New Horizons in Coatings and Thin Films
Room On Demand - Session F1
Nanomaterials and Nanofabrication

F1-1 Theory and Applications of Inverted Fireballs*, Gerhard Eichenhofer (eichenhofer@4a-plasma.eu),* 4A-PLASMA, Germany*; J. Gruenwald,* G-Labs, Austria

Inverted Fireballs have been proven to be a viable tool for large area surface modifications, especially for coating purposes [1, 2].This novel technology enables energy efficient deposition for various fields of applications.Its suitability for surface modifications in general and for deposition technologies in particular is owed to their very homogeneous plasma potential and their enhanced ion densities. It has been shown that a substantial increase in the degree of ionisation in the deposition plasma is feasible. This work will outline theoretical investigations into inverted fireballs, such as analytical models and particle-in-cell simulations [3-5] and the application of these findings to technologically relevant topics. Details of how these plasma phenomena can be utilisedin possible areas of surface technology, will be shown. Furthermore, it will be demonstrated that inverted FBs exhibit a number of plasma instabilities. However, they can be stabilised over a long period of time, which is necessary for industrial applications. It will also be outlined in this talk where the limitations of fireball research are at the moment and some ideas for future work on pulsed inverted FB deposition will be presented.

F1-2 Pulsed Aerosol Assisted Plasma Deposition: Influence of the Injection Parameters on ZnO/DLC Nanocomposite Thin Films*, Adèle Girardeau (adele.girardeau@laplace.univ-tlse.fr),* LAPLACE, LCC, France*; G. Carnide,* LAPLACE, LCC, IMRCP, France*; A. Mingotaud,* IMRCP, France*; M. CAVARROC,* Safran Tech, France*; M. Kahn,* LCC, France*; R. Clergereaux,* LAPLACE, France

Aerosol-assisted processes enable to deposit thin films, homogeneous [1, 2] or nanocomposite [3, 4, 5,6]. For example, the nebulization of colloidal solutions, *i.e.* liquid solutions containing nanoparticles, in different plasma processes has been widely used for nanocomposite thin film deposition. However, nanoparticles loaded droplets in the aerosol lead to the deposition of aggregated nanoparticles embedded in the matrix.

Recently, a new process of nanoparticles injection has been developed [7]. This method, called reactor-injector of nanoparticles, consists in synthesizing nanoparticles prior to their injection in the plasma in a pulsed injection regime. It enables to form nanocomposite thin films with really small (<10 nm in diameter) and highly dispersed nanoparticles embedded in the matrix [7].

This work aims to study the deposition of ZnO/DLC nanocomposite thin films in a low-pressure RF plasma. The main challenge of this process is to find the best compromise between the parameters for an efficient synthesis of ZnO nanoparticles and an optimal behaviour of low-pressure RF plasmas in a pulsed regime. It is shown that the operating window enables to deposit nanocomposite thin films with an extended range of volume fraction.

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F1-3 Design of Functional Nanoporous Ceramic Coatings via Infiltration of Polymer Templates*, Diana Berman (diana.berman@unt.edu),* University of North Texas, USA

Robust and efficient process for synthesis of various composition inorganic coatings with controlled nanoporosity and structure is highly desirable for design of efficient catalytic, purification, and detection systems. Recently, infiltration of a nanoporous polymer template with inorganic precursors using sequential infiltration synthesis (SIS) with inorganic vapor precursors followed by oxidative annealing was proposed as a new and efficient approach to create porous inorganic structures with tunable porosity and composition. The major limitations of the original water-based thermal SIS, though, are the thickness of the patterned structure being limited by vapor penetration depth of the precursors into the polymer template and the SIS material selection restricted by the availability of high vapor pressure precursors. Here, we propose a swelling-based modification to the SIS process that allows to overcome these limitations. We summarize the basics of the multi-step infiltration approach, the structure and properties of the resulting materials, and their functional potential for practical applications. We report ultra-high accessibility of the pores when porous films are prepared via the polymer swelling-assisted SIS. Using a quartz crystal microbalance (QCM) technique, we demonstrate increased solvent absorbing capabilities of highly porous ceramic films as a result of high interconnectivity of the pores in such structures. Our results show that the SIS can be been extended toward preparing conformal coatings, freestanding membranes, and powders consisting of metal or metal oxide nanoparticles embedded in a porous oxide matrix.

