by alternatively deposition of CrNy and thin layers of SiNy in order to stop the columnar-needle structure. Correlations are established between the mechanical properties of the Cr1-xSixN films and their morphology.

**G/PI.38** STRUCTURAL AND CORROSION BEHAVIOUR OF STOICHIOMETRIC AND SUBSTOICHIOMETRIC TiN THIN FILMS

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This paper reports on the preparation of substoichiometric TiNx thin films by dc reactive magnetron sputtering. Chemical composition of the coatings was obtained by Rutherford Backscattering Spectrometry (RBS). The coating thickness ranges from 1.7 to 4.2 µm and the nitrogen content varied between 0 and 55 at. %. The coating structure was characterized by SEM and X-ray diffraction (XRD). The characterisation of the corrosion resistance of the samples was carried out by electrochemical techniques and scanning electron microscopy (SEM) after immersion in synthetic sweat solutions. Results of XRD showed the development of the hexagonal a-Ti phase with strong [002] orientation for low nitrogen contents, where the N atoms fit into octahedral sites in the Ti lattice as the amount of nitrogen is increased. For nitrogen contents of 20 and 30 at. % the e-Ti2N phase appears with [200] orientation. The d-TiN phase becomes dominant as the nitrogen content is further increased. Corrosion experiments show a systematic dependence of the results in both the structure/composition (affected by the processing conditions) and the consequent changes in crystalline phases and the lattice distortion. A detailed analysis of this behaviour as a function of the processing conditions and the resultant structural features will be presented.

**G/PI.39** STUDY OF THIN HARD COATING OF TANTALIUM CARBIDES ON STEEL SUBSTRATES

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Hard tantalum carbide coatings were elaborated by depositing a tantalum layer (4 µm thickness) on carbon steel substrates and, subsequently, annealing the system in vacuum at temperatures from 600 to 1100°C. Structural characterization was assessed using X-ray diffraction and Auger electron spectroscopy (AES). The mechanical characterization was performed by measuring microhardness and adhesion. It is found that at annealing up to 800°C two carbides (Ta2C and TaC) are formed. Moreover, the microhardness and adhesion of the films increase significantly with increasing annealing temperature. At a given temperature, the microhardness increases, with the rise of the annealing time, to reach a maximum and then decreases. This behavior is discussed.

**G/PI.40** PLASMA DEPOSITION OF HYDROGENATED DIAMOND LIKE CARBON FILMS FROM CH4-Ar MIXTURES

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In the last two decades hydrogenated amorphous carbon (a-C:H) films have attracted a big scientific and technological interest for their low temperature deposition and their hybrid properties ranging from diamond-like, graphite-like to polymer-like. Nowadays, hydrogenated diamond-like carbon (HDLC) films are successfully utilized in several fields: as scratch-resistant and wear protective coatings on optical components, plastics, cutting tools, razor blades and magnetic recording media.

In this contribution, a-C:H coatings have been produced at room temperature by plasma enhanced chemical vapor deposition (PECVD) in a conventional ion etching reactor (RIE PLASMALAB DP800) using CH4/Ar mixtures. The substrates have been placed onto the cathode (r.f. powered electrode) to guarantee an efficient ion bombardment during the growth so that a DLC character has been conferred to the deposited films. The study of process parameters such as Ar addition (at 50 and 300 mTorr) and d.c. self-bias voltage will be presented and discussed. In particular, the Ar dilution is found to affect the deposition rate and the properties of the films. An optimum combination of the deposition parameters has been found for obtaining smooth, hard and high band gap HDLC coatings. Data relative to FTIR, UV-Vis, Raman spectroscopies and hardness measurements will be presented. The correlation between the deposition parameters and film properties (hydrogen content, structural, optical and mechanical properties) will be discussed.

**G/PI.41** SELECTIVE AREA DEPOSITION PERFORMED BY IONIZED MAGNETRON SPUTTERING

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This work is devoted to the study of thin film deposition by ionized magnetron sputtering (IMS). The deposition technique is based on classical r.f. magnetron cathode deposition assisted by an induced r.f. discharge generated by a r.f. powered coil (antenna), placed between the substrate and the cathode (target). Hence a highly density plasma with a high ionization degree can be obtained [1]. Moreover, a plasma can be generated by the antenna independently of the magnetron plasma.

In a previous paper [2], concerning the deposition of carbon nitride, by varying the power injected in the antenna, a very wide range of deposition conditions has been put in light : from no deposition on grounded conductive substrates (etching of the growing film) to a high deposition rate on insulating substrates (up to 50 nm/min) compared to magnetron sputtering alone (with the antenna " off). This is mainly caused by the wide variation of the plasma potential with the coil power, inducing an important variation of the ion bombardment of the substrate surface. Selective area deposition of carbon nitride is performed on processed substrates which consist of conductive and insulating successive lines. The typical width of the processed lines is about several tens of µm. The influence of the main deposition parameters (the r.f. coil power and the substrate bias voltage) are studied in this paper in order to determine etching and deposition rates.

[1] A.C. Vanderbecq, M. Wautelet, J.P. Dauchot, M. Hecq, A.M. Pointu, A. Ricard, J. Appl. Phys. 84 (1) (1998) 100.

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**G/PI.42** CHARACTERISATION OF REACTIVE UNBALANCED MAGNETRON SPUTTERED CHROMIUM OXYNITRIDE THIN FILMS WITH AIR

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The aim of this work is to study the stoichiometry of chromium oxynitride thin films deposited by reactive magnetron sputtering in presence of air with various relative humidities. RBS (Rutherford Backscattering Spectroscopy) and resonant nuclear reaction (RNRA) were used to determine the thickness and the composition of the films. Hydrogen and nitrogen profiles were obtained by Tof-SIMS and RNRA. The chemical bonds were investigated by XPS and LEEIXS. The chromium metallic and chromium compounds concentrations were measured versus the flow and relative humidity of the air. During sputtering in metallic mode, Cr2O3 stoichiometry is observed with low contents of CrN, CrO2 and (CrO2)3-N whereas in compound mode the CrO2 stoichiometry predominates.

**G/PI.43** CANCELLED

**G/PI.44** MICROSTRUCTURE AND TEXTURAL ASPECTS OF ZnNi LAYERS ELECTRODEPOSITED ON STEEL

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The ZnNi anticorrosion coatings with different chemical composition are electrodeposited on a steel substrate from sulphate-acetate bath in the controlled hydrodynamic conditions. The influence of electrocrystallization process parameters on microstructure (morphology, phase composition, texture) of ZnNi coatings were investigated. The dependence of crystallographic texture of ZnNi layers on the polycrystalline steel substrate and on the electrodeposition condition were analysed. Texture was analysed by means of X-ray method based on the back-reflection pole figures with different as well as constant information depth. Formation process of a residual texture of ZnNi layer and inheritance range of preferred orientation of the steel substrate were observed.

**G/PI.45** INTERACTION BETWEEN CRACKING,DELAMINATION AND BUCKLING IN BRITTLE THIN FILMS

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In this paper a comparison between calculated and experimentally observed interaction between cracking, delamination and buckling in thin brittle films is presented. The thin brittle films studied are well-defined amorphous carbon layers deposited on Al. The films differ in thickness, modulus, adhesion to the Al, and internal stress state. These films are subjected to uniaxial tensile deformation during which the abovementioned deformation mechanisms occur and are measured in-situ in an optical or scanning electron microscope. Similar deformation mechanisms are modelled. We use a simple description in terms of a network of linear springs with a distribution of breaking strengths. The model consists of a substrate,interface and coating region is set up in such a way that it alows the coating to break and buckle and the interface to delaminate. Results of experiment and simulation are compared. As an example, stress transfer from substrate to film through an interface zone is governed by a correlation length that can be assessed from the development of the crack density as a function of applied strain. Subsequently the shear modulus of the interface (zone) can be determined. Other issues that will be discussed are the interplay between the correlation length and coating homogeneity that determines the pattern of initiation and propagation of cracks, transitions from cracking to delamination, and the interplay between delamination and buckling.

**G/PI.46** INFLUENCE OF THE STRUCTURE OF THE COMPOSITE „NITRIDED LAYER / PVD COATING" ON THE DURABILITY OF FORGING DIES MADE OF STEEL DIN-1.2367

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The paper presents research results of the influence of the "nitrided layer / PVD coating" composite structure on the durability of forging dies made of steel DIN-1.2367. Five structures of the composite differing in the PVD coating material were investigated. Following types of PVD coatings were applied: TiN/Ti(C,N)gradient, (Ti,Cr)N, (CrN/TiN)x3, (Cr/CrN)x3, CrN. The investigated composites were created by means of the surface "duplex" treatment method in a two-stage separable cycle. The nitriding process was executed with the use of the regulated gas nitriding method, whereas the PVD coating creation was executed by means of the arc-vacuum method. The paper presents results of materials investigations (metallographic analysis, analysis of chemical composition depth profile, X-ray diffraction phase analysis, adhesion scratch tests and thermal fatigue tests) as well as the results of laboratory forging tests executed in different conditions (two different temperatures of forging material and two different temperatures of die) for forging dies covered with each of the investigated composites. The wear intensity of the investigated dies was assessed by means of precise there-dimensional measurements while the wear mechanisms were investigated by SEM and optical microscopy investigations. On the base of the received results authors determined the influence of the composite structure and its material properties on the mechanisms and intensity of forging dies destruction.

**G/PI.47** PREPARATION OF Al2O3 THIN FILMS ON STAINLESS STEEL BY ELECTROCHEMICAL DEPOSITION

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Alumina is widely employed as support for noble-metal automotive exhaust catalysts. With a view to practical use in catalytic converters, an electrochemical method for deposition of Al2O3 films on thin foils of stainless steel was developed. The films were deposited from AlCl3 salt diluted in alcohol solutions. On the basis of investigation on the process kinetics, the region of potentials at which deposition of good quality films takes place, was established.

The deposited layers are homogeneous, have an excellent adhesion to the substrate, a specific surface area of 25-30 m2/g and a thickness of about 5μm. The thickness growth is limited due to the isolating character of alumina. Examination by SEM shows a microstructure formed by small (75-150 nm) compacted spherical micro aggregates. XPS study has established that the Al2O3 film composition is close to the sesquioxide stoichiometry. Thermal treatment at 973 K leads to no change in structure and composition of the alumina films deposited on stainless steel.

**G/PI.48** ELECTROCHEMICAL DEPOSITION OF CeO2 ON ZrO2 and Al2O3 THIN FILMS FORMED ON STAINLESS STEEL

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Cerium oxide is widely employed as support and promoter for noble-metal automotive exhaust catalysts. Adding CeO2 to Al2O3 or ZrO2 supports significantly increases their thermal stability and allows storing and releasing oxygen under reaction conditions.

A new electrochemical method using a nonaqueous electrolyte is utilized for deposition of ceria on ZrO2/SS and Al2O3/SS substrates. SEM and XPS studies of the morphology, structure and chemical composition of the ceria films were performed. Cerium films were obtained in a solution of 0.3М CeCl3x7Н2О diluted in alcohol. The deposition was performed both in naturally aerated solution and deaerated medium (treated for 60 min with high-purity Ar). This was made to establish the effect of O2 on the deposition of ceria films. X-ray photoelectron spectroscopy was used to examine the nature of ceria overlayers on stainless steel, ZrO2/SS and Al2O3/SS substrates as a function of the preparation conditions. The results were attributed to different mechanisms of oxide formation in the deposited cerium films. In the case of naturally aerated solution, Ce2O3 is formed by the oxygen present in the electrolyte during the process of electrolysis. In deaerated medium Ce is deposited in the metal state which goes into the CeO2 oxide state when the deposited overlayers are exposed to air.

**G/PI.49** EFFECT OF HEAT TREATMENT ON THE THIN TITANIUM FILMS DEPOSITED ON STEEL SUBSTRATE BY CATHODIC PULVERIZATION METHOD

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In this work we have investigated the formation and growth of titanium carbides after reaction between thin titanium films (~ 7 µm) and steel substrates in the temperature range 400-1000°C. The pure titanium (99,99 %) thin films were deposited by cathodic pulverization method on the steel substrates with about 2%at of carbon. The samples have been exposed to vacuum annealing during 1h in the temperature range 400-1000°C. The effects of the heat treatment on the kinetic of titanium carbides formation and growth, morphology, mechanical characteristics have been investigated using X- ray diffraction (XRD), Auger electron spectroscopy (AES), Scanning electron microscopy (SEM) and Vickers microhardness method.

In the considered interval of temperatures, we found that only one phase of titanium carbides TiC forms and grows proportionally with temperature. The microhardness increase with annealing temperature. One notices for substrate an increase of the microhardness until a maximal value 600.52Kg/mm2 at the temperature 700°C then a relatively soft decrease. However coated samples microhardness values are more important and reaches their maximum 3200.23Kg/mm2 at 900°C then begins to decrease The observed increase of the microhardness with annealing temperature , is caused by the diffusion of substrate carbon toward the titanium layer and the formation and the growth of titanium carbide, witch depends to annealing temperature activing the process of diffusion and therefore the speed of advancement of forehead of reaction from interface toward the samples surface, as well as the concentration of carbon in the carbide TiC has their important influence on mechanical and physical properties.

**G/PI.50** THERMAL-DIFFUSION SYNTHESIS OF THICK MOLYBDENUM DISULPHIDE COATINGS ON STEEL SUBSTRATES

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Special attention has been paid to technologies of deposition of molybdenum disulphide (MoS2) coatings and films for last decade because of their outstanding tribological properties. Nowadays, PVD methods are known to be the most widespread ones in production of high-performance MoS2 coatings. Limited thickness of the coatings (usually not more than several microns) and necessity to deposit intermediate layers are main disadvantages of PVD methods.

The proposed method of thermal-diffusion synthesis of MoS2 coatings comprises two stages: formation of the molybdate and molybdenum oxide layer on the surface of the steel substrate and treatment of the substrate in the vaporous sulphur environment to form MoS2. The method ensures formation of transition layer between MoS2 coating and the substrate, which prevents spalling of the coating. Coatings on stainless steel and high-speed steel substrates were obtained. Thickness of the coatings was within 5-60 microns depending on material of the substrate and the synthesis parameters. Fretting examination of the coatings carried out under ambient conditions at 625 and 1250 MPa contact loads showed values of coefficient of friction 0.17 and 0.07 respectively.

**G/PI.51** EFFECT OF COMPLEXING AGENTS ON STRUCTURE AND MORPHOLOGY OF ELECTRODEPOSITED Zn-Ni PROTECTIVE COATINGS

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With the aim of preparing protective coatings, the conditions for electrodeposition of Zn-Ni alloy from sulphate electrolytes with different complexing agents have been developed. The effect of addition of trisodium citrate and sodium acetate on nickel and zinc deposition was studied in following systems: Ni(II)-citrate, Zn(II)-citrate, Ni(II)-acetate, Zn(II)-acetate, Ni(II)-Zn(II)-citrate, Ni(II)-Zn(II)-acetate. Based on determination of dominant species and their concentration in the baths examined and the polarization behaviour, the role of organic agent ions was explained. The corrosion behaviour of the coatings was evaluated in 5 % sodium chloride water solution using the polarization resistance and EDS techniques. SEM, AFM and XRD analyses showed that apart from chemical composition, the corrosion resistance of Zn-Ni coatings depends mainly on their microstructure, phase composition and structural parameters (texture and lattice imperfection). In the range in Ni content 0-16 % in Zn-Ni deposits the microstructure changes correspond to phase composition. The obtained Zn-Ni coatings characterise improved corrosion resistance in comparison with Zn layers deposited in the same conditions. In presence of citrate ions, layers containing less Ni were obtained with the same corrosion resistance as Ni-rich coatings deposited from acetate solution.

**G/PI.52** DEVELOPMENT OF THE SELF-HEALING IN-SITU IN LIQUID METAL FORMATTED COATINGS FOR HEAVY METAL COOLANTS APPLICATION

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The problem of corrosion protection of structure materials in liquid Pb-55%Bi and Pb is actual for prospective development in the field of making accelerator-driven systems (ADS) for transmutation of artificial radioactive isotopes.

The basic direction for the solution of this problem in Russia is the use of corrosion protective barriers (PCB) on basis of multi-alloyed oxides with a spinel structure. The possible way for PCB formation on steel surfaces in-situ in liquid metals is presented. It is established that the best corrosion protective properties of steels in liquid Pb-55%Bi and Pb have the coatings on silicon content steels. The conditions of forming the coatings, the features of their composition and structure, boundaries of keeping the protective properties of coatings in dependence on temperature and oxygen content in liquid metals are given. The condition for the self-healing of coatings are considered. It is also shown that the surface modification of steels by treatment with high power pulsed electron beams for some microseconds allows to expand the boundaries of the applicability of an oxide protection at the expense of complicating a spinel composition.

**G/PI.53** ELECTROCRYSTALLIZATION OF Ni-Mo COATINGS FROM COMPLEX CITRATE-AMMONIA ELECTROLYTES

E. Beltowska-Lehman, Institute of Metallurgy and Materials Science, Polish Academy of Sciences, 30-059 Krakow, 25 Reymonta Str., Poland

Alloys containing molybdenum are characterised by a high hardness, wear, corrosion resistance and good catalytic properties for hydrogen evolution. Binary Ni-Mo coatings can be electrodeposited at room temperature from aqueous electrolytes despite of the large difference in melting points of these metals and limited their mutual solubility. Ni-Mo coatings of different composition (0-40 wt% Mo) were electrodeposited from citrate-ammonia baths in potentiostatic regimes under controlled hydrodynamic conditions. The effect of electrolyte composition (pH, metallic species and complexing agent concentration) has been investigated on the alloy composition, the current efficiency and deposit quality. It has been shown that, when the molybdenum content increases, the cathodic efficiency markedly decreases and the quality of the deposits becomes worse and mass transport is an important parameter in deposition behaviour of Ni-Mo coatings. The surface morphology and preferred orientation of the deposits was strongly correlated with chemical composition. The relationship between electrodeposition parameters, structural properties and functionality has also been determined.

**G/PI.54** HARDNESS ENHANCEMENT BY COMPOSITIONALLY MODULATED STRUCTURE OF Ti/TiN/TiCN/CN MULTILAYER FILMS

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The first objective of the present paper is to investigate new hard coatings based on compositionally modulated Ti/TiN/TiCN/CN multilayer films deposited by dual ion beam technique using a combination of Ti, TiN, TiC and C targets and an Ar-N2 mixture discharge gas. The second objective is the evaluation of the physical and chemical characteristics of the multilayers in respect to their practical applications. Hardness, friction coefficient, adhesion, chemical resistance among other properties have been evaluated. Preparation parameters has been controlled to obtain microcrystalline or nanocrystalline films that combine ultrahard behaviour with good tribological and wear properties.

**G/PI.55** CONTRIBUTION TO THE STUDY OF CHROMIUM CARBIDES FORMED BY ANNEALING OF CHROMIUM THIN FILMS DEPOSITED ON STEEL SUBSTRATES

R. Gheriani(a), R. Halimi(b), R. Bensaha(b), (a)Physical laboratory of Materials, University of Ouargla, Algeria, (b)Unity of research, Materials and applications, University of Constantine, Algeria

The interaction between chromium thin films and steel substrate 100C6, containing about 1% mass of carbon is studied by scanning electronic microscopy (SEM), X rays diffraction (DRX) and by Auger electrons spectroscopy (AES).

Samples are constituted of substrates made of steel in the shape of a disk of 10 mms in diameter and 1 mm in thickness, on which we put, by cathodic pulverization, thin chromium films of ~0.68ľm in thickness, samples are thermally treated under vacuum (~10-6mbar) within the interval of temperatures of 400-1000°C. it's established that in the considered temperature interval, several composed forms; chromium carbide Cr7C3 and Cr23C6, forms and grows until the total consumption of chromium layer accompanied by a meaningful increase of the hardness and a change of color of samples free surface. The hardness increases with annealing temperature, reaches a maximum then decreases progressively, the growth of Hv is due to the diffusion of the carbon, and to the formation of chromium carbide. However, the decrease of Hv is associated to the diffusion of iron and the formation of iron oxide (Fe2O3), in the higher temperatures, we note the formation of chromium oxide (Cr 2O3). The formation of chromium carbides improve the surface materials properties, such as the resistance against chemical, mechanical, thermal solicitations. The mechanism of formation and growth of chromium carbides is discussed on the thermodynamic consideration basis.

## Session V: CVD/PECVD synthesized films and coatings
## Session chair: S. Luridiana, S. Mathur

**G-V.1** 14:30

EFFECT OF THE CARBON GAS PRECURSOR ON THE PROPERTIES OF NANOSTRUCTURED COPPER-CARBON FILMS PREPARED BY MICROWAVE PLASMA-ASSISTED PROCESSES

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Nanocrystalline copper/hydrogenated amorphous carbon (Cu/a-C:H) films have been deposited on silicon substrates using a distributed electron cyclotron resonance microwave plasma reactor. The microwave plasma-enhanced chemical vapor deposition process of carbon from argon-methane or argon-acetylene mixtures of various compositions was associated with the sputter deposition of copper from a copper target. The major objective of this work was to investigate the effect of the carbon gas precursor on the characteristics of Cu/a-C:H films deposited at ambient temperature. The morphology and surface topography of films as well as the residual stresses developed in the films were investigated as functions of the deposition parameters. The composition of films was determined by Rutherford backscattering spectroscopy, energy recoil detection analyses and nuclear reaction analyses. The structure of films and the size of copper crystallites incorporated in the a-C:H matrix were determined by X-ray diffraction (XRD) techniques. Grazing incidence angle X-ray scattering (GISAXS) was also performed to investigate the size distribution and distance of metal clusters as functions of the deposition parameters. A comparative study of the properties of films produced from CH4 and C2H2 was accomplished. The composition and structure of Cu/a-C:H films were found to be very dependent on the carbon gas precursor and composition of the gas phase.

**G-V.2** 14:50

SIOxCyHz POLYMERIC THIN FILMS PREPARED BY PECVD

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SiOxCyHz thin films have been deposited by remote plasma enhanced CVD at room temperature. These films have been studied by surface techniques like REELS, XPS, AFM and XANES with synchrotron radiation, and bulk techniques like RBS, ERDA, FT-IR and spectroscopic ellipsometry. The final stoichiometry of the films, ranging from inorganic silica to polymeric silicone-like, depended on the oxygen percentage in the plasma. The decomposition of the precursors in the plasma has been studied by optical emission spectroscopy. Results are obtained for two different experimental configurations, a first one consisting of an ECR source and a second being a surface-wave apparatus.

Whatever their stoichiometry, all the films were formed by an Si-O-Si basic skeleton. In addition, XANES spectra showed the existence of Si-C bonds in the structure of the films, while FT-IT show the presence of other organic groups. The optical properties of the deposited films determined by ellipsometry have been related with the composition and microstructure of the layers. This latter is shown to be highly dependent on experimental parameters like total pressure during deposition. Finally the oxidation behaviour with a plasma of the organic components of the films has been analysed by different techniques and simulated in situ in a XPS spectrophotometer. The results show the formation of a very dense silica layers with a high index of refraction.

**G-V.3** 15:10

PLASMA REACTIONS OF N2O ON HYDROGENATED AMORPHOUS CARBON FILMS BY PECVD METHOD

Y.T. Kim(a), S.G. Yoon(a), S.G. Yoon(b), S.C. Jung(b), S.J. Suh(a) and D.H. Yoon(a), (a)Department of Advanced Materials Engineering, Sungkyunkwan University, Suwon 440-746, Korea, (b)R & D Center Samsung Electromechanics, Suwon 442-743, Korea

Diamond-like carbon (DLC, a-C:H) films were deposited by r.f. plasma-enhanced chemical vapor deposition of methane(CH4)-nitrous oxide(N2O)-hydrogen(H2) mixtures onto silicon substrates. With increasing rf power, the nitrogen composition decreases while the oxygen composition increases, in a manner that the O/N ratio increases approximately linearly. The transmittances of the DLC films deposited with and without the addition of N2O were compared with each other in the visible light and ultraviolet light regions. The optical properties (the transmittance over a wide spectral range and refractive index) were determined by means of IR-spectroscopy and ellipsometric measurements. Surface morphology of DLC films with roughness below 10 Å was observed under atomic force microscopy (AFM).

**G-V.4** 15:30

CHARACTERIZATION OF DIAMOND-LIKE CARBON THIN FILMS PREPARED BY A MICROWAVE PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION METHOD

Won Seok Choi(a), Ilsub Chung(a), and Byungyou Hong(a,b), (a)School of Information and Communication Engineering, Sungkyunkwan University, Suwon 440-746, Korea, (b)Center for Advanced Plasma Surface Technology, Sungkyunkwan University, Suwon 440-746, Korea

We investigated the structural and electrical properties of diamond-like carbon(DLC) films grown with a RF plasma enhanced chemical vapor deposition(RF-PECVD) system. DLC thin films were prepared on the glass and silicon substrate with a methane(CH4) and hydrogen(H2) gas mixture. We have also checked optical and electrical properties of DLC thin films depend on the RF bias. Raman and FT-IR measurement shows the physical variation of DLC films. We have measure the hardness and optical band-gap with nano-intender and UV-visible, respectively. And we have investigated friction characteristics of DLC thin films with an atomic force microscope(AFM) in friction force microscope(FFM) mode.

**G-V.5** 15:50

MECHANICAL PROPERTIES OF PECVD HYDROGENATED AMORPHOUS CARBON COATINGS VIA NANOINDENTATION AND NANOSCRATCHING TECHNIQUES

P. Bruno, Dipartimento di Chimica, Università di Bari, Via Orabona 4, 70126 Bari, Italy, G. Cicala, IMIP-CNR w/o Dipartimento di Chimica, Università di Bari, Via Orabona 4, 70126 Bari, Italy, A.M. Losacco, Centro Laser, S.P. Casamassima km3, 70010 Valenzano (Bari), Italy, P. Decuzzi, Department of Mechanical Engineering and Engineering Management, Politecnico di Bari, Viale Japigia 182, 70126 Bari, Italy

The good combination of chemical and physical properties of hydrogenated amorphous carbon (a-C:H) coatings makes them suitable for mechanical, tribological, biomedical and microelectronic applications.

In this work, the mechanical properties of a-C:H films were determined by nanoindentation and nanoscratching techniques. The films were produced via plasma chemical vapour deposition (PECVD) from methane-argon gas mixtures. A nanoindenter with a Berkovich diamond tip was employed to estimate accurately mechanical properties of the coatings. Using the Oliver and Pharr approach, the load-penetration depth curves were determined with a maximum load of 1mN leading to penetration depth of 93nm, smaller than the 10% of actual film 1 µm thick. With a bias ranging between -30 and -300 V, the maximum Young's modulus (E) measured at the surface is of about 106 GPa, whilst the surface hardness (H) reaches 13 GPa. Continuous multi-cycle load tests were also carried out to estimate H, E at various depths and creep resistances. The films behave elastically with a little tendency to creep, both E and H increase with depth up to 135 and 17 GPa for the hardest sample, respectively. Finally, a scratch test was performed to assess the resistance to delamination. A sudden jump of the friction coefficient and penetration depth depicts clearly the point of delamination with a maximum rupture load of about 215 mN. The large values measured for H and E demonstrate the good diamond-like quality of the carbon films.

16:10 **BREAK**

## Session VI: Barrier and protective coatings
## Session chair: A. Biedunkiewicz, W. Gulbinski

**G-VI.1** 16:30 -Invited-

PLASMA ASSISTED DEPOSITION OF THIN FILM “SUPERBARRIERS” ON POLYMERS

**M.R. Wertheimer**, G. Dennler, Département de Génie Physique, École Polytechnique, Montréal QC H3C 3A7, Canada, G. Czeremuszkin and M. Latrèche, Nova Plasma Inc., Montréal QC H3S 2P2, Canada

Since their beginnings in the early 1990s, transparent ceramic permeation barrier coatings on polymers have been steadily gaining interest. Initially intended for food, beverage and pharmaceutical packaging, these coatings are now also of key importance to the emerging technology of organic-based microelectronic devices on flexible polymeric substrates, for example OLED or PLED displays. It is known that such films (for example SiO2 and Si3N4) reduce the measured OTR value ("Oxygen Transmission Rate") of a polymer only when their thickness, d, exceeds a certain critical value, dc (~10 nm). For d < dc, the coated polymer displays practically the same OTR value as the bare material.

During this lecture we present barrier characteristics of thin SiO2 and Si3N4 films prepared by PECVD (Plasma Enhanced Chemical Vapor Deposition) on various polymers. More particularly, we explain the absence of barrier properties for d < dc, limitations which exist when d > dc, namely sub-micron defects, and how to overcome these limitations in the quest for "superbarriers".

**G-VI.2** 17:00

INFLUENCE OF THERMAL TREATMENT AND ION IRRADIATION ON THE STRUCTURE OF TI-AL FILMS

B.N. Mukashev, S.E. Romankov, T.V. Volkova, D.M. Muhamedshina, Institute of Physics & Technology, 480082, Almaty 82, Kazakstan

Titanium aluminides based on TiAl and Ti3Al are potential materials for high temperature aerospace application. It is reasonable to develop processing strategies for protective and high temperature coating based on them. In the present work, we have created aluminium thin films on titanium substrates and investigated their microstructural evolution during annealing and ion irradiation by SEM and X-ray diffraction. When annealed, the aluminium atoms have been discovered to diffuse into the substrate. The redistribution of components near the surface takes place. During annealing the new intermediate metastable phases, which are stable only within the definite temperature range, have developed. Ion irradiation affects the kinetics of structural transformation.

**G-VI.3** 17:20

REACTIVE MAGNETRON SPUTTERING OF HARD Si-B-C-N FILMS WITH A CONTROLLED COMPOSITION

S. Potocky, J. Cizek, J. Vlcek, M. Kormunda, J. Houska, Department of Physics, University of West Bohemia, Univerzitni 22, 306 14 Plzen, Czech Republic, V. Perina, Nuclear Physics Institute, Academy of Sciences of the Czech Republic, 250 68 Rez near Praha, Czech Republic and J. Zemek, Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnicka 10, 162 53 Praha 6, Czech Republic

Si-B-C-N films of various compositions were deposited on Si(100) substrates by reactive dc magnetron co-sputtering of silicon, boron and carbon in nitrogen-argon gas mixtures using a composed C-Si-B target with variable Si/C area ratios and a fixed 20% boron fraction in the magnetron erosion track area. The total pressure and the discharge current on the magnetron target were held constant at p = 0.5 Pa and Im = 1 A, and the substrate temperature was adjusted at 600 °C by an ohmic heater or it was in the range from 180 to 250 °C without the heater. The rf induced negative substrate bias voltage, Ub, was varied from a floating potential of –15 V to –500 V. Elemental compositions of the films (determined by RBS and ERD), their surface bonding structure (XPS) and mechanical properties were primarily controlled by the Si fraction (5–75%) in the magnetron erosion track area, by the Ar concentration (0–75%) in the gas mixture and by the negative substrate bias voltage Ub. The energy and flux of ions bombarding the target and the growing films were estimated on the basis of the discharge characteristics measured for both the dc magnetron discharge (the cathode-anode voltages of the magnetron at Im = 1 A) and the rf discharge dominating in a deposition zone (the time-average rf powers absorbed by the plasma at the corresponding Ub values). The films, typically 1-2 μm thick, were found to be amorphous with hardness up to 50 GPa, good adhesion and promising tribological properties.

**G-VI.4** 17:40

EFFECT OF SiC COATING IN ABLATIVE AND MECHANICAL PROPERTIES OF CFRC COMPOSITES

Young-Jae Lee and Hyeok-Jong Joo, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan and Department of Polymer Science and Engineering, Chungnam National University, Taejon, Korea

Carbon fiber reinforced carbon (CFRC) composites has been used as a thermal insulator in aerospace applications (e.g., a rocket nozzle) but their relatively poor oxidation resistance at elevated temperature in oxidizing environment has limited the applications of the materials, resulting in the necessity of the diffusion barrier formation. Silicon carbide (SiC) is one of the prospective candidates for the diffusion barrier because it can offer not only high oxidation resistance but also a similar coefficient of thermal expansion (CTE) to that of carbon. A mismatch of CTE has often created a crack formation on coating, producing a catastrophic failure of the materials. 4D CFRC composites were prepared by PAN-based carbon fibers and coal-tar pitch as the reinforcement and the matrix, respectively. SiC coatings on the composites were produced by carbothermal reduction of a silicon compound mixture, the so-called pack cementation; the composites were immersed in a mixture of silicon compounds and heated at different temperature. The reaction time was also changed to optimize the process. The objectives here are to evaluate the effect of SiC coatings in ablative and mechanical properties of the composites and to optimize the process conditions. Flexural strength and modulus increased as the reaction temperature (up to 1850 C) and time (up to 6 hr) increased; it is thought to be that SiC coatings with a gradient increase the compatibility between the fibers and the matrix. The ablative property of the composites were measured by arc-plasma torch and presented in terms of ablation rate, weight, thickness and diameter. It seems to be that ablation is not simply proportional to oxidation inhibition and governed also by other properties.

**G-VI.5** 18:00

INORGANIC PROTECTIVE COATINGS FOR STAINLESS STEEL

K. Endres, M. Amlung, N. Niegisch, M. Mennig, H. Schmidt, Institut für Neue Materialien gem. GmbH, Saarbrücken, Germany

An inorganic coating on stainless steel based on nano SiO2 with a low alkali content (e. g. about 6 wt% for Na) has been developed. The coating solution is prepared from tetraethoxysilane, methyltriethoxysilane and sodium- and potassium hydroxide respectively according to the sol gel process. The coatings were applied by dip or spray coating on stainless steel, dried at 100°C and densified (500°C, 1 h). By using 29Si-NMR and by x-ray defraction it could be shown, that after densification only Q4 signals can be detected and that the patterns in the x-ray defraction show no sign of a crystalline material. Due to these results it can be concluded that a glass structure is formed. The nanoparticulate inorganic coating is insoluble in water and can be used as protective coating against acid but also alkaline attack. The coatings (thickness about 2 - 10 mm) prevent a tarnishing of the steel up to 500°C. The coatings have a good adhesion on the steel (GT0) and after 1000 cycles Taber Abrader test, the coated steel plates did not show any abrasion. The scratch hardness was 6 times higher than on uncoated steel. Due to the planarising properties, an improved cleaning behaviour of the coated steel surfaces against inorganic sediments and organic pollution could be proved. The flexibility of the coating was demonstrated by a bending test (bending radius of 2 cm) which showed that it can be deformed crack free. Application areas for the inorganic coatings could be household appliances, the area of automotive and architecture, as well as plant construction.

## Session VII: Nanostructured films
## Session chair: P.B. Barna, M. Sancrotti

**G-VII.1** 8:30 -Invited-

DEPOSITION AND CHARACTERIZATION OF NANOSTRUCTURED METAL-CARBON COMPOSITE FILMS

**Y. Pauleau**, National Polytechnic Institute of Grenoble, CNRS-LEMD, B.P. 166, 38042 Grenoble cedex 9, France

Nanostructured metal-carbon composite films consist of a matrix of various types of amorphous carbon (a-C) ranging from graphite-like sp2-bonded a-C, hydrogenated a-C or diamond-like tetrahedral a-C (DLC) with a significant fraction of sp3-bonded carbon atoms. The incorporation of a nanocrystalline phase such as metal or carbide in the a-C matrix can yield unique electrical, optical, magnetic, mechanical and tribological properties. In addition, metal containing DLC films may exhibit low residual stresses, good adhesion to various substrates, high hardness and toughness leading to very low friction coefficients under unlubricated sliding conditions against steel and sapphire counterparts, high wear resistance and simultaneously low friction even in humid environments. Various deposition techniques such as sputtering, arc discharge, plasma-enhanced chemical vapor deposition, sol-gel, pulsed laser ablation can be used to produce films containing metal clusters dispersed in the a-C matrix. The composition and microstructure of metal-carbon composite films depend greatly on the deposition technique and deposition conditions. The physical properties of films, in particular the mechanical characteristics and tribological behavior depend on various factors such as type of a-C, concentration of metal atoms, size and distance of metal clusters. These metal-carbon composite films may be used in a wide range of applications.

**G-VII.2** 9:00

FIB-SIMS ANALYSES OF NANOSTRUCTURED THIN FILMS

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Secondary Ion Mass Spectrometry with spatial resolution down to 20 nm was used to analyse thin carbon and titanium oxide films, from micro- to nano-scale level. Amorphous carbon films were produced both by a PACVD system from different mixtures of acetylene and tetrafluoromethane and cluster assembled from graphite cathodes, in He atmosphere, using a supersonic cluster beam apparatus. With the same apparatus titanium oxide films were obtained with a titanium cathode, in oxygen atmosphere.We acquired mass spectra, depth profiling and ion imaging of film surface. Contaminant distributions along the depth and on the surface were investigated. We found Na, Ca, K, O2, due to atmosphere contamination; their distribution is homogeneous along the surface and decreases rapidly with film depth, showing that no contaminants percolate into the film. Mass spectra highlight the mass distribution; in particular cluster mass distribution from cluster assembled films is shown. Surface images show the secondary ion distribution for F-, C2-, CN-, O-, TiO- and other ion compounds. Compositionally heterogeneous regions are evident mainly along defects, such as edges, on film surface, where the images show preferential accumulation of some elements.

**G-VII.3** 9:20

RELATION OF THE STRUCTURE AND MECHANICAL PROPERTIES OF CARBON-Ni AND CNx -Ni NANOCOMPOSITE FILMS

Gy. J. Kovács(a), G. Sáfrán(a), O. Geszti(a), T. Ujváry(b), I. Bertóti(b), G. Radnóczi(a), (a)Research Institute for Technical Physics and Materials Science, 1525 Budapest, P.O. Box 49, Hungary, (b)Research Laboratory of Materials and Environmental Chemistry, Chemical Research Center, H-1525 Budapest, P.O. Box 17. Hungary

DC sputtered Carbon/Nickel and Carbon-Nitride (CNx)/Nickel thin films were investigated by high resolution electron microscopy, X-ray microanalysis and nanoindentation to clarify the influence of nitrogen and Ni additions on the structure formation and mechanical properties. The films were deposited in argon or nitrogen plasma at temperatures from 25 to 800 oC onto Si substrates. The microstructures can be described as nanocomposites, built from Ni nanocrystals in a carbon or CNx matrix. The Ni nanopcrystals are normally rolled in 3-5 layer thick graphitic stacks of tubular shape, attributed to a catalyzer effect of the Ni. The structure of the matrix shows relatively high ordering in the form of curved graphite or CNx layer stacks, in which both nitrogen and Ni incorporation enhances the formation of ordered fraction of such type. Outside the above region the matrix was amorphous.

The mechanical properties of the films were found to be strongly dependent on the substrate temperature during growth. The highest nanohardness of 14 GPa was measured for the film, grown at 200 oC, while low values (2 GPa) were obtained for high temperature films. Structural, compositional and mechanical properties of the films will be described in detail and the relation between structure and mechanical properties will be discussed. Acknowledgement: This work was supported by the Hungarian National Science Foundation (OTKA T-30424) and by the EU under the contract No. ICAI-CT-2000-70029 and through the project New Fullerene-like Materials: RTN2-2001-00172.