F1-4 Improvement of Adhesion between NiTi Alloy and Diamond-like Carbon Filmby Bayesian Optimization*, Masafumi Toyonaga (m.tyng.keio@gmail.com),* Keio University, Japan*; T. Hasebe,* Keio University, Tokai University Hachioji Hospital, Japan*; S. Maegawa,* Tokai University Hachioji Hospital, Japan*; T. Matsumoto,* Keio University, Tokai University Hachioji Hospital, Japan*; A. Hotta, T. Suzuki,* Keio University, Japan

Surface coating is one of the most interesting methods for improving the mechanical, physical, chemical and biocompatible properties of materials and devices. Fluorine-incorporated diamond-like carbon (F-DLC) has received much attention as a coating material because of outstanding blood compatible properties which suppress fatal failure of the medical devices. However, it is well known that F-DLC thin films exhibit poor adhesion on metallic alloys and delamination or cracks are easy to occur after coating. In order to improve adhesion of F-DLC on metallic alloys, many scientific methods have been reported. Although some of these studies focused on introducing silicon-containing interlayers such as silicon-incorporated DLC (Si-DLC) between metallic alloys and F-DLC thin films to improve the adhesion properties, the film formation conditions of the interlayer that most improves the adhesion are not clear, and the method has not been established for optimizing the film formation conditions. Thus, we considered optimizing the structure of the interlayer using "Bayesian optimization", which is known as one of machine learning. In this study, we optimize the structure of Si-DLC interlayer by Bayesian optimization to apply F-DLC to low blood compatible nickel-titaniumu (NiTi) alloy, which has been attracting attention as a material for medical devices due to superelasticity and shape memory.

The purpose of this study is evaluating the effectiveness of Bayesian optimization for determining optimal structures of interlayers between metallic substrates and F-DLC, and developing high blood compatible NiTi alloy by improving adhesion properties of F-DLC.

Si-DLC and F-DLC were prepared on NiTi substrates using radio frequency plasma enhanced chemical vapor deposition (RF-PECVD) equipment. The adhesion properties between NiTi substrates and DLC thin films were evaluated by the scratch test, and the structures of Si-DLC interlayer were updated successively by Bayesian optimization on the obtained data. Total of 30 Si-DLC interlayers were produced, and the highest adhesion could be improved to about 53 mN, while the lowest adhesion was about 22 mN. The one with the highest and lowest adhesion were deposited on the NiTi stents, and after performing the crimp test and the fatigue test, the surface was observed by Scanning Electron Microscope (SEM). As a result, no delamination was observed in the interlayer derived by Bayesian optimization, whereas delamination occurred in the sample in which structure was not optimized.

Therefore, this study shows that adhesion properties between metallic material and DLC thin film can be improved by Bayesian optimization.

F1-5 Novel Type of Bent-Lattice Nanostructure in Crystallizing Amorphous Films Revealed by TEM: From Transrotational Microcrystals to Strain Nanoengineering and Novel Amorphous Models, *Vladimir Kolosov (kolosov@urfu.ru)*, Ural Federal University, Russian Federation

Exotic thin crystals with unexpected **transrotational nano**structures [1] have been discovered by transmission electron microscopy (TEM) for crystal growth in thin (10-100 nm) amorphous films of different chemical nature (oxides, chalcogenides, metals) prepared primarily by vacuum evaporation methods. We use TEM bend-contour method [2] combined with selected area electron diffraction. HREM, AFM and optical microinterferometry were used in due cases (preferentially for correlative microscopy).

The unusual phenomenon often can be observed ***in situ*** in TEM column during local e-beam heating or annealing: regular internal bending of crystal lattice planes in a growing crystal, Fig. 1 a-b. It is dislocation independent. Such **transrotation** (**trans**lation of the crystal unit cell is complicated by small **rotation** realized round an axis lying in the film plane) can result in strong regular lattice orientation gradients (up to 300 degrees/µm) of different geometries: cylindrical, ellipsoidal, toroidal, saddle, etc., Fig. 1b

The possible mechanisms of the phenomenon are discussed, Fig. 1d. Initial amorphous state and surface nucleation of the crystal growth are most essential factors. The last fact accompanied by anisotropy of crystal growth rate and obvious tendency for regular change of interatomic distances of the crystal propagating from the surface layers inside the bulk material resembles specific epitaxy, “vacuum epitaxy”. The transrotation phenomenon is the basis for novel lattice- rotation nanoengineering of functional, smart thin-film materials appropriate also for strain nanoengineering. Transrotational micro crystals have been eventually recognized by different authors in some thin film materials vital in applications, e.g. phase change materials (PCM) for memory [3-5].

New nanocrystalline “curved-lattice” concept for amorphous state is proposed: fine-grained structures with lattice curvature, Fig. 1e. Thus the great variety of different possible curved/transrotational lattice geometries inside fine crystal grains in the static model corresponds to different amorphous structures hardly distinguished by known methods. Going to 3D clusters of positive/negative curvature and dynamics we propose the hypothesis of “dilatons”, “contractons” pulsating or/and circulating in amorphous film.

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F1-6 Deposition of Cu and Pt Metallic Clusters onto Titanium Dioxide Nanoparticles by DC Magnetron Sputtering for Hydrogen Production, *Glen West (g.west@mmu.ac.uk)*, Manchester Metropolitan University, UK; *M. Bernareggi, G. Chiarello, E. Selli,* University of Milan, Italy; *A. Ferretti,* ISTM-CNR Lab Nanotechnology, Italy; *M. Ratova, P. Kelly,* Manchester Metropolitan University, UK

A novel technique using pulsed-DC magnetron sputtering has been employed to deposit metal nanoclusters directly onto titanium dioxide nano-particles. Deposition conditions and plasma compositions were varied to produce the desired Cu and/or Pt clusters on the particle surfaces. The nanoparticle powder was placed within an oscillating substrate holder, and a top-down sputter deposition arrangement allowed deposition onto the continuously rotating nanoparticles. HRTEM analyses revealed the presence of well-dispersed, sub-nanometric sized metal clusters, even following extended deposition times, while XRD analysis showed no modification of the TiO_2 crystal structure resulting from the process.

The coated powders were then tested for their ability to produce hydrogen from a methanol photo-steam reforming process via photocatalytic action. The photo-activity of the powders was increased by the presence of Pt clusters with respect to that of bare TiO_2. During Cu sputtering, the plasma composition was found to strongly affect the photoactivity of the materials produced. Copper when deposited as a lone co-catalyst in an Ar-only atmosphere imparted better photo-activity than Cu sputtered in Ar/O_2. When the deposition process coupled both Cu clusters and Pt clusters, an additive effect of the two metals in increasing TiO_2 photoactivity for hydrogen generation was observed under optimised conditions.

F1-7 Manipulation of Thin Films and Nanostructures on Weakly-interacting Substrates by Selective Surfactant Deployment, *A. Jamnig,* Linköping University, IFM, Nanoscale Engineering Division, Sweden; *N. Pliatsikas, M. Konpan,* Linköping University, IFM, Nanoscale Engineering Division; *J. Lu,* Linköping University, IFM, Thin Film Physics Division, Sweden; *J. Kovac,* Josef Stefan Institute; *G. Abadias,* University of Poitiers, PPRIME Institute, CNRS, France; *I. Petrov,* University of Illinois, USA, Linköping University, Sweden, USA; *J. Greene,* University of Illinois, USA, Linköping University, Sweden, National Taiwan Univ. Science & Technology, Taiwan, USA; ***Kostas Sarakinos (kostas.sarakinos@liu.se)***, Linköping University, Sweden