**G-VII.4** 9:40

STRUCTURE AND MECHANICAL PROPERTIES OF CrN/CrC NANOMETRIC MULTILAYERS

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Chromium nitride/ chromium carbide (CrN/CrC) multilayers, with periods between 10 and 100 nm, were deposited on M2 steel and silicon substrates using a single cathode r.f. magnetron sputtering system. The used target was pure chromium (99.99%) and the nitride/carbide multilayer structure was obtained by alternatively changing the sputtering gas composition between an Ar/N2 reactive mixture and another mixture with Ar and CH4. The deposition parameters were arranged to obtain optimized properties for both materials in individual coatings and then implemented in multilayered film deposition. X-ray diffraction allowed us a detailed characterization of the different phases obtained in both CrN and CrC individual coatings and CrN/CrC multilayers. Multilayers periodic structure was characterized by secondary ion mass spectrometry and electron microscopy. The mechanical properties such as hardness, residual stress and film adhesion in multilayers were analyzed by means of nanoindentation and microscracth techniques and their relations to period thickness are presented. These properties of the CrN/CrC multilayers are compared with those of CrN and CrC individual coatings.

**G-VII.5** 10:00

Ti-Si-C SPUTTER DEPOSITED THIN FILM COATINGS

Witold Gulbinski, Tomasz Suszko, Bogdan Warcholikski, Technical University of Koszalin, Faculty of Mechanical Engineering, Physics Department, Raclawicka 15-17, 75-620 Koszalin, Poland

Design concept of novel wear resistant and low friction nanocomposite materials is based on the formation of two- or multi-phase systems, which show a thermodynamically driven segregation into nanophase with grain size nanometer scale. Combination of materials (phases) in the single coating results in new properties which can meet an increasing level of requirements in modern applications. Thin film, Ti-Si-C system based coatings were deposited from elemental targets (Ti, Si) by double-source reactive, pulsed magnetron sputtering at silicon and steel substrates. Their structure, chemical and phase composition as well as pin-on-disc tested tribological properties in wide temperature range (20-7000C) were studied.

10:20 **BREAK**

## Session VIII: Mechanisms in energetic beam deposition

## Session chair: F. Fuso, B. Major

**G-VIII.1** 10:40 -Invited-

PROCESSES IN ION AND IN PHOTON INTERACTION WITH SURFACES

**Antonio Miotello**, INFM and Dipartimento di Fisica, Universita` di Trento, 38050 Povo, Trento, Italy

A comparison is made between the importance of the following categories of processes in ion-surface and laser-surface interactions: ballistic, thermal-spike, residual-defect-induced, and electronic. It is shown that ballistic processes are important for ion-induced sputtering, mixing, and composition change. On the contrary, thermal-spike processes are very important with laser-pulse sputtering. In the latter case one must distinguish between vaporization, phase explosion, hydrodynamic and photomechanical effects like exfoliation and spallation. On the other hand, normal boiling is unimportant owing to the negligible density of heterogeneous nuclei and because of extreme kinetic limitation. Residual defects are basic to all ion-surface interactions, but most especially to ion mixing. Finally, electronic processes are somewhat important to ion sputtering but have not yet been quantified for ion mixing or composition change. On the other hand, although electronic processes are very important indeed with laser-surface interactions, a basic qualification must be made: the primary laser-surface interactions are dominantly electronic, but most of the deposited energy is rapidly converted from excitation to heat, and it is for this reason that thermal-spike sputtering is so prominent. Finally, we consider the fact that laser sputtering has two aspects. These are the primary processes, which lead to particle expulsion, and the secondary processes, which arise due to collisions amongst the emitted particles.

**G-VIII.2** 11:10

HIGH TEMPERATURE NITROGEN PLASMA IMMERSION ION IMPLANTATION INTO MOLYBDENUM

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Refractory molybdenum, which shows a high corrosion and wear resistance, has applications in different areas, as chemical, aerospace and defence industry. Nevertheless, a higher surface hardness and sputter resistance are still demanded in several cases. The use of ion implantation allows the formation of a nitrided surface layer without changing the bulk properties. However, the diffusivity necessary to obtain thick layers beyond the ion implantation range of 100 nm or less is near - or below - the detection limit for temperatures up to 500 °C.

In this presentation, the diffusion behaviour of nitrogen and the phase formation in molybdenum are investigated for nitrogen plasma immersion ion implantation (PIII) in the temperature range from 550 to 750 °C. Heating by infrared radiation was used in addition to beam heating to obtain the desired temperatures. In this temperature range, a thermally activated diffusion with an activation energy near 1 eV was observed for the growth of a closed Mo2N layer, followed by a deeper diffusion tail into the material. A thickness of more than 10 µm can be obtained after several hours. The phase of the surface layer changed from cubic to tetragonal with increasing target temperature around 600 - 650 °C.

**G-VIII.3** 11:30

EXPANDING THERMAL PLASMA FOR FAST DEPOSITION OF SCRATCH-RESISTANT SiCxHyOz COATINGS ON POLYCARBONATE

Y. Barrell(a), M. Creatore(a), M. Schaepkens(b), C. D. Iacovangelo(b), M.C.M. van de Sanden(a), (a)Department of Applied Physics, Eindhoven University of Technology P.O.Box 513, 5600 MB Eindhoven, The Netherlands, (b)General Electric Global Research Center, Schenectady, New York, USA

Polycarbonate (PC) can be used in the transportation/architectural glazing industry to replace glass. However, PC is sensitive to scratching. To protect the PC it can be coated with abrasion resistant SiCxHyOz coatings using plasma-aided deposition methods. For industrial applications a fast, large-area deposition technique is required and the expanding thermal plasma set-up has proven to be successful for this application [1]. In this set-up a dc cascaded arc argon plasma is ignited at 0.1-0.4 bar and expands into the deposition chamber (0.1-0.3 mbar) through a nozzle, where O2 is injected. Hexamethyldisiloxane vapour is injected downstream by means of a ring. Due to the large pressure difference, the downstream properties do not influence the plasma characteristics. Moreover, due to the expansion the electron temperature drops to about 0.3 eV preventing electron impact dissociation to contribute to the plasma chemistry effectively. Instead, it is mainly controlled by charge exchange (with Ar+) and dissociative recombination reactions (with e-) in the expanding plasma. In this paper we present results from research performed to improve the understanding of how the gas phase and surface chemistry affect the growth of SiCxHyOz coatings. The chemistry is monitored using mass spectrometry and cavity ringdown spectroscopy. Chemical/optical characterisation of the coating is performed using FTIR, XPS and Spectroscopic Ellipsometry. Information on the mechanical performance of the film is also collected. These studies aim to further optimise the coating system.

[1] M. Schaepkens and C.D. Iacovangelo, "High-rate Large-area Plasma Deposition using Multiple Expanding Thermal Plasmas", AVS 49th International Symposium, Paper PS2-MoA7 (2002)

**G-VIII.4** 11:50

ION BEAM STUDIES OF TiNxOy THIN FILMS DEPOSITED BY REACTIVE MAGNETRON SPUTTERING

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Titanium oxynitride compounds exhibit interesting properties for applications in fields ranging from protective/decorative coatings to solar panels. The properties of TiNxOy are related to the oxide/nitride ratio and can be tailored playing with this ratio. In this work we studied the influence of substrate bias voltage and flow rate of reactive gases (a mixture of 95 % N2/5 % O2) on the properties of TiNxOy films. The films were deposited on steel and Si substrates at a constant temperature of 300 ºC by r.f. reactive magnetron sputtering. The depositions were carried out from a pure Ti target. The composition throughout the entire thickness was determined by Rutherford Backscatering Spectrometry (RBS). To get information on the profile of light elements (O, N) and detect the presence of hydrogen on the films, heavy ion elastic recoil detection analysis (HI-ERDA) was performed. The results indicate a nearly constant stoichiometry through all the entire analysed depth. The colouration varied from the shiny golden for low oxygen contents (characteristic of TiN films) to dark blue for higher oxygen contents. The electrical resistivity of the samples was obtained at room temperature and the values varied from about 120 mWcm for a sample with very low oxygen content to values up to 470 mWcm, for the highest oxygen contents.

**G-VIII.5** 12:10 CHARACTERIZATION BY ELECTRON SPIN RESONANCE OF DEFECTS IN a-C:H THIN FILMS. CORRELATION BETWEEN STRUCTURAL EVOLUTIONS AND OPTICAL PROPERTIES

E. Tomasella(a), M. Dubois(a), C. Meunier(b), L. Thomas(c), (a)Laboratoire des Matériaux Inorganiques, Université Blaise Pascal (Clermont-Ferrand II), UMR CNRS 6002, 24 Avenue des Landais, 63177 Aubière cedex, France, (b)CREST, UMR CNRS 6000, 4 place Tharradin, BP 71427, 25211 Montbéliard cedex, France, (c)Institut de Science et de Génie des Matériaux et Procédés, Université de Perpignan, UPR CNRS 8521, Technosud, Rambla de la Thermodynamique, 66100 Perpignan, France

Hydrogenated amorphous carbons (a-C:H) have recently received considerable attention because they posses interesting properties like extreme hardness, chemical inertness and optical transparency. The optical properties of a-C:H thin films prepared by r.f. plasma enhanced chemical vapor deposition from a CH4/Ar or CH4/He gas mixture have been previously investigated. The optical gap Eg and the Urbach tail parameter Eu have been determined by optical-ultraviolet absorption characteristics. The Urbach disorder parameter and the optical gap are important parameters to characterize a-C:H. These parameters depend on initial disorder, hydrogen content and sp3/sp2 ratio. Moreover, Elastic Recoil Detection Analysis, Infrared and Raman spectroscopies have been used to quantify respectively hydrogen content, the bonding and sp2 proportion carbon of thin films. This complete characterization was used to interpret the evolution of the defects states determined by Electron Spin Resonance (ESR) as a function of the film preparation (influence of the gas composition and the negative d.c bias voltage).

We have found that the optical band gap Eg of these films decreases with the loss of hydrogen (bonded and unbonded) and the increasing of sp2 content while Eu gap increases implicating a greater structural disorder. These results have been related to ESR analysis. We have shown in particular the decrease of the peak-to-peak linewidth, Hpp, as the hydrogen content decreases.

12:30 **LUNCH**

## Session IX: Mechanisms of film growth
Session chair: F. Maury, S. Dub

**G-IX.1** 14:00 -Invited-

SOLID STATE DE-WETTING OF VAPOR DEPOSITED FILMS ON PLANAR AND FIBER-SHAPED CARBON SUBSTRATES

**C. Eisenmenger-Sittner**, C. Schrank, E. Neubauer, H. Bangert, A. Bergauer, Technische Universität Wien, Institut für Festkörperphysik, E-138? Wiedner Hauptstrasse 8-10, 1040 Wien, Austria

In novel materials the interface zone between their components is a point of crucial importance in respect to mechanical or thermal contact. Copper-Carbon composites are an example for this material class. They have a potential for an application as heat sinks in electronic components, but joining the two materials is difficult.

Two critical processing steps determine the interfacial properties: first the deposition of Cu on the C surface at room temperature and second the heat treatment of the material during the compactation process. In this paper we investigate the adhesive properties of Cu-films on planar C-substrates and the de-wetting of Cu from C during heat treatment. De-wetting occurs well below the melting point of copper. It starts with hole formation and ends with the decomposition of the Cu-Film into isolated droplets. A similar behavior is observed on Carbon-fibers.

The above issues (interfacial adhesion and de-wetting) are investigated in dependence on several pre-treatment processes which were applied to the C-surface such as plasma-modification or the deposition of intermediate layers. The basic mechanisms of adhesion promotion and de-wetting are identified and the consequences of the experimental findings for the manufacturing of Cu-C composite materials are briefly discussed.

This Work is Supported by the Austrian FWF, Grant #P14534.

**G-IX.2** 14:30

IN-SITU AND REAL-TIME MONITORING OF THE ELECTRONIC PROPERTIES AND GROWTH EVOLUTION OF TiN FILMS

P. Patsalas and S. Logothetidis, Aristotle University of Thessaloniki, Department of Physics, Solid State Physics Section, 54124 Thessaloniki, Greece

Titanium Nitride (TiN) films have gained much interest due to their exceptional electronic properties and refractory character, which make them suitable for parts in high-power electronics. In this work, we implement in-situ and real-time Spectroscopic Ellipsometry (SE) to monitor the evolution of microstructure, composition and electronic properties of TiNx (1£x£1.12) films, 0.5-50 nm thick, during sputter growth on various substrates. We developed the appropriate methods of SE analysis to achieve sub-monolayer resolution. Effective Medium Theories (EMT) described the films in terms of their constituent materials and provided the evolution of composition, density, morphology (island density and size, surface roughness) and microstructure. The TiN growth mechanism is affected by the internal stresses, the substrate/film lattice match and the ion irradiation during growth. We found that TiN follows either island or layer-by-layer growth, depending on the substrate and ion irradiation conditions. We also found that a stress-relieved over-stoichiometric TiNx layer is grown before TiN, showing that the TiN island growth is a two-step process. We evaluate the evolution of the TiN's electronic properties [carrier concentration (2.5-5.5x1022 e/cm3) and resistivity (40-500 mW cm)] using a more sophisticated SE modeling, which describes the optical response of conduction and valence electrons, and we identified the low thickness limit for stable, conducting TiN layers.

**G-IX.3** 14:50

GROWTH MECHANISM OF SPUTTERED CARBON NITRIDE THIN FILMS

O. Durand-Drouhin (a), M. Lejeune(b), S. Charvet(a), A. Grosman(c), C. Ortega(c), M. Clin(a), M. Benlahsen(a), (a)Laboratoire de Physique de la Matière Condensée, Faculté des Sciences, 33 rue Saint-Leu, 80039 Amiens Cedex 1, France, (b)Institut für Photovoltaik (IPV) c/o Forschungszentrum Jülich GmbH 52425 Jülich, Germany, (c)Groupe de Physique des Solides (GPS), 2 Place Jussieu, 75251 Paris Cedex 05, France

High nitrogen content carbon nitride thin films were prepared using rf magnetron sputtering of a graphite target in pure nitrogen plasma. The deposition plasma has been characterised by mass spectroscopy, which led to the determination of the different species incoming on the substrate surface. TRIM calculations were performed to estimate the energy distribution of sputtered carbonated particles. Microstructural, mechanical and optical properties of the as-deposited films were determined using a combination of techniques such as Raman, infrared and optical spectroscopies and stress measurements. Combining in- and ex-situ informations allowed us to consider a growth model in which the terminal bond (CN triple bond) is the key parameter. The significant amount of CN triple bond agrees well with a porosity of the films. The reaction between the growing surface, the plasma ions and the incoming CNx particles, can be modified by altering the nature, the flow and the energy of the CNx sputtered species through the target selfbias. This leads to the modification of the incorporation of nitrogen inside the films (amount and bonding) and can explain the observed evolution of the physical properties of the films.

**G-IX.4** 15:10

SELF-ORGANIZED LAYERED STRUCTURE OF COPPER-CARBON COMPOSITE FILMS DEPOSITED BY PLASMA-ASSISTED TECHNIQUES UNDER LOW ENERGY ION BOMBARDMENT

F. Misjak, A. Kovacs, P.B. Barna, F. Thiery, Y. Pauleau and J.J. Grob

Copper-carbon composite films have been deposited on Si substrates. The microwave plasma-enhanced chemical vapor deposition process of carbon from Ar-CH4 mixtures containing 10, 30 and 50 % of CH4 was associated with the sputter deposition of copper from a Cu target. The energy of incident ions on the surface of films was about 10 eV and independent of the gas phase composition. The structure of the films was investigated by Rutherford backscattering spectroscopy (RBS), X-ray diffraction, high resolution and analytical transmission electron microscopy (TEM), and electron diffraction of cross sectional specimens. The C and Cu contents (20 and 80 at.%, respectively) in the films were found to be independent of the gas phase composition. The RBS data indicated a periodic change of the Cu and C concentrations along the film thickness, in particular in Cu-C films prepared with 30 and 50 % of CH4. The TEM analysis of films supported the existence of this structure. In all samples a continuous polycrystalline Cu layer formed on the substrate and was covered with a small grained Cu-C composite layer. For films deposited with 30 and 50 % of CH4, this Cu-C composite layer was followed by a second continuous polycrystalline Cu layer covered with a second Cu-C composite layer with higher grain size. The growth of these self-organised layered structures can be attributed to segregation phenomena of species (Cu or C) and the repeated formation of the phases of the segregated species.

**G-IX.5** 15:30

FORMATION OF Al-Al4C3 COMPOSITE STRUCTURES IN CO-DEPOSITED THIN FILMS

D. Biro, A, Kovács, F. Misják, P.B. Barna, Research Institute for Technical Physics and Materials Science of HAS, Thin Film Physics, P.O.Box 49, 1525 Budapest, Hungary

Formation mechanisms of composite structures in co-deposited Al-C thin films have been investigated. Experiments were carried out in an all metal vacuum system evacuated by turbo molecular pump. The 25 and 80 nm thick films were prepared at room temperature and 3500 C substrate temperatures on a-C films supported by electron microscopic microgrids. For cross sectional TEM investigations samples were deposited simultaneously on Si wafers covered by thermally grown SiO2. Al and C were sputtered by separate unbalanced magnetron sputter guns in argon atmosphere at 2,5 10-1Pa pressure. The structure of the films was investigated by XRD, in plane and cross sectional transmission electron microscopy and selected area electron diffraction. Metallic Al and intermetallic Al4C3 phases were identified in all samples. In samples deposited at room temperature the Al4C3 phase was amorphous or nanocrystalline, while in samples deposited at 3500 C it was large crystalline. The grain size of Al films deposited at room temperature decreased with increasing concentration of C indicating that the carbide phase formed a layer on the surface of growing Al crystals limiting both the crystal and the grain growth. A composite structure is formed at this temperature in which the carbide phase is situated at the grain boundaries. At 3500C the carbide phase formed well detectable individual crystals situated on the surface of the Al crystals. The density and size of carbide crystals increased with increasing concentration of C. The formation of these composite structures can be explained by the segregation of C species to the surface of growing Al crystals forming carbide layer or three dimensional carbide crystals.

**G-IX.6** 15:50

MODELING OF THERMALLY SPRAYED COATINGS ON LIGHT METAL SUBSTRATES – LAYER GROWTH AND RESIDUAL STRESS FORMATION

M. Escribano, R. Gadow, M. Wenzelburger, Institute for Manufacturing Technologies of Ceramic Components and Composites, University of Stuttgart, Allmandring 7b, 70569 Stuttgart, Germany

Automotive lightweight engineering is a key requirement for fuel saving and reduction of emissions. The substitution of cast iron engine blocks by light metal components yield significant weight savings. Protective coatings are essential for aluminium components to resist mechanical and tribological loads in engine applications. Layer composites can be manufactured by thermal spraying techniques.

Light metals and ceramic coating materials show a principal mismatch in their thermophysical and mechanical properties. Due to the complex heat and mass transfer processes which are characteristic for the thermal spray technique, this leads to the formation of residual stresses in the composite. Residual stress analysis is essential for the optimization of the manufacturing process and reliability of the components operating behaviour. Numerical finite element analysis (FEA) provides the facility to examine stress formation depending on temporary heat distribution in the component during the manufacturing process by means of real time simulation. A cylinder liner tube is modeled, and inside coating processes are simulated. To analyze the influence of heat transfer during manufacturing, different simultaneous cooling techniques were adopted to the model. Finally, the FEA results were validated by experimental measurements with the microhole drilling and milling method. This yields a deeper understanding and effective optimization of manufacturing processes.

16:10 **BREAK**

## Session X: Multilayer coatings
## Session chair: S. Orlando, C. Eisenmenger-Sittner

**G-X.1** 16:30 -Invited-

STRUCTURE AND PROPERTIES OF MULTICOMPONENT AND COMPOSITE LAYERS PRODUCED BY SURFACE TREATMENT METHODS

**Tadeusz Wierzchon**, Warsaw University of Technology, Faculty of Materials Science and Engineering,02-507 Warsaw, Woloska 141, Poland

A prospective line in the advances of surface engineering is the development of new methods for producing multicomponent and composite surface layers. These new methods, known as multiplex or hybrid, combine various surface treatment techniques and, thereby, permit fabricating new constructional and functional materials in which the microstructure, chemical composition, phase composition, and residual stress state of the surface layer can be controlled so as to modify, according to the current needs, the performance properties of these materials. It should be emphasised that the multiplex processes are not mere combinations of surface treatments, since they are expected to produce composite layers that form a multilayer system in which the advantageous properties of the individual layers, which could not be achieved in the substrate material or in the surface layer itself, are complementary to one another.

The paper presents, by way of example, two methods of duplex surface treatment intended to produce composite and multicomponent layers of the types: nitrided layer + Ti(N,C,O) formed on steels by a combination of glow discharge assisted nitriding and the PACVD process with the participation of a reactive atmosphere composed of Ti(OC3H7)4 vapours, and Al2O3+TiAl3+TiAl+Ti3Al formed on the Ti6Al2Cr2Mo titanium alloy using the PVD deposition of Al-coating and glow discharge assisted treatment. The paper also discusses the results of examinations of the structure, chemical composition, phase composition of the layers the results of the measurements of their properties, such as the resistance to corrosion and to frictional wear.

**G-X.2** 17:00

CHEMICAL VAPOUR DEPOSITION OF PyC-SixCy-SiC-Si3N4 MUL-TILAYER WITH GRADED C...SiC TRANSITION

E. Roos, K. Maile, K. Berreth, A. Lyutovich, University of Stuttgart, Stuttgart, Germany, R. Weiss, Schunk-Company, Giessen, Germany, T. Perova, A. Moore, University of Dublin, Trinity College, Dublin, Ireland

A multilayer protective coating of C/C-SiC composites was proposed and realised by Chemical Vapour Deposition (CVD). It consists of pyrocarbon for bonding and to smooth the substrate surface, then a controlled graded SixCy transition coating to the Si3N4 layer, that provides oxidation and corrosion protective properties. This complete layer stack is deposited in a single growth process in a horizontal "Cold Wall" reactor chamber with HF-heating under atmospheric and at low pressure. The pyrolytic carbon film is obtained by CH4 cracking in a hydrogen atmosphere at 1200°C. The graded SixCy and SiC coatings were deposited from CH4 and SiCl4/H2 mixtures by steering the CH4/SiCl4 ratio. Si3N4 is obtained by the reaction of SiCl4 with NH3. For the investigation of the layer microstructure and the chemical composition, optical microscopy, SEM, EDX, EPMA, ESCA, and micro-Raman spectroscopy are in use. The size of PyC crystallites ranges from 8 to 10 nm and is highly ordered. Cubic -SiC and some hex-agonal (4H-SiC and 6H -SiC) SixCy are formed in the transition layers. The investigation of sample cross-sections by line-scan e-probe and Ra-man spectroscopy shows the distribution of elements and their composi-tion according to the controlled deposition process. ESCA gives evidence of the interaction between Si and N and the formation of Si3N4.

**G-X.3** 17:20

NANOMETER-SCALE MULTILAYER COATINGS COMBINING A SOFT METALLIC PHASE AND A HARD NITRIDE PHASE

Y.Y. Tse, A. Michel, C. Tromas, D. Babonneau, G. Abadias, Laboratoire de Métallurgie Physique, UMR CNRS 6630, Université de Poitiers, BP 30179, 86962 Futuroscope-Chasseneuil, France

Metal/Nitride composite films, either in the form of biphase nano-composites or multilayers, have attracted considerable interest for their increased mechanical properties. The present study reports on the microstructure and mechanical properties of Me/TiN (Me=Cu or Ag) multilayers coatings, with bilayer period ranging between 2.5 and 50 nm, deposited on Si and MgO substrates by dual ion beam sputtering. Both high-angle X-ray diffraction (XRD), X-ray reflectivity combined with GISAXS measurements and Transmission Electron Microscopy (TEM) techniques were used to globally characterise the multilayers structure as well as the nature of the interfaces. For TiN/Cu, a cube-on-cube epitaxial growth is observed along the [001] growth direction, whereas a (001) preferred orientation is found in TiN/Ag, as confirmed by TEM. In both cases, low-angle XRD spectra exhibited a large number of superlattice reflections, while high-angle spectra do not revealed such features, indicating that although a good reproducibility is achieved along the growth direction with relatively sharp interfaces, the structural coherency length is rather small.

The effects of interface and bilayer thickness on hardness were investigated by depth-sensing nanoindentation. For TiN/Cu, the hardness is found to increase between 8 and 17 GPa, when the bilayer period decrease from 50 to 2.8 nm. The influence of the substrate (Si or MgO) on the measured hardness is discussed and the results compared with existing theoretical models for hardness enhancement.

**G-X.4** 17:40

STRESS AND TEXTURE EVOLUTION OF NI/AL AND RU/AL MULTI-FILM BY LASER INTERFERNCE IRRADIATION

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Due to the corresponding intermetallic compounds, Ni/Al and Ru/Al multi-layered thin film systems are important to protect the mechanical and chemical impact on the bulk component. The mechanical properties of these tough intermetallic compounds, NiAl and RuAl, can be further improved by combining with other stiff phases. Especially, if the surface composite can be made in such a way that the different phases are arranged periodically with a preferred orientation, micro-scaled period and reticulated phase interfaces, the mechanical properties would be optimised. Such optimised surface composites have been archived by laser interference irradiation.

In this study, the thin film systems with different thickness are produced by physical vapour deposition and subsequently irradiated by the interference pattern of two or more coherent laser beams. The microstructure and grain growth evolution of the Ni/Al and Ru/Al film systems during laser irradiation have been analysed. The stress and texture distribution after interference irradiation have been thoroughly investigated by high resolution x-ray diffraction. The corresponding hardness and plasma erosion resistance of the structured composite films have also been studied.

**G-X.5** 18:00

A MECHANICAL STUDY OF W2N/W SUPERLATTICES

L. Maillé, P. Aubert, C. Sant, P. Garnier, Université d'Evry Val d'Essonne, Laboratoire d'Etude des Milieux Nanométriques, Rue du Père Jarlan, 91025 Evry cedex, France

In this paper, the structure of W2N/W superlattices has been related to their mechanical properties. Symmetric period system with period thicknesses ranging from 2 nm to 80 nm of W2N/W have been studied. Samples have been grown on <100> silicon substrates by reactive RF-sputtering, with a pure tungsten target. Films are deposited using Argon (for W) and Argon/(10%)N2 gas mixture (for W2N) at a total pressure of 0,5 Pa. The structural study was investigated by X-Ray Diffraction. Period thickness, density and interfacial roughness were deduced from X-Ray Reflectometry patterns. W thin films are crystallized with nanosize grains and W2N layer are amorphous. W2N/W is so an amorphous/nanocrystalline multilayers system. Hardness and Young modulus have been measured by nanoindentation technique combined with Atomic Force Microscopy. The hardness of the symmetric superlattices is around 18 GPa +/- 2 GPa. This hardness is upper than W (13,7 GPa +/- 1,6 GPa) and W2N (14,3 GPa +/- 0,9 GPa) monolayers ones prepared under the same condition. First experimental results of asymmetric period are presented to determine the influence of W and W2N monolayer on the hardness.

**G-X.6** 18:20

STUDY OF THE STRUCTURAL AND OPTICAL PROPERTIES OF AlN / ZrN / AlN LOW-E COATING

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AlN / ZrN / AlN multilayers are deposited by magnetron sputtering onto borosilicate glass wafers. These kinds of multilayers has a great reflectivity in the IR range and a good transmission in the Visible range. The synthesised films are analysed in-situ by XPS (X-Ray Photoelectron Spectroscopy). XPS profiles are used to analysed the interfaces. We have observed the influence of the plasma parameters (total pressure, nitrogen partial pressure, target current, bias voltage,..) on the properties of the films (roughness, intermixing, resistivity, cristallinity,...). Then we have correlated these results with the properties of the coating (optical properties, adhesion, weathering,...). The negative bias voltage has a great influence on the roughness and resistivity of the ZrN layer. We have located an optimum value. The layers intermixing at the interfaces is strongly dependant on the sputtered atoms energy at the surface of the growing film. This energy is controlled by the target current, the total working pressure and the substrate bias voltage.

18:30-20:00 POSTER SESSION II

**G/PII.01** THICKNESS DISTRIBUTION OF GAS PHASE COATINGS IN CONFINED CHANNELS

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Process of coating deposition from a gaseous substance inside confined channels is scrutinised theoretically. The variation of coating thickness along channel axis was modelled in the form of a boundary-value problem for two regimes of gas flow: molecular and viscous ones. Invariant parameters of similarity were discovered for the channels of various geometrical types and sizes as well as various deposition conditions as a result of solving the boundary-value problem. Analytical expressions for some specific types of deposition reaction are derived describing the thickness distribution. Numerical solutions of the boundary-value problem for other reaction types are obtained and presented in a graphic form. The results of analysis allow predicting the coating thickness distribution and choosing appropriate deposition parameters to deposit the coatings of the required conformity. The results obtained are supposed to be applied to some real objects like filters, membranes, capillaries, separate pipes, gaps and others.

**G/PII.02** SURFACE MODIFICATION AND ALLOYING OF METALLIC MATERIALS WITH LOW-ENERGY HIGH-CURRENT ELECTRON BEAMS

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New methods for surface modification and alloying of metallic materials are described which are based on the irradiation of materials with a pulsed (2-3 mks)low-energy (10-40 keV), high-current (up to 50 kA, 1- 40 J/cm2) electron beam (LEHCEB). Based on study of the microstructure evolution and simulations of temperature fields, it has been shown that the pulsed melting induced by e-beam irradiation makes it possible to realize the liquid-phase dissolving of second-phase particles in the surface layer of thickness ~ 1 mkm, and the superfast (~10E9 K/s) quench-ing from liquid state results in the formation of nanosized and submicron nonequilibrium micro-structure, which gradually go to the matrix. These effects together with the surface cleaning and smoothing make it possible to improve the material properties such as the corrosion resistance of stainless steels (SS) and Ti alloys, the fatigue strength of Ti alloys, the wear resistance of cutting tools made of high-speed steels and hard alloys, and the electric strength of vacuum insulation. The characteristics of surface alloys formed by pulsed melting of some film-substrate systems (Al/Fe, Ti/Fe, etc.) are considered. These methods hold promise due to the considerable im-provement of the surface properties and the advantages of LEHCEB sources (reliability, high efficiency, low cost, nondangerous X-radiation levels)over pulsed lasers and high-power ion beam sources currently used for surface treatment of materials.

**G/PII.03** MICROSTRUCTURE OF SURFACE LAYERS OF AUSTENITIC STAINLESS STEELS IRRADIATED WITH LOW-ENERGY, HIGH-CURRENT ELECTRON BEAMS

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The surface morphology, chemical composition, and microstructure evolution occurring in the surface layer (up to 0.5 mkm) of austenitic stainless steels (304L and 316L) subjected to pulsed electron beam melting have been studied using OM, AES and TEM. Melting was induced by a low-energy (20-30 keV), high-current electron beam (2.5 mks, 2-10 J/cm2). The main reason for the crater formation is the local overheating followed by explosive ejection of material at the sites of localization of second phases. The seats of microcraters might be associated with low-melting-point submicron particles of FeS2. The intensity of cratering for plate stock samples is substantially lower than that for rod stock ones. Multiply repeated pulsed melting of SS 304L (plate) and 316L (rod) almost completely suppresses cratering and reduces the surface roughness compared to the original (upon cutting) surface condition. The surface smoothing is accompa-nied by removal of O, C, and N impurities from the near-surface layer (~ 50 nm). As a result of fast quenching from liquid state, in the near-surface layer of thickness ~ 0,5 mkm, single-phase (fcc) microstructure is formed with a grain size of 0.2-0.6 mkm, which is almost two orders of magnitude lower than that in the original state. The formation of single-phase homogeneous microstructure with a low density of impurities offers the possibility to considerably enhance the electric strength of vacuum insulation and the corrosion resistance of SS.

**G/PII.04** ELABORATION OF A FIRE RETARDANT COATING FOR POLYAMIDE-6 USING COLD PLASMA POLYMERIZATION OF A FLUORINATED ACRYLATE

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Perfluoroalkyl(meth)acrylates homo and coplymers are widely used for many applications, requiring hydrophobic properties, thermal and chemical stability.

In order to improve the flame retardancy properties of polyamide 6, the monomer 1,1,2,2 tetrahydrofluorodecylacrylate was graft-polymerized onto polyamide-6 samples using a low-pressure microwave plasma process. The chemical composition and the thermal stability of treated polyamide, were characterized by X-ray photoelectron spectroscopy and thermal gravimetry analysis respectively. The surface morphology was examined by scanning electron microscopy. The fire retardancy performances of polyamide-6 coated with fluorinated polyacrylate were evaluated using the cone calorimeter. The deposits are efficient fire retardant coatings. The rate of heat released for the coated PA-6 is decreased by 50% compared to virgin PA6.

**G/PII.05** PROTECTIVE COATINGS FOR Hg1-xCdxTe LAYERS

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The abstract deals with the problem of performing protective coatings for photonic layers and structures based on Hg1-xCdxTe (MCT). Anodic oxide coatings (AOC) were grown on the corresponding samples in order to obtain the structure AOC/MCT. The work investigates distribution of chemical elements on the depth of such semiconductor hetero-systems by method of electron Auger-spectroscopy. We have obtained Auger-spectra and profiles of Cd, Hg, Te, O, C element distribution in systems MCT/AOC studied from both sides in depth of 0.5-1.0mm of the sample surface; AOC have varied by the technological modes of the preparation. The similar studies were carried out after the etching processes realized by 5 keV Ar+-ion beam under Ar-pressure in vacuum chamber about 7×10-3Pa. The probe beam energy was estimated to be about 5 keV under the spot diameter 5-10mm. It is found that AOC layer with 70 nm thickness of a good quality is prepared with CdSO4-electrolite assistance.

**G/PII.06** THICK SILICA FILMS VIA SOL-GEL PROCESS IN THE PRESENT OF METHYLCELLULOSE

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Silica and silica-titania optical coatings made by the sol-gel technique are attractive for their potential use in integrated optics and are compatible with the silica-on-silicon technology. However, a major problem with the pure inorganic system is cracking in the heating process, which limits the thickness of the films. While interest continues in the conventional inorganic materials, hybrid organic/inorganic materials are currently being subjected to more intense development. Here we reported the fabrication of thick silica single layer via sol-gel process in the present of some prepolymerized organic compounds. SEM, AFM, TGA, DTA, UV-VIS, and FTIR studies were performed to investigate the composition and microstructure of the coatings. Relative dense, crack-free and transparent SiO2 films were achieved via spin deposition using a solution containing suitable amount of MC of average molecular weight of 63000. Cross-sectional scanning electron microscopy images of the films show the thickness of the films with different treatments, such as 3.2um for the film prepared by 5 times successive spin-coating, 1.8um for the film by single spin-coating and 0.93um for the single layer heated at 600°C. It is found that the organic components in the composite films tend to decomposition in the range of 200-600°C, and the water in the film is driven out with heat treatment higher than 800°C for 15 min due to the dense film structure.

**G/PII.07** COLUMNAR GRAIN GROWTH OF YTTRIA-STABILIZED-ZIRCONIA IN INDUCTIVELY COUPLED PLASMA SPRAYING

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YSZ was deposited by 7mm thick with inductively coupled plasma spraying (ICP) and a theory of nucleation and solidification of YSZ were introduced. The concentration was homogeneous within a particle, but different from particle to particle. The solute rejection by diffusion was occurred in a layer during solidification, but the interface condition of GqmGc led columnar grains to facilitate. The microstructure of the bottom part showed small equiaxed grains. In the middle part, large columnar grains, about 100㎛ thick and 300㎛ long, were developed through the layers with strong adhesion. Heat of droplets, latent heat of solidification, small pore array in the splat boundaries, and low thermal conductivity retard the heat transfer, and thus thick and long columnar grains could be facilitated. The long columnar grain growth through the layers was supposed to be possible, when the previously solidified surface of the deposit acts as seed.

**G/PII.08** STRUCTURE AND MECHANICAL PROPERTIES OF MAGNETRON SPUTTERED ZR-TI-CU-N FILMS

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The article presents a detailed analysis of the structure-hardness relations in Zr-Cu-N and Zr-Ti-Cu-N films with low and high Ti content. These films were sputter deposited using an dc unbalanced magnetron equipped with a composed target, i.e. a round plate of diameter 100 mm made of ZrCu (90/10 at.%) alloy with a Ti (99.5%) fixing ring. The use of the Ti fixing ring of two internal diameters (70 or 50 mm) makes it possible to prepare Zr-Ti-Cu-N films with different Ti content, approximately with 15 or 50 at.%, respectively. The properties of the Zr-Ti-Cu-N films were compared with those of Zr-Cu-N films reactively sputtered from the same magnetron but equipped with a ZrCu (90/10 at.%) target in a mixture of argon and nitrogen at a total pressure pT=pAr+pN2=0.7 Pa. It was found that (i) nanostructured Zr-Cu-N and Zr-Ti-Cu-N films can form superhard materials with hardness H greater than 40 GPa, (ii) there is a strong correlation between the structure and the hardness of the films, (iii) the films with a maximum hardness Hmax are composed of a mixture of grains of different crystallographic orientations and (iv) there is no correlation between Hmax of superhard films, their stoichiometry x=N/(Zr+Ti) and Ti content in the film.

**G/PII.09** THE EFFECT OF CRYSTAL STRUCTURE AND MORPHOLOGY ON THE OPTICAL PROPERTIES OF CrN FILMS

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Chromium Nitrides (CrN, Cr2N) are promising for protective coatings due to their exceptional mechanical properties and chemical stability. We study the microstructure of various CrxNy (1<x<2, y~1), coatings grown by unbalanced reactive magnetron sputtering (UBRMS), using X-Ray Diffraction (XRD) and X-Ray Reflectivity (XRR). The CrxNy coatings consist of various Cr-N phases, depending on the growth conditions. XRD has shown that a Cr adhesion layer below CrxNy eliminates the stress and promotes the growth of bigger grains. XRR determined the film density, which can be used also for the phase identification. We found that the UBRMS can produce single-phase CrN, Cr2N coatings with density, hardness and elastic modulus (measured by nanoidentation) equivalent to the corresponding single-crystals. The optical properties of the coatings were studied by Spectroscopic Ellipsometry (SE) from IR (0.1 eV) to ultraviolet-UV (6.5 eV) spectral region. Results for CrxNy for such a wide spectral range are presented for the first time. Our coatings exhibited the higher absolute values of the dielectric function in the literature, meaning that they are denser. Thus, combining the structural analysis and SE data we identified the single-phase (Cr, CrN, Cr2N) coatings and their optical properties and we established an optical data database for the Cr-N system. The variations of optical properties of CrxNy coatings with the microstructure have been evaluated from SE data using the combined Drude-Lorentz model, which provides the conduction electron density and the energy positions of interband transitions.

**G/PII.10** EFFECTS OF NON-DEPOSITING SPECIES DURING THE SPUTTER GROWTH OF BORON NITRIDE AND AMORPHOUS CARBON FILMS

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The so far studies of Boron Nitride (BN) and amorphous Carbon (a-C)growth have been focused to bulk processes like the subplantation and densification (SD) mechanisms, which are due the depositing energetic species. In the case of sputter deposition the incorporation of inert, non-depositing, energetic species have not gained much attention so far. We present a study of the effect of Ar+ irradiation during sputter growth of BN and a-C. Using characterization techniques with different sampling depth we managed to distinguish the surface and bulk properties of the films. We found that the BN and a-C growth are not identical. BN growth follows very well the SD model for ion energies below the threshold of Ar+ subplantation into BN. However, our analysis does not confirm the existence of an sp2 (h-BN) overlayer, as it is expected by SD, possibly due to the surface etching by non-penetrating, heavy Ar+ ions. The film stress follows the prediction of the SD model for films with stress higher than a threshold of 5 GPa. For ion energies higher than the threshold for Ar+ subplantation, the Ar+ penetrate into BN and disrupts the B-N bonds resulting to defective BN structures and enhancement of h-BN, but retaining high stress and promotes the stability of C impurities and the formation of C-N bonds. On the other hand, in a-C films sp3-bonded C is formed in a wider window of Ar+ ion energy (80-100 eV) due to the combination of the SD mechanism and surface activated sp3 formation.