The ability to control the size and shape of noble-metal nanostructures and the morphology of noble-metal films on weakly-interacting substrates, including 2D materials and oxides, is essential for the fabrication of high-performance enabling devices. The use of less-noble-metal and gaseous surfactants is a known strategy for manipulating growth of noble-metal layers, but the mechanisms by which surfactant atoms affect the complex structure-forming processes are not yet understood. In this work, we study the effect of nitrogen (N_2) gas on the morphological evolution of magnetron-sputter-deposited silver (Ag) thin films on silicon dioxide substrates. We find that presence of N_2 in a mixed argon (Ar)/N_2 gas atmosphere, throughout all film-formation stages, promotes 2D growth and smooth film surface, while the continuous-layer electrical resistivity increases, compared to Ag films grown in pure argon (Ar) ambient. Using a combination of real-time *in situ* film growth monitoring and *ex situ* characterization, we conclude that N_2 is physisorbed on the film growth surface and promotes 2D morphology by suppressing island coalescence rates during initial growth stages. Moreover, our data suggest that physisorbed N_2 causes interruption of local epitaxial growth on Ag crystals, which leads to repeated nucleation and explains the increased electrical resistivity of continuous films. Using these insights, we deposit Ag films by deploying N_2 selectively, either during the early growth stages or after coalescence completion. We show that early N_2 deployment leads to a 2D morphology without affecting the Ag-layer resistivity, while post-coalescence introduction of N_2 in the gas atmosphere further promotes formation of 3D nanostructures and roughness at the film growth front. The knowledge generated in the present study is relevant for the development of single-step growth manipulation strategies in which gaseous and less-noble-metal surfactant species can be deployed with high temporal and spatial precision to selectively target and modify the rates of key structure-forming processes.

New Horizons in Coatings and Thin Films
Room On Demand - Session F2

High Entropy and Other Multi-principal-element Materials

F2-1 Combinatorial Design of High Entropy Alloys: A Rational Approach in Thin Film*, **Elise Garel (elise.garel@grenoble-inp.fr)**, H. Van Landeghem, R. Boichot,* SIMAP, Grenoble-INP, CNRS, France

High entropy alloys (HEAs) have been studied since 2004 for their exceptional mechanical properties. While conventional alloys are composed of one or two main elements plus addition elements, HEAs are designed with five or more principal elements. The development strategy of these alloys usually focuses on the interior region of the composition space. Among them, refractory high entropy alloys (RHEAs) are studied as an alternative to nickel superalloys that could, for instance, be used in aerospace or for energy production.

Improving the properties of a RHEA by the usual method of trial-and-error requires synthesizing and characterizing many different bulk alloys to cover the entire composition space. For five elements, exploring a 5 to 35% molar fraction range, with a variation of 0.1%, would represent 2.43×10^{12} possible samples to make. Thus, using this historical approach, with such a space to explore, new interesting alloys (probably not optimized) would be discovered essentially by applying a rule of thumb.

This study aims at developing a method to systematically explore an entire n-elements composition space with the minimum number of experiments, focusing on the particular quinary alloy Zr-Ti-Nb-Mo-Cr. Linear gradients of composition are synthesized by depositing thin films through a modified confocal Magnetron Sputtering deposition technique, choosing each set of targets so that these gradients pass by at least three points of an augmented centroid mixture design, to guarantee a uniform screening.

In a n-elements space, it has been demonstrated that there are $(3^n-2^{n+1}+1)/2$ possible gradients, that pass several times by each point of the mixture design. For five elements, there are 90 potential samples to deposit. It is then possible, depending on the preference of the experimenter – such as exploring preferentially the centre or the borders of the composition space - to choose a certain number of gradients among all the possibilities. In the case of a five elements RHEA, about 20 samples (meaning 20 experiments) are enough to screen the entire composition space.

All of these deposited alloys are to be characterized (composition, micro-hardness and phases) to build a database that links composition, structure and properties. A Machine Learning approach is tested to evaluate whether or not it is possible to build a reliable predictive model that would allow to define the RHEA compositions that optimize the alloy properties.

Ultimately, samples of optimized compositions would be cast in ingots in order to confirm on bulk samples the properties discovered with the thin film approach.

F2-2 Systematic Investigation of the Impact of Pure Metal Addition on AlCuMgZn Multi Principal Element Alloys*, **Johannes Kirschner (johannes.kirschner@tuwien.ac.at)**, R. Gaschl,* Vienna University of Technology, Austria*; J. Bernardi,* USTEM, Vienna Technical University, Austria*; C. Eisenmenger-Sittner,* Vienna University of Technology, Austria*; C. Simson,* LKR Leichtmetallkompetenzzentrum Ranshofen, Austria

The design and synthesis of new materials and alloys is a crucial element in various technical areas, from the design of more energy-efficient mobility solutions to the construction of mechanically more robust alloys. Multi-Principal Element Alloys (MPEAs) show great potential as previous studies have shown that certain quaternary and quinary alloys containing approximately equal amounts of their constituents were superior to conventional alloys. The prediction of compatible elements and their optimal composition, especially in the area of light metals, represents a major challenge in this field and up to date, there is a lack of reliable models and concepts.