**G/PII.11** THE CHEMICAL STRUCTURE OF CARBON NITRIDE FILMS FABRICATED BY PULSED PLASMA-ASSISTED CHEMICAL VAPOUR DEPOSITION

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Carbon nitride films have been grown by a novel CVD technique in which high power activation is achieved by glow discharge plasma generation with pulses of nanosecond lifetime in a modified excimer laser head. The effect of the N2/CH4 flow ratio (RT, total pressure: 300 Pa) and the substrate temperature (CH4: 13 sccm, N2: 39 sccm, total pressure: 300 Pa) on the chemical composition of the films is followed by XPS. At room temperature nitrogen incorporation is proportional to the nitrogen partial pressure with N/C values exceeding 0.4. Though the N content of the films steeply decreases with increasing substrate temperature, even those grown above 800C do contain a few at.%. The changes in the relative abundance of the individual spectral components of the C1s and N1s lines as a function of nitrogen partial pressure and substrate temperature are interpreted in terms of changes in the chemical environment of the nitrogen and carbon atoms. Comparison of the results of the XPS analysis with pieces of information on the microstructure and changes in local composition of the films derived from parallel SEM & X-ray microanalyses suggests that the films consist of a great variety of carbon microstructures of different shape and dimension sitting on a rather thin layer of higher nitrogen content.

**G/PII.12** KINETICS AND MECHANISMS OF THE SURFASE OXIDATION OF ALFA-Fe WITH PREVALING CUBICAL TEXTURE

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The objective of this work was to investigate the kinetics of the thin pro-tective oxide film growth on the surface of alfa-Fe with prevailing cubical texture at temperatures 643-773 K. It was determined that the initial stage of the kinetics is described by logarithmic function of the dependence of film thickness - time oxidation. A space-charge-limited growth model, based on the classical oxidation theory of Cabrera-Mott is introduced. We proposed that self deceleration of the film growth is caused by attenuation of the electric intensity because of the shielding influence of the space charge of the ionic and electronic species in the oxide plasma. The loga-rithmic law of the oxide film growth was derived. It was shown that the kinetics of oxidation is described by this law until the influence of electric field on the transport of ionic species predominate over their thermal mo-tion. The consequences of the introduced model corresponded to literature data. The results of the investigations were used in developing the surface oxi-dation technology of electric steel sheets.

**G/PII.13** SPUTTERED ZnO THIN FILMS: STRUCTURAL STUDY AND APPLICATION AS A PHOTOPROTECTIVE COATING ON POLYCARBONATE

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Thin films of zinc oxide (ZnO) were deposited on silicon substrates in a sputtering unit equipped with a radio-frequency generator (13.56 MHz) and using an Ar/O2 mixture as the sputtering gas.

The first part of this work was to study the structure and the composition of the samples by X-ray diffraction (XRD) and Rutherford Backscattering Spectroscopy (RBS) respectively. It was found that the deposits are polycrystalline with an hexagonal würtzite structure and have a crystallographic c-axis orientation perpendicular to the substrate surface. When the thickness of the thin films increases from 25 to 600 nm, the grain size and the density increase whereas the O/Zn ratio decreases. In the second part of this work, ZnO coatings were deposited on polycarbonate (PC) in order to protect this polymer against the solar ultraviolet (UV) radiations. Samples have been irradiated in artificial accelerated conditions with a polychromatic light ( > 300 nm) and photodegradation have been measured by infrared and UV-visible spectroscopies. ZnO coatings decrease the degradation rate and the photo-yellowing of PC. It was shown that the efficiency of the ceramic depends on the thickness and the structural properties of the coating. As a conclusion ZnO coatings can improve the long term behaviour of PC for outdoor applications.

**G/PII.14 oral presentation G-VIII.5**

**G/PII.15** CORRELATION BETWEEN THE STRUCTURE AND MICROSTRUCTURE WITH THE OPTICAL PROPERTIES OF M/TiO2 THIN FILMS

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M/TiO2 thin films (M : V and Si) with different compositions and microstructures have been prepared by Ion Beam Induced and plasma enhanced CVD. The evolution upon annealing of the structure and microstructure of these thin films has been followed by different techniques, including EXAFS to determine the local environment around the cations. The possible segregation of the constituent phases has been investigated by using different structural techniques including XRD, FT-IR, this latter employed to analyze the vibrational modes of the TiO2 structure. Depending on the annealing conditions and the metal cation M, different patterns of crystallization into anatase and rutile have been found. Optical properties of the films (absorption coefficient and refraction index, n) have been determined by transmission UV-vis absorption spectrossopy and by ellipsometry. A clear correlation has been found between the magnitude of the refraction index, the composition and microstructre of the samples. Changes in the absorption threshold edge on the segregation of the constitutent oxides has been also observed in V-TiO2 thin films. A direct correlation between the refraction index values and the Auger parameter of Ti and Si in the Si-TiO2 oxides determined by XPS and n permits to correlate microscopic and macroscopic properties of the films.

**G/PII.16** CHEMICAL AND THERMAL TREATMENT OF PEDOT-PSS THIN FILMS FOR USE IN ORGANIC LIGHT EMITTING DIODES

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To prevent organic light emitting diodes (OLEDs) from fast degradation caused by the electrode contact, a thin interfacial layer can be used between the anode (usually indium tin oxide or ITO) and the emitter. The performance of the devices will depend on the chemical stability, the optical transparency and the electrical properties of the interfacial film.

In this work, we have examined the behaviour of poly (3,4-ethylenedioxythiophene)-poly (styrenesulfonic acid) or PEDOT-PSS thin films using thermal and chemical treatments in order to optimise its use as an interfacial layer in OLEDs. Best results have been obtained by a combination of a thermal treatment and an acid treatment of the PEDOT-PSS film, resulting in a highly transparent and conducting layer, which can efficiently be used to increase the stability of the devices.

**G/PII.17** STRUCTURAL CHARACTERIZATION AND MECHANICAL PROPERTIES OF Ti-Zr-N COATINGS, DEPOSITED BY VACUUM ARC

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The multilayer (30-150 bilayer) system TiN/ZrN and triple nitride system Ti-Zr-N were formed by vacuum-arc deposition on carbon steel and silicon substrates. Obtained TiN/ZrN films consist of TiN and ZrN nitride layers with cubic structure and (111)-preferred orientation. For modulation period 20 nm superlattice peak were found. The residual stresses of multilayers are of a compressing type and their absolute value increase with decreasing the modulation period (to – 15 GPa). Nanohardness of multilayers TiN/ZrN increase (to 29 GPa) and modulus of elasticity decrease (291 GPa) with decreasing modulation period in compare with mononitride ZrN films (25 GPa and 349 GPa, correspondingly).

The Ti-Zr-N coatings were deposited at different bias voltage. The microstructure, composition and nanohardness were studied. XRD investigation shown that (Ti,Zr)N solid solution was formed. The (Ti,Zr)N grain are columnar as revealed in the SEM measurements. The residual stresses are mainly compressive and their values depend on bias voltage. The nanohardness of the (Ti,Zr)N coatings reached 40,5 GPa.

**G/PII.18** INTUMESCENT PAINTS: FIRE PROTECTIVE COATINGS FOR METALLICAL SUBSTRATES

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The protection of metallic materials against fire has become an important issue in the construction industry. Indeed, in case of fire such materials distort leading to the destruction of building structures and as a consequence to dramatic human and economical losses. Utilization of intumescent coatings is a way to achieve such protection.

Intumescent coatings form on heating an expanded multicellular layer, which acts as thermal barrier, retarding heat penetration to the substrate. Intumescent paints consist of intumescent additives linked together by a binder. In this study, the relationship between the polymer binder characteristics and the protective behaviour of intumescent coatings is investigated. Linear and crosslinked substituted styrene/acrylic copolymers are studied. The effect of the nature of the monomer on the chemical reactivity between the binder and the intumescent system is investigated. It is found that the thermal stability increases when the ratio of substituted styrene increased in the copolymer. Such observation has been explained elucidating the mechanism of degradation of the systems using solid-state NMR and FTIR analysis. Finally, the efficiency of thermal insulation of intumescent coatings prepared with these copolymers is evaluated. It is found that the thermal insulation is greatly improved when using a mixture of linear and crosslinked copolymers.

**G/PII.19** STRUCTURAL CHANGES IN Zr-Si-N FILMS VERSUS THEIR SILICON CONTENT

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Zr-Si-N films are deposited on silicon and steel substrates by DC magnetron sputtering of a Zr-Si composite target in Ar-N2 reactive mixtures. The silicon concentration in the films is adjusted by the variation of the number of Si chips located on the target erosion zone. The films are characterised by X-ray diffraction (XRD), electron probe microanalysis, Fourier transform infrared spectroscopy (FTIR), X-ray photoemission spectroscopy (XPS) and depth sensing indentation. At very low silicon content, no Si-N bond is observed by FTIR. Thus, silicon is probably present in the ZrN lattice as confirmed by the strong increase of the compressive stresses of the films. For an intermediate range of the silicon concentration, nanocomposite films are synthesised: ZrN grains oriented in the [200] direction are detected by XRD and an amorphous silicon nitride phase is evidenced by FTIR and XPS. The increase of the silicon content induces the amorphisation of the Zr-Si-N films. Finally, the Si content strongly influences the hardness of Zr-Si-N films ; values in the range from 20 to 45 GPa were measured.

**G/PII.20** STUDY OF NEW FLUORINE-CONTAINING EPOXY RESIN FOR LOW DIELECTRIC CONSTANT

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The fluorine-containing polymers which have good chemical resistance, water impermeability and low coefficient of friction, dielectric constant, become important in optical communication and microelectronics. In this work, the fluorine-containing epoxy resin, 2-diglycidylether of benzotrifluoride (DGEBTF) was prepared by reaction of 2-chlorobenzotrifluoride with glycerol diglycidylether in the presence of pyridine catalyst. As a result, the chemical structure of DGEBTF was confirmed by FT-IR, 13C NMR, and 19F NMR spectroscopy. The curing behaviors and dielectric constant of DGEBTF/DDM and DGEBA/DDM systems were investigated using dynamic DSC and dielectric spectrometer, respectively. The dielectric constant values of DGEBTF/DDM system were 15% lower than those of DGEBA/DDM system. Also, the glass transition temperature (Tg) and thermal stability factors of the cured specimens were investigated by dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA), respectively. For the evaluation of mechanical properties, the fracture toughness and impact tests were performed by using the casted specimens. The KIC and impact strength of the DGEBTF/DDM and DGEBA/DDM systems were 5.63 MPa×m1/2, 50 kN/m2 and 3.53 MPa×m1/2, 26 kN/m2, respectively. The introduction of trifluoromethyl (CF3) group into the chain of the epoxy resin, resulted in improving the dielectric and mechanical properties and lowered the Tg and thermal stability of the studied DGEBTF/DDM system.

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**G/PII.21** MATERIALS SURFACE MODIFICATION USING QUASI-STATIONARY PLASMA ACCELERATORS

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Broad opportunities for modification of microstructure and morphology of surface layers of various materials are opened up through the application of plasma flows generated by quasi-stationary plasma accelerators of a new generation. Parameters of such a plasma provide the rapid heating of surface and maintaining necessary temperature levels until completion of physico-chemical transformations. Exposure of a silicon wafer to a medium-power plasma flow results in the melting of a sample surface followed by modification of the material down to a depth of ~ 10 micrometers, and in creating of regular submicron structures. Their formation during fast crystallization phase of silicon molten layer occurs at high temperature gradients and in the presence of developed thermoelastic stresses and induced electromagnetic fields. Exposed to a high-power plasma flow were carbon steel details of large size and complex shape. According to results of investigations, three zones comprising a modified layer and differing essentially in structure (latent-acicular martensite zone, hardness 11 GPa, martensite and bainite zone, hardness 9 Gpa, and bainite ferrite zone, hardness 4 GPa), and transition zone (whose microhardness falls with depth from 3.5 GPa to that of basic metal) are formed in a surface layer.

**G/PII.22** EVOLUTION OF SURFACE MORPHOLOGY DURING ION NITRIDING OF ALUMINIUM

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Surface evolution plays an essential role in thin film deposition and surface modification processes. In general, a higher ion energy and a higher substrate temperature lead to surfaces with a reduced roughness and larger crystallite size, due to a higher particle mobility.

However, investigations of nitrogen implantation at elevated temperatures into Al show a completely different behaviour. A rather smooth surface was observed after 15 keV nitrogen implantation in Al below 250 °C. Whereas a significant increase of the surface roughness was found for the implantation at the same energy and higher substrate temperatures beyond 350 °C, which would indicate a negative activation energy for this material system. In the intermediate range, a surface roughness changing strongly from grain to grain was observed. A reduction of the ion energy to 1 keV did not change the observed results. No stringent theoretical explanation of the experiments can be presented at the moment. Albeit, it is hypothesised that the dominant process is the thermally activated aluminium diffusion towards the surface, starting at grain boundaries and defects, while being influenced by the surface sputtering of the incoming ions.

**G/PII.23** CHARACTERISATION OF PLASMA GENERATED IN VACUUM ARC WITH ZIRCONIUM CATHODE IN A REACTIVE GAS ATMOSPHERE

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The application of the cathodic arc plasma for the deposition of zirconium compounds has attracted considerable interest in recent years. The structure and properties of arc plasma deposited coatings strongly depend on chemical and physical process parameters i.e. cathode material, arc current, composition and pressure of working atmosphere. A meaningful and wide information about plasma state can provide optical emission spectroscopy as in-situ, non-intrusive analysis technique. We performed spectroscopic study on zirconium arc working in the N2 and N2+C2H2 atmospheres. For comparison, a pure zirconium vapour vacuum arc discharge was also investigated. A multi-source arc device constructed as industrial unit was used. Intensities of emission spectra of zirconium (Zr I, Zr II, Zr III, Zr IV), molecular nitrogen (N2, N2+) and CH radical have been recorded and investigated as a function of arc current and nitrogen pressure. Relative concentrations of atomic and molecular species (both neutral and ionized) have been measured under various experimental conditions. The excitation temperatures, ionization degrees and electron density have been determined from line intensities. The results are crucial for understanding possible mechanisms of plasma processes. The mechanisms of production, excitation and ionization of plasma species are discussed.

**G/PII.24** PULSED LASER ABLATION DEPOSITION (PLAD): A NEW DEPOSITION CONFIGURATION FOR THE SYNTHESIS OF THICK AND UNIFORM FILMS

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The roughening of the target surface during long laser irradiation of solid targets is responsible of the plume deflection effect and, hence, of displacements of films thickness distributions. The target roughening is also responsible of the emission of microscopic particulates. Several solutions have been suggested to reduce the target surface roughening such as the rotation and translation of the target and the laser beam scanning over a large-diameter rotating target. Nevertheless, the surface alteration is an intrinsic shortcoming of the PLAD technique and it is cannot be eliminated. Therefore, the conventional configuration (substrate parallel and frontal to the target surface) is not suited for the deposition of uniform films and less than ever of thick films, hence, new deposition geometries, termed off-axis configurations, have been suggested and reported in literature. These new configurations appear to be the best solution for obtaining films with acceptable thickness profile, but they suffer of very low deposition rate. In this complex scenario, we set up a new laser deposition configuration, termed dynamic off-axis configuration, for the preparation of uniform and thick films. In this new deposition configuration the substrate position is computer controlled and continuously follows the deflected plume axis. This deposition geometry was used to deposit films of Si and hydroxyapatite, which exhibited both high deposition rate and high thickness profile. The deposition rate obtained in the new approach was averagely three times higher than that measured in the conventional configuration. The thickness homogeneity in the two arrangements was also compared and discussed.

**G/PII.25** COMPOSITE STRUCTURES IN CO-DEPOSITED Al-Pt THIN FILMS

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The effect of the Al concentration in the condensing vapour beam on the simultaneously nucleating and growing phases was investigated. The films were deposited at 350 °C on a-C layer supported by electron microscopic microgrids. The Pt was evaporated from the e-beam source while the Al from the thermally heated tungsten wire source. A specific arrangement of the Al and Pt sources and substrate holder resulted in a variation of the Al concentration (0-65 at.%) in the condensing vapour beam within a 20 ?m wide substrate surface area. The thickness of the film was 30 nm. The samples were investigated by analytical and high resolution transmission electron microscopy and selected area electron diffraction in plan-view. The local composition of the samples was analysed by energy dispersive X-ray microanalysis (EDS). The sequence of coexisting phases was changing with the local concentration of Al in the vapour beam. Al3Pt2 and metallic Al was coexisting in the area of 65 at.% Al. With decreasing Al concentration the domains of composite structures of Al3Pt2, AlPt2 and metallic Pt with varying concentration followed each other. The formation of this composite phases can be interpreted by the considering the model for the nucleation and growth of binary alloy particles [1], by the process induced segregation of component's species not consumed by the growth of primary phases and by the delayed nucleation of secondary phases as well as by the competitive growth of coexisting phases.

[1] R.Anton et al, Phys. Rev.B, Vol.41 17 (1990) 11875

**G/PII.26** OPTICAL EMISSION DIAGNOSTICS OF CATHODIC ARC PLASMA USED FOR DEPOSITION OF TiN AND Ti(C,N) COATINGS

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The main advantages of the vacuum cathodic arc as a deposition technique lie in the properties of the arc plasma (high ionization degree and ion multiplicity, the moderate energy of ions). However, the fundamental plasma parameters and processes underlying the benefits have not been established so far and knowledge about arc spectroscopy is also unsatisfactory. This work is concerned with plasmas of the titanium vacuum arcs working in N2, C2H2 and mixtures of N2+C2H2 as ambient gases. An industrial device supplied with nine arc sources with directly cooled cathodes, high voltage systems of arc ignition and two electromagnetic systems allowing to localise cathode spots on the cathode working surface was used. The plasma has been investigated by emission spectroscopy methods. Concentrations of excited species, excitation temperatures (atoms, ions), ionisation degrees and electron density have been obtained from intensities of emission spectra recorded in the wide spectral range (200-800 nm). The plasma parameters are measured versus the arc current (from 60A to 100 A), the nitrogen pressure (0,002 mbar - 0,02 mbar) and the content of C2H2 in N2+C2H2 mixture (from 5% to 30%). Relations between the spectroscopy data determined here and their dependencies on discharge parameters have been shown. Possibilities of the application of the spectroscopic results for optimising the process of TiN and Ti(C,N) deposition are discussed.

**G/PII.27** a-SIC:H FILMS AS PERSPECTIVE WEAR-RESISTANT COATINGS

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Amorphous hydrogenated silicon carbide (a-SiC:H) films have been deposited from methyltrichlorosilane (MTCS) in a 40.56 MHz PECVD reactor with an additional bias at a substrate. The substrates were crystalline silicon wafers and cutting hard alloy tools. Substrate temperatures were varied in the range of 200-600 0C. The films were annealed at 450 and 600 0C for 1 h. The as-deposited films consist of about 60-70 at% Si, 20-30 at% C, up to 8 at% O and 0.8 % Cl. It was found that the increase of the MTCS flow rate and the substrate temperature promote the creation of the poly-crystalline coatings. The thickness of the coatings was about 0.3-0.5 mm. Film morphology investigations have shown that the coatings are homogeneous, and the substrate-coating zone points to the high adhesion of the coating to the substrate. From nano-indentation tests it follows that a-SiC:H coatings demonstrate the hardness up to 12 GPa and elastic modulus of 144 GPa. The annealed at 600 0C samples show the hardness, which is by 20% higher then the one of the as-deposited films. A preliminary tribological test have reveled that the wear-resistance of the tools covered by the annealed a-SiC:H coatings is four times higher that the one of the un-covered tools. So, despite the comparatively low hardness, the a-SiC:H films demonstrate good tribological properties, which make them suitable for applying as the low-cost wear-resistant coatings. The possible mechanisms describing the tribological properties of the a-SiC:H films are discussed. The further ways for improving the wear-resistant properties of the films are suggested.

**G/PII.28** TIGHT-BINDING MOLECULAR-DYNAMICS SIMULATIONS OF a-SiC:H

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The atomic and electronic distributions in a-SiC:H are studied using a sp3s* tight-binding force model with molecular dynamics simulations. Parameters of the repulsion pair-wise potential are determined from ab initio pseudo-potential calculations. Both un-hydrogenated and hydrogenated samples are generated from dilute vapors condensed at 1900 and 800 K, respectively. To improve the amorphous structure, a-SiC:H sample was annealed at 650 K. A plausible model of the inter-atomic interaction and electronic distribution in a-SiC:H is suggested. According to this model, hydrogen preferably surrounds the carbon atoms creating C-H and C-H2 bonds. The silicon atoms form only mono-hydride groups. H-H correlations point to clustering, especially in the annealed sample. The hydrogen bonds are shown in the electronic spectrum as sharp resonance peaks in both the valence and conduction bands. The resonance-peak distribution depends strongly on the surrounding of the atom that interacts with hydrogen. Hydrogen atoms passivate weak bonds provided the final tetrahedral configuration is formed. The computed characteristics are in rather good agreement with the available experimental data on a-SiC:H and with the results on a-SiC and a-Si:H from ab initio pseudo-potential calculations. However, in contrast to experiment, no an appreciable increase in hetero-nuclear bonds with hydrogenation was revealed.

**G/PII.29** oral presentation IX.4

**G/PII.30** Cancelled

**G/PII.31** BORON NITRIDE AND SILICON NITRIDE MULTILAYERED THIN FILMS DEPOSITED BY RF PLASMA REACTIVE PULSED LASER ABLATION

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Multilayered thin films of boron nitride and silicon nitride have been deposited by reactive pulsed laser ablation of boron and silicon targets in presence of a 13,56 MHz radio frequency (RF) nitrogen plasma. The gaseous species have been deposited at several substrate temperatures, using the on-axis configuration, on Si (100).

Thin films have been characterized by Scanning Electron Microscopy and X-Ray Diffraction. The influence of silicon nitride intermediate layer thickness on the growth of the BN surface layer has been investigated. The optimization of the multilayer adhesion and the thin film cristallization have been obtained varying convenientely the depostion parameters, in particular the substrate temperature and the nitrogen gas pressure.

**G/PII.32** USE OF AN AUGER PARAMETER FOR CHARACTERIZING THE Mg CHEMICAL STATE IN DIFFERENT MATERIALS

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Metallic, oxide and hydroxide environments of magnesium are clearly identified by X-ray Photoelectron Spectroscopy from chemical shift of Mg 1s and Mg 2p photopeaks. Unfortunately Mg3N2 cannot be distinguished from MgO through these two peaks. In this work, we give evidence that it is possible to unambiguously identified magnesium nitride from magnesion oxide thanks to Mg Auger parameter (a) defined as the difference between the kinetic energy of MgKLL Auger peak and the kinetic energy of Mg 1s photopeak. The value obtained for Mg3N2 (a = 1000.0 eV) is quite different from the one observed for MgO (a = 998.6 eV). Values obtained for metallic Mg and for Mg(OH)2 are respectively equal to 1004.2 and 997.5 eV.

This parameter is then used in order to characterize the modification of the Mg chemical environment in the Al-5083 aluminum alloy (containing 5 % Mg) nitrided by a Distributed Electron Cyclotron Resonance nitrogen plasma.

**G/PII.33** DLC FILMS ON LITAO3 FOR SAW DEVICES

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DLC films are a promising material for packaging of SAW devices because they inherit some very attractive properties of diamond such as high hardness, high Young modulus, good friction properties, chemical inertness and especially properties that are relevant for SAW devices : high sound velocity, low sound propagation loss, low density, low permittivity and high resistivity. However, some structural and chemical incompatibility of carbon based films to common oxides dictate the need for modifications of the interfacial layers and generally a SiC buffer layer is used to ensure a reasonable adhesion of soft DLC films on piezoelectric surfaces.

In this work, we study the modification of the piezoelectric surface after immersing in a methane plasma, the adhesion of DLC films without a buffer layer and the patterning of the DLC films needed for opening windows for deposition of other materials or metallization level access. Rutherford Backscattering Spectroscopy and Elastic Recoil Detection Analysis is used to determine the composition of the films , X-ray Photoelectron emission Spectroscopy allows the determination of the binding state of carbon on the LiTaO3 substrate. From nanoscratch tests we evaluate the adhesion by measuring the critical loads for first elastic cracking and first delamination. X-ray reflectometry is used to obtain electron density profiles and in particular it yields knowledge of the interfacial layer created during deposition (thickness, electron density, roughness).

**G/PII.34** SOLID LUBRICATION LAYERS PREPARED BY LASER EMBEDDING

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Laser embedding was investigated for production of solid lubrication layers on metallic surfaces including aluminium alloy and stainless steel. Composite of alumina and molybdenum disulfide was pre-deposited on the metallic surfaces using conventional flame spraying, and then treated using a CW CO2 laser under various laser power levels, beam sizes and traverse velocities. The microstructure of the laser-treated layers was characterized with scanning electron microscopy and energy dispersive X-ray spectroscopy. The tribological properties of the laser-embedded solid lubrication layers were measured employing a friction and wear tester. It was found that the homogenous laser-embedded solid lubrication layers reduced the friction and wear when compared with the original metallic surfaces. The relationships between the process parameters, microstructure and tribological properties of the laser-embedded layers were discussed.

**G/PII.35** DIAMOND NUCLEATION ON CHEMICALLY MODIFIED SILICON USING HFCVD

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Scratching and seeding are simple and effective pretreatment methods for the enhancement of diamond nucleation but these thechniques cause surface damage and cannot be easily applied to substrates of complex geometry and shape. We investigated the nucleation of diamond films grown on silicon substrates with different surface pretreatments: (i) by classical scratching with diamond powder and (ii) using adamantane derivate molecules as interlayer. After successful deposition of diamond (MPCVD) on a pretreated silicon substrate with divinyladamantane (DVA) molecules (1,2) we have tried to improve the homogeneous diamond nucleation in various pretreatment conditions of silicon (111) substrat. Low-pressure diamond growth was performed via HFCVD and an interferometric method was used for the in-situ observation of growth. Different method analysis: SEM, XRD, XPS and Raman were used to study nucleation and growth.

1. A. Giraud, T. Jenny, E. Leroy et al. Chemical nucleation for CVD diamond growth J. Am. Chem. Soc 123, 2271-2272
2. L. Giraud, V. Hubert, T. Jenny 2,2 Divinyladamantane: a new substrate for the modification of silicon surface Tetrahedron 54,11899-11906

**G/PII.36** THE INFLUENCE OF THE N2-H2 MIXTURE COMPOSITION ON THE SPECTROSCOPIC AND TEMPORAL BEHAVIOUR OF GLOW DISCHARGE CHARACTERISTICS IN PULSE-SUPPLIED NITRIDING PROCESSES

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The purpose of the research was to determine correlation between I-V characteristics of pulsed glow discharge (f=2 kHz, Δ=95%) and the temporal evolution of active elements concentration in the generated plasma. Experiments were carried out in an industrial arc-vacuum device adapted to execution of continuous "duplex" surface treatment processes. Investigated processes of plasma nitriding were executed at constant pressure (3 mbar) of N2-H2 atmosphere within wide range of N2 content (from 5% to 100%). Current and voltage of the discharge were automatically adjusted by the control system in such a way that the substrate temperature was kept constant at chosen value of 570oC, enabling, depending on the atmosphere composition, creation in the iron substrates nitrided layers of different structures: from single-phase layer, containing diffusion zone a-Fe(N) only, to three-phase one containing both diffusion zone a-Fe(N) and two-layer compound zone e+g'. Optical emission spectra of generated plasma as well as temporal courses of selected emitters intensities (N2(C), N2+(B), Hα) were recorded in the vicinity of the substrate. On the basis of the obtained results the correlation between power supply parameters, gas composition and temporal evolution of the relative concentrations of the selected active species was determined. It was shown that the kinetics of the investigated emitter is strongly controlled by electrons. Results of spectral investigations were also correlated with the composition of nitrided layers created in the substrates made of steel DIN-1.2367.

**G/PII.37** DEPOSITION OF BORON NITRIDE BY PVD METHODS: TRANSITION FROM h-BN to c-BN

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A cross section TEM image of a cubic boron nitride film reveals the well-known layered structure: amorphous BN, textured turbostratic BN with c-axis parallel to substrate, textured nanocrystalline (111) c-BN planes and turbostratic BN upper layer. The thickness of the sp2 layer depends on deposition conditions and in the case of IBAD techniques lies between 10 and 30 nm. A lack of knowledge about this turbostratic BN layer with c-axis parallel to substrate is mainly due to its small thickens and to the fact that it is buried layer. Nevertheless, we consider that it is possible to obtain films with the same features using deposition conditions as close as possible to those for h-BN to c-BN transition. Pure hBN films with thickness up to 200 nm were deposited and analysed using stress, density and HRTEM measurements. These sp2 films have compressive stress up to 10 GPa, density up to 3.2 g/cm3 and a rhombohedral structure.

**G/PII.38** A COMPARATIVE XAS AND XPS STUDY OF PULSED LASER DEPOSITED CNx FILMS

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We present a comparative XAS and XPS study on CNx films prepared by pulsed laser deposition (PLD) at room temperature. The C1s and N1s core levels as well as the C and N K edges display many contributions which give valuable information on the true nature of the carbon-carbon and carbon-nitrogen bonds. The combined use of these two probes reveal to be be powerful to elucidate the nature of bonds in CNx materials. We therefore develop a procedure from the analysis of the individual lines of the C1s and N1s core levels, and the C and N K edges, respectively, with the use of either literature or experimental references. We therefore propose an assignment of these lines that involve a clear separation of the pyridinic, pyrrolic and nitrile contributions in nitrogen. This interpretation is tested on CNx films when changing the most important parameters of the PLD process (laser fluence, nitrogen pressure, target-to-substrate distance).

**G/PII.39** PHOTOPROTECTION OF POLY(ETHYLENE-NAPHTHALATE) BY ZINC OXIDE COATING

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Zinc oxide coatings were deposited on poly(ethylene-naphthalate) (PEN) film by r.f cathodic magnetron sputtering. The peeling test showed a good adhesion of the assembly for optimised conditions (total pressure, partial pressure of oxygen, power).

The barrier properties of the coating were investigated by measuring the gas diffusion through the assembly. The diffusion of oxygen, carbon dioxide and nitrogen is greatly lowered by ZnO coatings. The photo-protective properties of zinc oxide coatings (200 nm thick) deposited in various conditions on PEN films (25 µm thick) were studied. Assemblies were irradiated in artificial conditions (wavelength > 300 nm) corresponding to a medium acceleration of the outdoor ageing. Photodegradation was followed using infrared and UV-visible spectroscopies. The rate of photooxidation of PEN was measured in the region of hydroxylated photoproducts (3800-3000 cm-1) which corresponds to the vibration domain of alcohols, hydroperoxides and carboxylic acids groups. The extent of photo-yellowing was determined by measuring the increase of absorbance at 400 nm. Results indicate that the photodegradation of PEN films is strongly decreased by the presence of ZnO coatings. Best results are obtained when deposits occur at high power, weak partial pressure of oxygen and low total pressure.

**G/PII.40** THE ELECTROLESS DEPOSITION OF NICKEL ON SIC PARTICLES FOR ALUMINUM MATRIX COMPOSITES

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Nickel coatings have been deposited by electroless method on SiC powder particles. Three different SiC powder grades, in terms of average particle size, were chosen, i.e. 8, 14 and 70 µm. The coating process was performed in few steps consisting of the SiC powder cleaning by acetone, its sensitization by HCl aqueous solution containing Sn++, followed by its activation by HCl aqueous solution containing Pd++, and finally- hydrometallurgical nickel deposition using aqueous solution containing Ni++, as a nickel carrier. The influence of the deposition conditions on the coating layer properties was studied. The thickness, morphology and microstructure of the layers were controlled by the growth conditions. SEM and digital image analyzing techniques were used for those purposes. Since the Ni-coated SiC powders were produced as a reinforcement for Al matrix composites, their compatibility as compared with the uncoated SiC powders was also controlled by metallography.

**G/PII.41** STRUCTURAL AND MECHANICAL PROPERTIES OF SPUTTERED CUBIC AND HEXAGONAL NbNx THIN FILMS

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NbNx films with 0.61≤ x ≤ 1.06 were prepared by reactive magnetron sputtering of a Nb metal target in an Ar/N2 atmosphere at a total pressure of 0.4 Pa. Different nitrogen partial pressures PN2 and substrate temperatures Ts were used. The films were characterized by x-ray diffraction, electron probe microanalysis, scanning electron microscopy and nano-indentation measurements.

The films deposited without substrate heating contain a pure cubic phase for 0.61≤ x ≤0.96 (3%≤ PN2 ≤11%) while, for 0.98≤ x ≤1.06 (13%≤ PN2 ≤21%), they include a mixture of the hexagonal ε-NbN and cubic δ-NbN phases. The average grain size, determined by X-ray diffraction in the Bragg Brentano geometry, increases from 3 nm to 15 nm as x increases from 0.61 to 0.96. With larger x ratio, it sharply decreases with the appearance of the second phase. The hardness values correlate with the grain size variation. Compact poorly crystallized films exhibit high hardness values of about 32 GPa. The increase in Ts for films prepared at PN2 = 15% leads to the decrease of x and enhances the film density. The deposited films contain mixed phase (ε-NbN and δ-NbN). Film deposited at Ts = 400°C exhibit a hardness of 33 GPa and a Young modulus of 370 GPa. The deposition of films at various PN2 and Ts = 400°C leads to the formation of a pure hexagonal phase for 0.97≤ x ≤1.00 (21%≤ PN2 ≤30%) whereas mixed phases (ε-NbN and δ-NbN) are obtained for 1.00≤ x ≤1.06 (33%≤ PN2 ≤40%).

**G/PII.42** GRAIN STRUCTURE OF SPUTTER-DEPOSITED TUNGSTEN CARBIDE THIN FILMS

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The structure of tungsten-carbon thin films, deposited onto monocrystalline silicon substrates by reactive magnetron sputtering (argon + benzene) in a wide range of preparation parameters has been investigated by GISAXS. Substrates were in a fixed position relative to the two adjacent cylindrical magnetrons. Benzene partial pressure was varied from 1% to 10% of the total working gas pressure. A series of samples were prepared, with the substrate temperature held at RT, 200°C, and 400°C, and the substrate potential held at floating potential or biased -70 V with respect to discharge plasma.

The bulk particle contribution to the scattering was investigated outside of the specular plane, applying two dimensional CCD detector. For the higher values of the benzene partial pressure, the generated films consist of densely packed tungsten carbide grains with an amorphous, carbon rich matrix in between, while the lower benzene pressure in some cases resulted in isolated carbon rich particles buried in tungsten carbide. Since it is known from earlier measurements that all the preparation parameters also influence the film chemical composition, relatively complex dependence of particle sizes on the benzene partial pressure can be explained as a function of the relative carbon content.

**G/PII.43** KINETIC OF TANTALUM CARBIDES FORMATION BY VACUUM ANNEALING OF THIN TANTALUM LAYER ON STEEL SUBSTRATES

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Tantalum carbides present some attracting physical and mechanical properties as high melting point, extreme hardness, low coefficient of friction, chemical inertness, oxidation resistance, and good electrical conductivity. These properties make them an ideal candidate for many industrial applications like wear resistant coatings, cutting and drilling tools. In the present work we are intending to elaborate and to study thin film coating of tantalum carbides on steel substrates. The procedure used in order to prepare the samples consist on depositing, by electron gun evaporation, a thin film ( 4µm thickness) of tantalum on steel substrates containing 1 %wt. of carbon, then, annealing the system (substrate/coating) in vacuum at a temperature at which the carbon of the substrate may diffuse into the Ta metallic film. This fact leads to the formation of tantalum carbides. The effects of the annealing on the kinetic of tantalum carbides formation and morphology have been investigated using X- ray diffraction (XRD), secondary ion mass spectroscopy (SIMS) and scanning electron microscopy (SEM). It is found that at annealing up to 800°C the compounds Ta2C and TaC are formed. During the subsequent heat treatement from 900°C to 1100°C the final TaC phase grows at the expense of the Ta2C phase. The final coating layer has a golden color and presents a columnar structure. The formation mechanisms are discussed.

**G/PII.44** MOLECULAR MODELLING OF INTERFACE OCCURRENCE OF Ti(C,N,O) - Fe COMPOSITE

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High demands that are posed to modern materials exposed to the action of thermal, mechanical or chemical loads oblige one to seek new solutions and technologies. Compliance with these expectations requires designing the composite materials without structural notches, and the application of gradient materials. Transient zone, determining the interphase compound, is an essential element of each composite. Interaction forces creating transient structural zones determine value of the adhesion forces. Among all forces determining the adhesion the strongest are the forces of a chemical bond. Therefore, the molecular modelling should be a valuable method to investigate and design the composites.

In presented research the conditions of coat adhesion of the Ti (C,N,O)-type to steel substrate are taken into consideration. Using standard quantum-chemistry program, the energies of the following systems (clusters) - Fe-?-N-Ti, Fe-?-C-Ti and Fe-?-O-Ti - are calculated. The aim of the analysis was to determine the conditions for preparation of initial substrate, which are advantageous for the process of coat formation. This analysis confirmed benefits arising from nitriding as initial treatment of the steel. The results obtained do agree with experimental results. The Ti(C,N,O) - nitrided steel composite research results which where done in sol-gel method were presented.

**G/PII.45** Er-YLF COATING OF Si-BASED SUBSTRATES BY PULSED LASER DEPOSITION

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Recently, thin films of materials with specific optical properties have attracted large interest for their possible use in optoelectronics and photonics devices. Within this frame, rare earth doped fluorides play a special role due to their marked nonlinear effects. Physical techniques able to efficiently coat substrates with thin fluoride films are often cumbersome, due to the high sensitivity of the material properties on its stoichiometry and structure. We have used pulsed laser ablation in ultra-high vacuum to deposit Er-doped fluorides onto Si-based substrates. The bulk material used during the ablation process was a YLF crystal doped with 30% Er. It was grown with Czochraski technique from high purity materials. In-situ diagnostics of the laser ablation, accomplished by plume optical emission spectroscopy, showed the occurrence of an efficient and clean fragmentation of the target into elemental species, expected to favor the realization of films with the required properties. The deposited samples have been analyzed by using different techniques. In particular, their optical emission has been investigated under UV and NIR excitation, revealing promising features in view of their exploitation in the area of photonics.

**G/PII.46** BORON NITRIDE THIN FILMS DEPOSITED BY RF PLASMA REACTIVE PULSED LASER ABLATION AS INTERLAYER BETWEEN WC-Co HARD METALS AND CVD DIAMOND FILMS

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Thin films of boron nitride have been obtained by reactive pulsed laser ablation of a boron target in the presence of a 13,56 MHz radio frequency (RF) nitrogen plasma. The films have been deposited at several substrate temperatures, using the on-axis configuration, on WC-Co cutting tools, after Co removal by chemical etching (HF/HNO3). Diamond polycrystalline films of increasing thickness have been deposited by HF-CVD at different methane percentages.

Cross sections of the coated samples have been characterized by Scanning Electron Microscopy, and the stress values of these structures have been studied by Raman spectroscopy. The boron nitride thin film crystallisation and the adhesion optimisation of the whole structure to the substrate have been obtained by varying the deposition parameters, such as the substrate temperature and the nitrogen gas pressure.

**G/PII.47** INFLUENCE OF X-RAY ILLUMINATION ON THIN METAL CARBON FILMS

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Thin Metal - Carbon multi-layers were deposited on silicon substrates using pulse-laser deposition [1]. X-ray reflectivity measurements up to 0.9Å-1 were performed in order to determine structural properties of those samples. Series of reflectivity measurements executed on the same sample showed a permanent of layer parameters. To study this behaviour in more detail, reflectivity measurements were executed in-situ and ex-situ taking the sample under non-ambient conditions.