Multi-component layers (thickness of 10 µm) were co-deposited by magnetron sputtering and thereafter thermally treated to reveal the complex correlation between chemical composition, crystallography, mechanical properties and morphology. Quaternary systems including the elements Al, Mg, Zn and Cu were chosen to prepare samples in different compositions on a single substrate. Special emphasis was given to the increase of the relative Cu content with approximately the same ratios of the other alloying materials. Scanning electron microscopy in combination with energy dispersive X-ray spectroscopy and X-ray diffraction showed that the addition and increase of Cu have immense effects on the crystallographic phase formation. A wide concentration range in the Cu rich regime was observed (Cu content > 65 at%), in which a single phase system was formed. This range is characterized by significant indentation hardness variations and changes in microstructure. The obtained results were compared with the effects of the quantitative variation of the other constituents to evaluate the impact of different metals and metal classes (alkaline earth metals, transition metals, post-transition metals) on the system properties. Furthermore, the effects of the addition of a 5th element on the structure and crystallography of the alloy were investigated. These results establish a better understanding of the correlation between different metals in a complex system and expand the concept of high entropy alloys to the class of light metals to develop low density alloys. They should also provide valuable information for alloy synthesis using traditional methods such as melt synthesis.

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F2-3 Improving Phase Stability, Hardness and Oxidation Resistance of Reactive Magnetron Sputtered $(Al_vCr_wNb_xTa_yTi_z)N$ Thin Films by Si-alloying*, **Andreas Kretschmer (andreas.kretschmer@tuwien.ac.at)**,* Institute of Materials Science and Technology, TU Wien, Austria*; K. Yalamanchili,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; H. Rudigier,* OC Oerlikon Management AG, Switzerland, Liechtenstein*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

High-entropy alloyed nitrides are promising materials for hard coatings. One major drawback is a lack of oxidation resistance in most coatings, which limits high-temperature applications in ambient conditions. In this work we report a method to increase the oxidation resistance while also improving thermal stability of the alloy, and higher resistance to the hardness drop induced by elevated temperature annealing.

$(Al_vCr_wNb_xTa_yTi_z)N$ coatings were formed in a cubic (c) solid solution in thin film form by reactive magnetron sputtering in N_2-atmosphere using a powder metallurgically prepared metal target (Plansee) with nominal composition of 20 at% of each element. Si was alloyed by placing different numbers of pieces (about 2x2x0.4 mm^3 each) of Si on the cathode racetrack during deposition. The hardness and indentation modulus of the as-deposited samples were 32.6 ± 2.0 GPa and 462 ± 23 GPa without Si, and 35.4 ± 1.1 GPa and 328 ± 14 GPa with Si, respectively. X-Ray Diffraction (XRD) measurements of the samples after vacuum annealing to temperatures up to 1200 °C revealed that Si delays the decomposition from 1000 °C to 1200 °C. After vacuum annealing to 1100 °C we measured a hardness of 30.3 ± 2.5 GPa and 38.1 ± 1.3 GPa as well as an indentation modulus of 445 ± 25 GPa and 430 ± 11 GPa for the samples without and with Si, respectively.

We gauged the oxidation resistance of the coatings by placing the samples in a furnace in ambient air at 850 °C for 0.5, 1, 5, 10, 30 and 100 h. After these durations we extracted the samples from the hot zone and analysed them with XRD and Energy-Dispersive-X-Ray-Analysis. With increasing Si-content the oxidation resistance improved significantly.

Based on our results we can conclude that this type of high entropy nitride coatings, especially when alloyed with Si, provides excellent thermomechanical properties as well as oxidation resistance.