Traditional layered-structure model based calculations did not lead to satisfying agreement between measurement and simulation. The so-called inverse method applied on this investigation solved the analytical problem. The matching electron-density profiles (EPD) were obtained by analysing the height-height correlation function [2] and applying an inversion algorithm [3]. The measurements, the inversion algorithm, the resulting EPS's and their unambiguousness will be discussed.

[1] - R. Dietsch et al., Appl. Surf. Sci.: in press, 7993 (2002)
[2] - C.-J. Yu et al, Phys. Rev. Lett.: 82, 2326 (1999)
[3] - K. M. Zimmermann et al., Phys. Rev. B: 62, 10377 (2000)

**G/PII.48** REAL-TIME SENSING OF STOICHIOMETRY AND MONITORING OF SILICON OXIDE DEPOSITION PROCESSES

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Multi-Wavelength Ellipsometry in Vis-far UV energy range has been applied for the study and control of the stoichiometry (x) and optical properties of SiOx films, grown on c-Si substrates by electron-beam evaporation technique, using different source materials (SiO2, SiO or SiOx). The ellipsometric data collected in real-time correspond to 32 different wavelengths covering the range from 1.5 up to 6.5 eV, and are fitted by applying the Tauc-Lorentz model. The calculated optical parameters such as Penn Gap w0, the fundamental band gap wg, as well as the e¥ and the constant value of refractive index are directly correlated to x values (given by ex-situ X-ray Photoelectron studies), but also with the films' quality (e.g., microvoid content). More specifically, the w0 values exhibit a linear relationship to x values, whereas the n values exhibit a more complicated one due to the fact that these are influenced by both stoichiometry and microvoid content or composition. In addition, the close monitoring of the deposition processes with a sampling time as low as 100 ms, provides the ability to study the growth mechanisms which are discussed in terms of the source material and the predominant precursors during deposition. Therefore this methodology reveals the potential for real-time control of SiOx films' growth of desirable stoichiometry or a functionally graded one, meeting specific demands for microelectronics or other industrial applications.

**G/PII.49** NOVEL POLYMER BASED CONVERSION COATINGS FOR THE INHIBITION OF THE CORROSION OF ALUMINIUM ALLOYS

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Aluminium is a reactive metal that owes its corrosion resistance to a thin, protective oxide surface layer, which is generally stable in air and aqueous solutions. Although Aluminium Oxide is generally protective, pores and other defects caused from alloying elements can lead to localised corrosion. This type of corrosion is characterised by the formation of pits. The great importance of this metal in our world, makes the need to protect it against corrosion greater. Methods of low cost and non-toxic substances are still in researching process.

Recently our laboratory developed a novel polypyrrole based coating, which can be formed on the aluminum surface from an aqueous pyrrole solution of Fluorozirconic Acid neutralized with Zinc Oxide. The composite layer is consisted from Polypyrrole (Ppy) chemisorbed on Titanium and Zinc Oxides and exhibits advanced corrosion resistance. For the investigation of the structure and the corrosion mechanism of the composite corrosion resistant layer we use a Photo-Electron Emission Microscope (PEEM). PEEM is especially suitable because it can deliver topographic contrast as well as elemental contrast and chemical information in connection with a variable X-ray source. The structure of the corrosion resistant layer was investigated before and after accelerated corrosion tests. Our results pointed out the important role of Titanium Oxide and Zinc on the corrosion resistance of our Ppy conversion coating on Aluminium.

**G/PII.50** NANOMECHANICAL PROPERTIES OF ELECTRON BEAM EVAPORATED SILICON OXIDE THIN FILMS ON POLYMERIC SUBSTRATES

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Thin films of silicon oxide (SiOx) have outstanding properties for the protection of metals and polymers and they are widely used as SiO2 in microelectronics, optoelectronics and optics. SiOx films offer several advantages: they are transparent and chemically inert, absorb UV radiation, and have sufficient mechanical properties to protect polymeric substrates. Silicon oxide films on polymers are extensively investigated for application in semiconductor technology, food and pharmaceutical packaging industries, and more recently in encapsulation of organic-based displays. Furthermore, thin SiOx films onto polymeric substrates can replace many plastic-packaging multilayers (~10 μm), for its simplicity and reduced environmental concerns. The microstructure and optical properties of such films have been studied, but their nanomechanical behavior on polymeric substrates has been much less investigated. The present work reports on the nanomechanical properties of SiOx films, 50 - 150 nm thick, (with x between 1.5 and 1.8) deposited by Electron Beam Evaporation onto poly(ethylene terephthalate) (PET) membranes. The nanomechanical properties of both SiOx films and PET were examined in light of depth-sensing nanoindentation experiments, under conditions of maximum contact load in the range of 0.5-12 mΝ. The continuous stiffness measurement technique was used to monitor the hardness (H) and the elastic modulus (E) as a function of the penetration depth. The SiOx/PET system exhibit a hardness of 3 GPa, increased by a factor of 9 compared to the PET hardness, while the elastic modulus was found to increase by a factor of 5 and provide sufficient adhesion to the PET substrate. The H and E are compared with the barrier properties for oxygen and water of the SiOx/PET system.

**G/PII.51** COMPARISON OF THE NANOMECHANICAL AND NANOSCRATCH PERFORMANCE OF ANTISCRATCH LAYERS ON ORGANIC LENSES

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The combination of transparency, toughness and light weight makes polycarbonate (PC) very attractive for eyewear applications. However, PCs are easily scratched in the normal use environment because of their softness. Antiscratch layers, based on PC, can significantly alter surface sensitive properties of polymers, including hardness and scratch/wear resistance. In this work the nanomechanical and nanoscratching performance of three commercial available antiscratch layers are compared, as protective overcoatings of organic lenses. Their protective character is defined in terms of their wear resistance and sufficient hardness. The nano-scratch behavior of the antiscratch layers is investigated using a Nano Indenter XP system with a lateral force measuring attachment. The hardness (H) and elastic modulus (E) of the layers were determined using the continuous stiffness measurements (CSM) technique, under conditions of maximum contact load in the range of 0.05 mN. Low load (6 mN) scratch tests were used to evaluate the scratch resistance and the friction coefficient of the antiscratch layers. We focused on the adhesion and deformation response of the layers to compare their nanoscratch behavior. The scratch process revealed a fully elastic recovery/deformation of the antiscratch layers. Testing under a normal load of 6 mN resulted in slight grooving at the layer surface; however, in-situ profiling of the scratch trace showed no evidence of failure. The coefficient of friction (ì) was found in the range 0.1 – 0.3, and in the case of the harder layer was found to decrease with the normal load applied. The nanoscratch results are compared with abrasion tests performed using sandpapers and abrasive materials of various particle sizes that are typically used in the industry to evaluate the mechanical performance of the antiscratch layers of organic lenses.

**G/PII.52** MICROSTRUCTURAL CHARACTERIZATION OF CNx-TiN/Ti GRADIENT-MULTILAYERED COATINGS

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A good mechanical performance of CNx-based hard coatings grown onto steel components requires an optimal adhesion to the substrates. In the present work, the CNx films have been joined to the AISI M2 steel substrates through a TiN/Ti functionally gradient underlayer. Three types of CNx-TiN/Ti graded systems were deposited by means of magnetron sputtering technique in different growing conditions and the adhesion properties were evaluated by scratch-tests. Chemical and structural characterization at the nanoscale for these systems were carried out by grazing incidence x-ray diffraction (GIXRD), transmission electron microscopy (TEM), energy dispersive x-ray analysis (EDAX), energy filtered TEM (EFTEM), and electron energy loss spectroscopy (EELS). This complete microcharacterization of the multilayered CNx-TiN/Ti systems coupled with the observed adhesion properties has allowed to identify relationships between the deposition conditions and the material chemistry and structure, in order to reach the desired coating performance. A gradual enrichment in nitrogen and nitride phases was detected from the metallic substrate to the CNx top layer affording higher critical load for delamination.

**G/PII.53** AL, GA, IN-DOPED ZINC OXIDE THIN FILMS BY SOL-GEL METHOD

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Transparent and conductive high preferential c-axis oriented ZnO thin films doped with Al, Ga or In have been prepared by sol-gel method using aluminium, gallium or indium salts as cation source, 2-methoxiethanol as solvent and monoethanolamine as sol stabilize. Film deposition was performed by dip-coating technique at a withdrawal rate of 1,5 cm min-1 on Corning 1737 glass substrate.

The influence of doping element, heating treatment and annealing in reducing atmosphere on the microstructure as well as on the electrical and optical properties of the thin films is discussed.

**G/PII.54** CORRELATION BETWEEN MECHANICAL AND ELECTRICAL PROPERTIES OF SILICON OXIDE DEPOSITED BY PECVD-TEOS AT LOW TEMPERATURE

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The PECVD/TEOS process can control the physical properties of the silicon oxide films. It is known that good electrical characteristics are obtained using a high ion bombardment during the deposition process, which results in denser films. The ion bombardment avoids the incorporation of undesired TEOS subproducts during deposition process. At the early stages of deposition process, when the oxide-substrate interface is being formed, an effective ion bombardment is needed to decrease its exposition to TEOS vapor or sub-products and/or remove its from the surface. However, if the ion bombardment is too high, the substrate surface is excessively exposed to the plasma, increasing the interface roughness.

In this work, we show the results obtained to the deposited silicon oxide under different ion bombardment conditions. For TEOS dilutions in oxygen in the range from 0.2 to 3%, a similar oxide stoichiometry and vibrational spectra were obtained for all samples. These results could not explain the observed differences in stress and electrical measurements. Higher stressed samples could be associated with less trapped charges inside the film and with higher electric breakdown strengths. Samples made under similar conditions exhibited different electrical behaviors depending to the treatment of interface by plasma. From all results, it was possible to identify the contribution of the interface and film in the improvement of the oxide film electrical properties.

**G/PII.55** MORPHOLOGY AND TEXTURE OF BN THIN LAYERS DEPOSITED USING ArF AND KrF EXCIMER LASERS

Waldemar Mroz, Miroslaw Jelinek, Boguslaw Major and Artur Prokopiuk, Tomas Kocourek, Jan Bonarski, Military Universitu of Technology, Institute of Optoelectronic, 2 Kaliskiego St., 00-908 Warsaw, Poland

Excimers of ArF and KrF types were used for ablation of h-BN and deposition on Ti substrates heated up to the 700 oC. The films deposited were subjected to X-ray diffraction (XRD), atomic force microscope (AFM), scanning electron microscope (SEM) and transmission electron microscope (TEM) examinations and microstructure, texture and residual stresses of the macro and micro types were under examinations. Contribution of deposition parameters to the a-BN, h-BN and c-BN formation was studied. Possible mechanism of solidification from plasma was discussed on the basis of the surface topography observed on AFM patterns. Texture on the pole figures and the orientation distribution function (ODF) for the deposited films and substrates used was discussed in the way of preferred orientation and for possible contribution of crystallographic orientation of substrates to the texture developed in deposited films. The film foils obtained from the cross-section of the deposited layers were studied in respect to the interface between the film and substrates, which was related to adhesion. Residual stresses of the macro type on the basis of the diffraction line sifting and micro stresses and crystallites sizes on the basis of the diffraction line broadening were under discussion.

**G/PII.56** THE AFM INVESTIGATIONS OF LASER DEPOSITED FeAL FILMS ON Cu AND CRYSTALLINE Si SUBSTRATES

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Intermetallic coatings were produced by ablation of the FeAl alloys using a KrF laser (lambda = 0.248 um, t ~ 20ns). The laser fluence was changed from 4 J/cm2 to 12 J/cm2, the substrate temperatures from 200C to 7000C.

To study the surface topography and morphology of FeAl layers deposited on Si and Cu substrates an atomic force microscopy operating in the tapping mode was used. The AFM investigations have shown that the homogeneity, shape and size of grains were dependent on substrate temperature and ion's energy moreover the kind of substrate (Cu or Si) determine the type of layer nucleation. The measurements have shown that in high substrate's temperature and high energy density conditions, process of growth FeAl layer on Cu substrate was similar to proposed in the 3D model (a large number of islands composed from small clusters) whereas layers deposited on Si substrates have grown rather in the Stranski-Krastanow mode (terraces of FeAL with separated islands on they). In case of high energy density and room temperature - the film is not homogenous and there are different zones on sample surface. The results of measurements of films' growth under other: energy density and temperature condition will be also discussed.the basis of the diffraction line broadening were under discussion.

**G/PII.57** SYNTHESIS AND CHARACTERISATION OF A NEW INORGANIC-ORGANIC POLYURETHANE TYPE COMPOSITE MATERIAL BY SOL-GEL PROCESSING

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An inorganic-organic composite material was synthesized by using a blocked isocyanatotrialkoxysilane. The blocking permitted the hydrolysis and condensation of the alkoxysilane without affecting the isocyanato grouping. After finishing the inorganic condensation reaction, the isocyanato grouping was thermally deblocked and reacted with 1,5-pentandiole. The reactions were characterized by FT-IR and 13C-NMR-spectroscopy. The system was used for the fabrication of thermally cured coatings. The composite coatings showed remarkably enhanced abrasion resistance compared to the pure PU system.

**G/PII.58** CARBON MATERIAL DEPOSITION BY REMOTE RF PLASMA BEAM

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Carbon based thin films and structures are largely used in various fields and open opportunities for development of new applications in microelectronics, optics, nanotechnology. A large variety of deposition techniques were reported aiming to obtain films or micro and nanostructures with well defined characteristics. Even in the frame of the same technique the material properties can change drastically with the experimental conditions. We have investigated the dependence of material morphology and composition upon the experimental conditions in the case of a remote plasma beam RF deposition system. Hydrogenated and nitrogenated films were obtained by PECVD with carbon species supplied by acetylene gas injected into an Ar or Ar/N2 plasma stream, respectively. Also, nitrogenated films were deposited while carbon species supplied by graphite surfaces in contact with nitrogen containing discharge. The material characterization was conducted by Fourier Transform Infrared Absorption Spectroscopy, Optical Absorption Spectroscopy in ultraviolet and visible, X-Ray Diffraction and Electron Microscopy techniques. The growing of amorphous films or films consisting of an amorphous matrix embedded with crystalline nanoparticles was noticed. Depending on the plasma power, pressure, precursor flow rate and downstream substrate position carbon particulates of various size and morphology were obtained.

**G/PII.59** SOL-GEL PROTECTIVE COATINGS FOR INTERSTITIAL FIBEROPTIC LASER APPLICATOR

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Recently, much effort has been directed towards the development of low invasive or non-invasive optical techniques to interrogate the human body for medical purposes. There is an increasing interest in the use of optical techniques for applications such as local treatment of tumors carried out by guiding a laser applicator into the tumor. The applicator should scatter the laser radiation homogeneously into the area of pathologic lesion to be treated. The aim of our study was to examine the influence of material structure on optical properties of sol-gel coatings of an interstitial laser applicator.

The applicator was made from 200 micron fiber. The jacket of the fiber was removed mechanically prior to the etching process of fiber clad. After that the sol-gel layer was deposited on the core. Silica sol-gel layers were made of silica sol-gel precursor TEOS (tetraethoxysilane) and alcohol as a solvent in the process of acid-base hydrolysis. We produced the layers with various molar factor R (5, 15, 32, 50) denoting the ratio of number of solvent moles to number of precursor moles. For each material the microstructure was examined by mean of laser light scattering method enabling to determine the pores size in range of the used wavelength. Additionally, the refraction index *n* was measured. The refraction index of sol-gel layer is an important factor determining the laser light distribution from the applicator tip. We stated that the refraction index depends upon the pore size and amount of pores (porosity) in the material. This, however, depends on the method of coating preparation, meaning the R factor. In this way by changing R we are able to produce the sol-gel coating with tailored optical properties.

**G/PII.60** SEM STRUCTURE AND THE PROPERTIES OF ASP2060 STEEL AFTER LASER MELTING

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In this work the structure and the properties of ASP2060 steel after laser melting is described. During the laser process the different energy of Nd:YAG laser beam (2-5.6J) was applied. Scanning Electron Microscopy (SEM) and X-ray Energy Dispersive Spectroscopy (EDS) were used to investigate structure and chemical composition of the surface layer. The hardness and wear resistance measurements were performed during the investigation. The laser melting resulted in chemical homogenization and refinement of the steel surface. The microstructural investigation showed that the laser melted zone had a cell structure with the carbide ($M_6C$, MC) network precipitated at the cells boundaries. The substructure of these cells consisted of ultra fine dendritic structure.

The results of investigation show, that in the laser melted zone was achieved increase of hardness level (~800 HV0.65 and ~250- HV0.65 in the matrix) and of wear resistance (2-3 times higher than in the matrix).

**G/PII.61** DOSE DEPENDENCIES OF MECHANICAL CHARACTERISTICS OF IRRADIATED POLYMERIC MATERIALS

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We studied mechanical characteristics of post-irradiated polyimid and lavsan films. The radiating influence was carried out under normal conditions by fast electrons, which were generated by the linear accelerator with energy 2MeV and power of bunch 3 kilowatts. The radiation dozes of lavsan varied from 50 Gu up to 5 MGu. It is determined that losses of plasticity occurred at D 500 Gu. The radiation dozes of polyimid films varied from 5 up to 100 MGu. For dozes 20-40 MGu the anomalous effects are found out: hardening of films on 25-30 % with the simultaneous triple or fourfold increase of its relative deformation.

**G/PII.62** INFLUENCE THE FAST ELECTRONS ON THE OPTICAL CHARACTERISTICS OF THE POLYIMID AND LAVSAN FILMS

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We studied optical characteristics of polyimid and lavsan films, which were irradiated by relativistic electrons with energy 2 MeV of dozes from 50 Gu up to 100 MGu. The researches carried out in the wave-length range of 200-1500 nm. It is determined that light-transmission factor depends on radiation doze and energy of photons. The structural changes in irradiated polyimids are disclosed and identified by the method IR – spectroscopy.

## Session XI Advanced mechanical properties
## Session chair: E. Alves, P. Patsalas

**G-XI.1** 8:30

DEPOSITION OF CERAMIC LAYERS ON CARBON FIBERS BY CONTINUOUS LIQUID PHASE COATING

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Carbon fibers are widely used as reinforcement fibers for composite materials. Especially in the case of ceramic matrix composites (CMCs) and metal matrix composites (MMCs) the protection of the fiber is very important to avoid hot corrosion, fiber oxidation or formation of carbides during high temperature manufacturing processes or high temperature application. Controlling the fiber-matrix-interface properties by deposition of coatings increases the tensile strength of the composites. Continuous liquid phase coating of commercial fiber strands with ceramic or carbon precursors solutions with subsequent drying, curing, pyrolysis and calcination is a cost efficient process to deposit dense and homogenous coatings. The precursor systems tested were silazanes, siloxanes, borasilazanes, phenolic resins and coal tar pitch. Scanning electron microscopy showed that the resulting fiber strands were monofilamentwise coated. Tensile tests of the coated fibers specimens were performed according DIN 65382 A. The parameters of the pilot plant were systematically varied in order to obtain optimum tensile strength. The output of the plant 200 - 350 m/d 12k roving, 800 tex) is sufficient to produce enough material for manufacturing of composite samples in pilot plant scale. The coated carbon fibers were applied as reinforcement fibers in ceramic composites, both as unidirectional reinforcement or chopped.

**G-XI.2** 8:50

STRUCTURE AND PROPERTIES OF CRYSTALLINE TIO2 LAYERS DEPOSITED BY REACTIVE PULSED MAGNETRON SPUTTERING WITHOUT SUBSTRATE HEATING

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Crystalline TiO2 layers could be deposited by reactive pulsed magnetron sputtering without additional substrate heating on glass and silicon substrates using a long term stable process with high deposition rate.