F2-4 Carbon Containing Multicomponent Alloys with High Hardness, Ductility and Corrosion Resistance*, **León Zendejas Medina (leon.zendejas.medina@kemi.uu.se)**,* Uppsala University, Sverige*; G. Lindwall,* KTH - Royal Institute of Technology, Sweden*; E. Pascalidou,* Uppsala University, Sweden*; L. Riekehr,* Uppsala University, Angstrom Laboratory, Sweden*; M. Tavares da Costa,* Uppsala University, Sweden*; S. Fritze,* Uppsala University, Angstrom Laboratory, Sweden*; K. Gamstedt,* Uppsala University, Sweden*; L. Nyholm, U. Jansson,* Uppsala University, Angstrom Laboratory, Sweden

The development of fuel cells is a field in need of new multifunctional materials for corrosive environments. The cell components need to withstand the high potentials and low pH in the cell while simultaneously meeting many additional material requirements. In this study, we focus on finding coatings for corrosion protection of bipolar plates in PEM fuel cells. The high demands on the corrosion resistance must be combined with high mechanical stability and formability, to allow for roll-to-roll deposition followed by stamping to a customized pattern of flow channels. The coatings must, therefore, meet high demands on three points: corrosion resistance, hardness, and ductility.

To achieve this, we have explored carbon addition to multicomponent films deposited by magnetron sputtering. Adding carbon is a known way to overcome the hardness-ductility trade-off [1] and improve the corrosion resistance of thin films, as long as the formation of crystalline carbides is avoided. The Cantor alloy, CrMnFeCoNi, was chosen as a starting point due to the high concentration of weak carbide forming elements. The alloy composition, combined with the high quenching rate during sputter deposition, improves the chances of carbide suppression.

The selection of new compositions was first explored by thermodynamic calculations using CALPHAD. The films were characterized using a range of techniques, from XRD, SEM, EDS, TEM, XPS to HAXPES and XAS at a synchrotron. Electrochemical measurements and mass spectrometry were used to understand the corrosion mechanisms. Nanoindentation was used to obtain mechanical parameters, while fragmentation tests on polyimide substrates were performed to investigate the crack resistance [2].

The addition of carbon to the alloy resulted in the amorphization of the material, starting from 6 at-% C, with no evidence of free carbon or a segregated carbide phase. The change in structure was accompanied by an increase in both hardness and crack resistance, and the addition of carbon greatly improved the corrosion resistance. In the second part of the study, Mo and W were added to the alloy as a way to increase the corrosion resistance further. The effects on structure and material properties will be presented in more detail.

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F2-5 Structural and Mechanical Properties of AlTiTaZr(-N) Medium Entropy Films (MEF) Obtained by DC Magnetron Sputtering in Dynamic Mode*, **Mohamed El Garah (mohamed.el_garah@utt.fr)**, S. Achache,* LASMIS, CNRS- Université Technologique de Troyes, France*; A. Michau, F. Schuster,* CEA, Université Paris-Saclay, France*; F. Sanchette,* LASMIS, CNRS-Université Technologique de Troyes, France

Since their introduction by Yeh and Cantor[1, 2], High Entropy Alloys (HEAs) reveal attractive physical and chemical properties. Similar to that, High Entropy Films (HEFs) have been also reported to possess excellent mechanical and physical properties such as good wear[3] and corrosion resistance[4] as well as an excellent thermal stability.[5] They open up new promising possibilities to various functional material applications; especially they can be used as protective coatings to deal with extreme environments.

New AlTiTaZr medium entropy films (MEFs) are elaborated by using direct current magnetron sputtering of four pure metallic targets. The films are deposited in various argon-nitrogen gas mixtures on glass, silicon and sapphire positioned in the center and in the target's axis of a rotating substrates holder. Crystallographic structure evolution, as a function of the nitrogen content, is predicted by calculating the phase selection criteria. The theoretical predicted structures are consistent with X-ray diffraction analysis results. Without nitrogen, the films are amorphous, and by increasing the N_2 content in the gas mixture, they are single phased faces centered cubic (FCC). A {200} preferential growth of AlTiTaZr(-N) films is favored in the targets axis position with increased nitrogen flow rate, whereas those in the center position of substrates holder grow preferentially with {111} planes parallel to the substrates surface.

Hardness and Young's modulus are improved with increasing of the nitrogen flow. The highest values were obtained for those in the targets axis position and reach 24.64 GPa and 148.4 GPa for the hardness and the Young's modulus, respectively. These films were annealed at 600 °C and 900 °C in vacuum and their thermal stability is discussed.

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F2-6 Mechanical Properties of Multilayered NbMoTaW Alloy Films with Cyclic Gradient Concentration*, Y. Chen,* ***Chun-Yen Chen (lover0614revol@gmail.com)***, National Taiwan Ocean University, Taiwan

Conventional High-entropy alloy films have been fabricated through sputtering using a target of multi-principal-element materials with equal proportions in chemical compositions. In this study, NbMoTaW alloy films were prepared using a four-gun cosputtering apparatus with four pure-element targets. Moreover, the rotation speeds of the substrate holder were controlled at 1–30 rpm, which resulted in that the films exhibited a multilayer structure stacked with cyclic gradient concentration. The uniformity of the multilayered alloy films was improved with increasing the substrate holder rotation speed. The mechanical properties and crystalline phases of the NbMoTaW alloy films were investigated. The results indicated that the NbMoTaW alloy films prepared with a substrate holder rotation speed of 30 rpm exhibited a single body centered cubic(bcc) phase, a hardness of 12.9 GPa, and a Young's modulus of 287 GPa. The phase evolved into a combination of plural bcc phases as the substrate holder rotation speed was decreased to 1–10 rpm. All the NbMoTaW alloy films exhibited a Young's modulus level of 282–289 GPa. The NbMoTaW alloy films prepared at 10 rpm exhibited a high hardness of 14.1 GPa.

F2-7 Unveiling Microplasticity Mechanisms in Metallic Glasses with the Help of Polymer-supported Thin Films*, **Oleksandr Glushko (oleksandr.glushko@unileoben.ac.at)**,* Montanuniversität Leoben, Leoben, Austria*; C. Mitterer, J. Eckert,* Montanuniversität Leoben, Austria

The main, if not only, mechanism of plastic deformation in metallic glasses is *shear banding* – formation of strongly localized bands with high shear displacement within them. Despite at least a decade of intense research, shear bands are still not fully understood. This unfortunate situation can be explained by the fact that shear banding is a very fast kinetic process which can hardly be temporally resolved in an in-situ experiment. Additionally, the high amount of elastic energy which is released upon shear band propagation leads to catastrophic fracture of free-standing tensile samples through propagation of a single shear band across the whole specimen. Here, we use polymer-supported thin film metallic glasses (TFMGs) to capture the dynamics of shear bands under tensile loading.

By means of in-situ resistance measurements, in-situ optical microscopy as well as quasi-in-situ SEM and FIB characterization, different stages of evolution of shear bands and cracks with increasing strain are detected and described. Two distinct types of shear bands appear in polymer-supported $Pd_{80}Si_{20}$ and $Au_{60}Ag_{20}Si_{20}$ (deposited by co-sputtering) TFMGs with increasing strain: (i) the "out-of-plane" shear bands (the direction of shear is not in the film plane) which are formed at about 2% strain and develop quickly into through-thickness cracks and (ii) in-plane shear bands (the direction of shear is within the film plane) which appear after crack density saturation (at about 10% strain) and do not lead to crack formation. If the film thickness is reduced below 15 nm, the formation of shear bands is suppressed and the film can deform up to strains of about 6% elasto-plastically (i.e. without cracking) showing formation of homogeneously distributed short nanocracks at higher strains [1]. It is demonstrated, that with increasing applied strain, new in-plane shear bands can easily intersect the existing ones, whereupon the intersected shear bands become inactive and cannot carry further plastic deformation. This mechanism can lead to effective strain hardening of metallic glasses. Not intersected shear bands are shown to be softer than the non-deformed matrix and the deformation is localized there if the sample is unloaded and re-loaded.

Presented results demonstrate that formation of shear bands of specific type in thin film metallic glasses under tensile loading does not always lead to film failure. The "only" problem is to learn how to promote formation of favorable shear bands and suppress formation of unfavorable shear bands.