XRD investigations have revealed that a variation of pulse mode between unipolar and bipolar allows the deposition of layers with anatase and rutile structure, respectively. The SEM micrographs of anatase layers show faceted crystallites on the surface as well as in the fracture. In comparison the rutile layers have a smoother surface and a more glassy like fracture. Cross-section TEM investigations on samples with anatase or rutile phase have shown that the growth of the layers starts with an amorphous sub-layer. With increasing distance from the substrate the nucleation of first crystallites can be recognized. The lateral size of the columnar grains lies between 100 and 200 nm for both anatase and rutile films. In contrast, the dislocation density of the rutile phase is drastically higher than in films with anatase structure. Spectroscopic ellipsometry measurements have shown that no absorption is present in the visible spectrum range. The refractive index (550 nm) is about 2.5 for anatase and 2.7 for rutile layers, respectively. The hardness and Young's modulus measured by nanoindentation is about 8 and 170 GPa for anatase and 17 and 260 GPa for rutile layers. Layers with anatase structure are well suited for photocatalytic applications using the hydrophilic, self-cleaning and antifogging properties. Rutile layers can be used as optical layers with high refractive index and as protective layers with good mechanical properties.

**G-XI.3** 9:10 Cancelled

**G-XI.4** 9:30

STRUCTURE / PROPERTY RELATIONS FOR TI1-XALXN COATINGS WITH DIFFERENT AL CONTENTS

Kerstin Kutschej, Materials Center Leoben, Franz-Josef-Strasse 13, 8700 Leoben, Austria, Paul Heinz Mayrhofer, Department of Physical Metallurgy and Materials Testing, University of Leoben, Franz-Josef-Strasse 18, 8700 Leoben, Austria, Martin Kathrein, Plansee Tizit AG, 6600 Reutte, Austria, Christian Mitterer, Department of Physical Metallurgy and Materials Testing, Franz-Josef-Strasse 18, University of Leoben, 8700 Leoben, Austria

Ti1-xAlxN hard coatings are already successfully applied for cutting tool applications with extreme conditions. Special emphasis in this field is laid on high hardness, oxidation resistance and superior tribological properties. Numerous individual studies have already been conducted, however, the aim of this work was to present a comprehensive study of the influence of the Ti/Al ratio on structures and properties of the coatings. A D.C. magnetron sputtering system was used to deposit the coatings in an Ar+N2 discharge at various N2 partial pressures and bias voltages onto high speed steel substrates. Ti-Al targets with 50, 60, 67 and 75 at% Al were powder metallurgically produced. Scanning electron microscopy, wave length dispersive electron probe microanalysis and X-ray diffraction were used for structural and chemical characterisation of the coatings. Additionally, mechanical properties were characterised by a computer-controlled microhardness tester. The tribological properties of the coatings at room temperature and elevated temperatures up to 700°C were evaluated with a ball-on-disc tribometer.

**G-XI.5** 9:50

HARDNESS EVALUATION OF W-Si-N SPUTTERED COATINGS AFTER THERMAL DEGRADATION IN OXIDANTE ATMOSPHERE

C. Louro, N. Bagagem, ICEMS, Departamento de Engenharia Mecânica - Polo II – FCTUC, Universidade de Coimbra, Pinhal de Marrocos, 3030 Coimbra, Portugal

Coatings for mechanical applications, especially for cutting operations, must perform under extreme conditions, which oblige to some particularly coating properties like thermochemical stability, hardness and fracture toughness.

Previous research works, shows that W-Si-N sputtered coatings posse these properties. W-Si-N coatings can present crystalline or amorphous structures. In general, the higher the content of Si and/orN higher is the probability to obtain amorphous structures. This fact is determinant on the hardness of the coatings. Amorphous coatings are softer than crystalline ones. However, if amorphous coatings are crystallised by thermal annealing, very high hardness can be reached, even higher than that found for crystalline films. Concerning the oxidation resistance, the best behaviour is observed for films with the highest silicon content with amorphous structure. These antagonic results seems to be a problem for practical applications of W-Si-N films since it is expected simultaneously very high hardness and oxidation resistance. Thus, the aim of this research work was to study the influence of chemical degradation on the mechanical properties of the non degraded zones of sputtered amorphous W-Si-N coatings. For this, an ultramicroindentation technique was used after removal the oxide scales. The results obtained indicate that the oxidation process don't lead to mechanical degradation of the non-oxidised film. In fact the hardness increases with increasing oxidation temperature, similar to that observed previously during thermal annealing.

10:10 **BREAK**

## Session XII: Laser beam processing
## Session chair: J. Kusinski, V. Rotshtein

**G-XII.1** 10:50

FEMTOSECOND PULSED LASER DEPOSITION OF TITANIUM CARBIDE THIN FILMS

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Thin films of refractory materials are widely used as wear-resistant coatings for industrial purposes. In particular titanium carbide is a semi metallic ceramic with some peculiar properties as high thermal stability, hardness and corrosion resistance. Among the various techniques suitable for film deposition of materials, pulsed laser deposition (PLD) has been demonstrated to be very promising for the realization of coatings with good properties for technological applications. In the recent period the increasing availability of ultrashort pulsed lasers have opened up new possibilities in the PLD field. Following previous studies on other refractory systems, we have decided to study the laser ablation of TiC by using a frequency doubled Nd:glass laser with a pulse duration of 250 fs. The results evidence large differences in the plasma characteristics in the case of fs or ns ablation. In particular, in the femtosecond plume the energy and velocity distribution of neutral and ionised particles are very different in respect to those found in the nanosecond plume. Also the ablation mechanism seems to be very different, including, in the case of femtosecond ablation, the delayed emission from the target of large and slow particles. The characteristics of the plasma are clearly related to the morphology of the deposited films and preliminary results show a nanostructure consisting of a large number of spherical particles with diameters ranging from 50 to 200 nm.

**G-XII.2** 11:10

PULSED LASER DEPOSITION OF ADVANCED TITANIUM NITRIDE THIN LAYERS

Boguslaw Major, Institute of Metallurgy and Materials Sciences, Polish Academy of Sciences, Cracow, Poland, Waldemar Mroz, Institute of Optoelectronic MUT, Warsaw, Poland, Tadeusz Wierzchon, Faculty of Materials Science, Warsaw University of Technology,Warsaw, Poland, Wolfgang Waldhauser, Jurgen Lackner, Reinhold Ebner, Materials Center Leoben, Austria

Titanium nitride thin layers were fabricated by PLD using a Nd:YAG laser on both metallic (ferritic steel) and polyurethane substrates by ablation of pure titanium in nitrogen environment.On-axis and off-axis geometry of deposition was applied. Residual stresses were measured in the TiN showing the compressive values in the range of -6 to -8 GPa for the on-axis growth while of about -2.8 GPa for the off-axis position. Crystallographic texture examinations showed the {110}<112> main texture component in the substrate while differences were stated in the TiN phase in respect to the geometry of deposition. In the case of the on-axis growth, the mostly axial texture with the plane {110} parallel to the surface with tendency to the {110}<011> was observed, while for the off-axis growth, the very pronounced {112}<223> dominant orientation was stated. Examinations of crystalline size and lattice strain were carried out on the basis of the diffraction line broadening. Deposition of the TiN at ambient conditions on the polyurethane substrate revealed uniform thin layers. Residual stresses showed the compressive values of about -1500 MPa. The measured texture was stated to be close random. Morphology of deposited layers was examined by means of AFM and revealed similarity to the 3D growth mechanism.

**G-XII.3** 11:30

ROOM TEMPERATURE PULSED LASER DEPOSITIOM OF TITANIUM OXIDE COATINGS FOR INDUSTRIAL TRIBOLOGICAL APPLICATIONS J.M. Lackner, W. Waldhauser, R. Ebner, Laser Center Leoben, Leoben, Austria and B. Major, Institute of Metallurgy and Materials Sciences, Polish Academy of Sciences, Cracow, Poland and T. Schöberl, Erich-Schmid-Institute, Austrian Academy of Sciences, Leoben, Austria

Titanium oxide (TiO (sub x)) coatings exhibit extraordinary tribological properties due to their possibility of solid lubrication, but very few is known about the relationship between structure and mechanical resp. tribological properties of room temperature deposited coatings. In the present work this gap was closed by employing the room temperature pulsed laser deposition (PLD) process. The substrates surfaces have been situated parallel and perpendicular to the ablated pure titanium targets. The combination of a four-beam PLD evaporator with a suitable movement of the substrates resulted in a high rate film growth on large surfaces. The structure of the coatings investigated is a mixture of monoclinic beta-TiO(sub 2) and amorphous phases. The ratio of the phases, the hardness and the elastic constants depend strongly on the target-substrate arrangement and the O(sub 2) pressure applied. Due to the very high adhesion of the coatings and their very smooth surfaces the coatings exhibit low friction coefficients of about 0.4 and wear rates of lower than 10E-15 $m^3/Nm$, turning out that titanium oxide films deposited by PLD are very promising candidates for wear protection and tribological applications.

**G-XII.4** 11:50

LASER ABLATION OF CERAMIC OXIDES IN THE PRESENCE OF A RF PULSED OXYGEN PLASMA

M. Cantoro, N. Coppedè, A. Camposeo, F. Cervelli, F. Fuso, M. Allegrini, E. Arimondo, INFM, Dipartimento di Fisica Enrico Fermi, Università di Pisa, Via Buonarroti 2, 56127 Pisa, Italy

Pulsed laser ablation and deposition is a well-established technique for the growth of ceramic oxide coatings. Typically, the process is accomplished in a low-pressure molecular oxygen atmosphere, with the main aim to increase the oxygen content of the film and to stabilize its structure. The mechanism is inherently related to molecular oxygen fragmentation and formation of oxygen-containing molecules and clusters during the expansion of the ablated material. In some specific applications, however, an excessive exposure to oxygen during the deposition process can be detrimental, as, for instance, when a metal substrate must be coated. In fact, formation of non-stoichiometric oxides at the substrate surface can easily lead to structural and morphological defects at the microscopic and macroscopic scale. In order to control and limit the exposure to oxygen, we have implemented in our pulsed laser deposition setup a RF oxygen plasma source, which can operate in either CW or pulsed regime. A detailed in-situ diagnostics carried out during laser ablation of ceramic and metal targets, has been accomplished by optical absorption spectroscopy with time- and space-resolved capabilities. Results suggest that the system is efficient in limiting exposure to oxygen while providing the atomic oxygen local density required for the attainment of the correct film stoichiometry.

Work supported by CNR through Progetto Applicativo "Applicazioni della supeconduttività ad alta Tc".

**G-XII.5** 12:10

LASER MODIFICATION OF MICROSTRUCTURE AND PROPERTIES OF ARC SPRAYED COATINGS OBTAINED FROM Fe-Cr-B BASED CORED WIRES

B. Wielage(a), A. Wank(a), H. Pokhmurska(a), W. Kalita(b), M. Student(c), V. Dovhunyk(c), (a)Chemnitz University of Technology, Institute of Composite Materials, Chemnitz, Germany, (b)Institute of Fundamental Technical Research, Polish Academy of Science, Warsaw, Poland, (c)G.V. Karpenko Physico-Mechanical Institute of National Academy of Sciences of Ukraine, Lviv, Ukraine

Cored wires of Fe-Cr-B base system for arc spraying of renovation and protective coatings on the parts made from steel and aluminium alloys with the aim of increasing their wear resistance and restoring the geometrical dimensions. Wires were covered with a low carbon steel cover of 0,4 mm thickness with 1,6-2,0 mm in diameter with the filling mixture of different composition including iron/chromium/boron, aluminum, magnesium powders. The irradiation of CW CO2 laser was use to modify the structure of as-sprayed coatings. Depending on the regimes of laser treatment different effects, from surface glazing to metallurgical bounding formation, were observed. In all cases structure of the remelted coating is uniform, porous loss, with very fine grains. Such coatings, besides the increasing of microhardness, demonstrate much better corrosion performance.

The influence of laser parameters, laser treatment geometry, different protecting atmospheres, presence of antireflection coating on the microstructure, phase composition, residual stresses and undesirable crack formation was investigated. Microhardness and abrasive wear resistance of the laser modified coatings were studied. In was shown that laser treatment of arc sprayed coatings obtained from cored wires based on Fe-Cr-B system allows to rise the microhardness of modified layers and abrasive wear resistance in the range of 40% and in the same time to increase their corrosion resistance.

## Session XIII: Structure-properties correlation
## Session chair: G. Abadias, V. Uglov

**G-XIII.1** 14:00 -Invited-

DECORATIVE COATINGS DEPOSITED BY COLUMNAR ARC DEPOSITION
**K.W. Marszalek**, AGH University, al.Mickiewicza 30, 30-059 Cracow, Poland
Among the different coatings the decorative ones and the esthetic significance of its application plays inreasingly important role.Sometimes decorative features of the coated surface are the main functional feature but in most cases are additional to the others functional features like hardness, corrosion protection or optical properties. The author presents an overview of the materials used for deposition of thin film decorative coatings. The survey of the coating applications for which the decorative function plays a primary or additional role is also shown.The significance of the technology choice for the particular application is discussed. The advatages and disadvantages of the columnar arc deposition in comparison to thermal evaporation and magnetron sputtering are presented. The role of the columnar arc as a source of high enery and strongly ionized plasma as well as arc spot moving mechanism and different source construction are presented.The arc spot parameters like electrical field, current density, temperature and pressure within the spot area are reviewed. A few industrial arc deposition systems for production of decorative coatings are presented.

**G-XIII.2** 14:30

THE RELATION BETWEEN THE DEGREE OF DENSIFICATION AND THE MECHANICAL PROPERTIES OF SI02- COATINGS
Susan Enders, MPI for Metals Research, Stuttgart, Peter Grau, Dept. of Physics, M.-Luther University, Halle, Germany
The mechanical properties, like hardness, Young`s modulus, frictional behavior of SiO2 films derived from the Sol-Gel process and deposited on various substrates, were measured by use of nanoindentation / scratching techniques.
It is known, that these films may achieve different densification states and thus differ in their microstructure due to variations in the heat treatment. Aim of our investigations is to reveal the relationship between microstructure and mechanical performance of the coatings. However, in indentation tests the exact film properties are difficult to determine, because of the substrate influence. From previous tests on coated systems it is known, that the substrate will affect the results even if the indentation depth is less than one-tenth of the film thickness. Therefore, we developed an analytical model, which allows the separation between the properties of the coating and the substrate independent of the film thickness and the ratio in hardness between film and substrate. Further, with this model gradients in hardness and Young´s modulus of the film, substrate and compound with dependence to the penetration depth are determined as well. The so obtained results show clearly the influence of the processing conditions on the mechanical properties of the films and provide individual mechanical parameters for further comparison.

**G-XIII.3** 14:50

Cancelled

**G-XIII.4** 15:10

GRADED REFRACTIVE INDEX LAYER SYSTEMS FOR ANTIREFLECTIVE COATINGS AND RUGATE FILTERS DEPOSITED BY REACTIVE PULSE MAGNETRON SPUTTERING
H. Bartzsch, S. Lange, P. Frach, K. Goedicke, Fraunhofer- Institut für Elektronenstrahl- und Plasmatechik (FEP), Winterbergstr. 28, 01277 Dresden, Germany
Reactive pulse magnetron sputtering enables the long term stable deposition of compound films by sputtering of a metal target in a mixture of inert and reactive gas. It also allows to deposit multicomponent films such as SixNyOz or AlxNyOz using mixtures of different reactive gases such as oxygen and nitrogen. Gradient layers with varying composition and refractive index in growth direction can be obtained by changing the gas mixing ratio during the deposition.
In this paper the application of this new technology to the fabrication of antireflective coatings and rugate filters is reported. The possibility of freely choosing intermediate refractive indices gives a new degree of freedom for the design of an antireflective (AR) coating with a simple and robust design. The reflectivity of the deposited AR coatings consisting of a twofold gradient SixNyOz film is less than 0.5% in the wavelength range between 450nm and 620nm. Rugate filters composed of a film with sinusoidal oscillating refractive index have been produced at high precision by reactive sputtering in a varying reactive gas mixture using appropriate process control. An example of a deposited rugate filter has a reflectivity > 99.9% at 550nm with a narrow band width of 60nm and a transmission greater than 80% below 500nm and above 600nm. Both Ar-coatings and rugate filters are produced by stationary sputtering at only one deposition station without interruption of the plasma process thus guaranteeing a very stable and efficient process. The applied hardware allows coating of 8" substrates with film thickness uniformity of +/-1%.

**G-XIII.5** 15:30

COMBINED XAS AND XPS ANALYSIS OF THE CORROSION PROTECTION OF ULTRATHIN PROTECTIVE COATINGS FOR MAGNETIC STORAGE DEVICES

P. Bernhard(a), Ch. Ziethen(1), R. Ohr(b), H. Hilgers(b), G. Schoenhense(a), (a)Johannes Gutenberg-Universitaet, Institut fuer Physik, 55099 Mainz, Germany, (b)IBM Speichersysteme Deutschland GmbH, 55131 Mainz, Germany

The X-ray Absorption Spectroscopy (XAS) is an established method in today?s materials research, which can also be used for chemical analysis of buried layers. Determination of its fine structure (XANES - X-ray Absorption Near Edge Structure) allows a prediction of the bonding condition of the detected elements [1]. A second approach to investigate the buried layers is done by XPS.

We used both methods subsequently under the same conditions and on the same sample area with a lateral resolution < 1 µm to investigate the corrosion protection of ultrathin protecting carbon layers [2]. These layers are used in the hard discs production to protect the magnetic film from corrosion and wear. The decrease of the layer thickness is one aim in current development of hard disc coatings as it leads to a further increase of the storage density. As the functional properties of the protecting layers must stay unchanged, the investigation of the corrosion protection in interrelation of the layer thickness is essential. To learn about this interrelation, we concentrated on the absorption edge of Co L2/L3 (for XAS) and on the 2p XPS-Spectra of Co and Co-oxide.

[1] Ch. Ziethen et al., Diamond Rel. Mat., 11, 2002 (1068)

[2] Projects BMBF, FKZ 13N7759 and FKZ 13N7863

**G-XIII.6** 15:50

EVALUATION OF MODIFICATIONS INDUCED ON PORE NETWORK AND STRUCTURE OF PARTIALLY STABILIZED ZIRCONIA MANUFACTURED VIA HYBRID PLASMA SPRAY PROCESS

Guy Antou, F. Hlawka, A. Cornet, LISS, Ecole Nationale Supérieure des Arts et Industries de Strasbourg, 24 Bd de la Victoire, 67084 Strasbourg Cedex, France, G. Montavon, C. Coddet, LERMPS, Université de Technologie de Belfort-Montbéliard, site de Sévenans, 90010 Belfort Cedex, France, F. Machi, IREPA-Laser, Pôle API, Parc Technologique, 67400 Illkirch, France

Thermal barrier coatings (TBCs) constituted by Yttria Partially Stabilized Zirconia (i.e., Y-PSZ, ZrO2 + 7wt% Y2O3) and a metallic bond layer (i.e., MCrAlY where M represents a combination of Ni and Co) are extensively used to improve the performance of hot-section components of gas turbines.

Air plasma spray (APS) and in-situ laser irradiation by diode laser processes are combined to modify structural characteristics of TBCs. The existence of interconnected porosity and segmented cracks in APS TBCs not only influences their mechanical properties, but also deteriorates the oxidation and corrosion resistance of the component. So, one of the purposes of combined laser treatments is to reduce the porosity level. The dependence between the microstructure of TBCs, which was modified by laser treatment and corrosion resistance has been evaluated by an electrochemical test. Results show that, for a laser energy density ranging from 1.7 to 1.9 J.mm-2, the pore network connectivity level decreases. Scanning electron microscopy observation revealed also that laser treatment induces a change of the microstructure from lamellar to columnar dendritic. Intensive image analysis was also performed to further quantify the pore characteristics (i.e., nature, orientation, percentage, etc.). Moreover, no phase transition was noticeable: the metastable tetragonal phase still remains the predominant phase after laser treatment.

16:10 Symposium concluding remarks