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F2-8 Phase Formation and Structural Properties of AlSiTaTiZr Multicomponent Thin Film Alloys*, **Felipe Cemin (lipecemin@gmail.com)**, M. Jimenez,* UNICAMP, Brazil*; L. Leidens,* Universidade de Caxias do Sul, Brazil*; R. Merlo,* UNICAMP, Brazil*; C. Figueroa,* Universidade de Caxias do Sul, Brazil*; F. Alvarez,* UNICAMP, Brazil

The increasing demand for advanced materials combining unique and unusual properties has encouraged the study of new multicomponent alloys. High entropy alloys (HEA) were originally designed as simple solid-solution structures composed of at least five principal elements (3d transition metals) in near-equiatomic composition, yielding exceptional mechanical properties. In recent years, the field has grown to include refractory and noble metals as well as low-density elements. Moreover, these alloys now include intermetallic phases, ceramic compounds, thin films, architected microlattices, *etc*. When considering HEA thin layers composed by functional elements such as Ti, W, and Zr, the as-deposited product is often amorphous (or nanocrystalline), due to the relatively large atomic size difference (resulting in sluggish diffusion) and ‘rapid quenching’ effect in sputtering deposition, prompting glassy metal formation.

In the pursuit of understanding these new materials in the non-bulk, thin film form, we have investigated key parameters leading to film crystallization and phase formation in an AlSiTaTiZr multicomponent system, due to its potential application in the field of high-temperature, oxidation-resistant coating materials. Therefore, metallic films were grown by radio-frequency magnetron sputtering at different deposition conditions with the goal to tune adatom diffusivity, grain nucleation, and ultimately the microstructure and properties of the films. Although the deposition method is essentially controlled by kinetic factors, thermodynamic calculations can help to predict possible phase formation. Therefore, thermodynamic simulations using the CALPHAD method were employed in post-annealed samples. The chemical composition of the films was controlled by proper designing of a sectioned, circular target containing slices (“pizza shaped target”) of different elements. This approach differs from most of strategies using powder targets or co-deposition methods (multiple metal targets). The chemical bonds were analyzed by XPS revealing the presence of silicides and aluminades of the transition metals in both amorphous and crystalline metallic samples. Moreover, a microstructural characterization was performed using XRD and AFM. Post-thermal annealing prompts the metallic glass structure into a complex crystalline structure of several coexistent compounds, expected by thermodynamic calculations. Special focus is given to the entropy and enthalpy role on the phase formation and stability.

F2-9 XPS Core-Level Shifts, Local Lattice Distortions and Charge Transfer in HfNbTiVZr Refractory High Entropy Alloy, ***Luis Casillas-Trujillo (luis.casillas.trujillo@liu.se)***, Linköping University, IFM, Sweden; *B. Osinger, R. Lindblad, D. Karlsson, S. Fritze, K. von Fieandt,* Uppsala University, Angstrom Laboratory, Sweden; *B. Alling,* Linköping University, IFM, Sweden; *U. Jansson,* Uppsala University, Angstrom Laboratory, Sweden; *I. Abrikosov,* Linköping University, IFM, Sweden; *E. Lewin,* Uppsala University, Angstrom Laboratory, Sweden

Ab-initio simulations of HfNbTiVZr high-entropy alloy using density functional theory (DFT) have been combined with experimental studies of the thin film material using X-ray photoelectron spectroscopy (XPS) to investigate lattice distortions, charge transfer and XPS core level shifts in the alloy. The lattice distortions obtained from the DFT simulations show that the size mismatch among the constituent elements is reduced in the alloy, causing a considerable reduction of the assumed lattice distortion effect commonly estimated with metallic radii. We show that this size reduction is due to the charge redistribution caused by the different local chemical environments, which was evaluated using a fixed sphere model that compared the relaxed, non-relaxed, and elemental reference structures. Finally, the theoretical core level shifts (CLS) values calculated from the DFT-simulated high entropy alloy show good agreement with the experimentally observed core level binding energy shifts, as well as peak broadening due to a range of chemical surroundings obtained by XPS measurements of a thin film deposited by sputter deposition.

New Horizons in Coatings and Thin Films
Room On Demand - Session F3

2D Materials: Synthesis, Characterization, and Applications

F3-1 Low-Temperature Synthesis of Vertically Standing Graphene by Microwave-Chemical Vapour Deposition, *I. Vasconcelos Joviano dos Santos,* ***Justyna Kulczyk-Malecka (J.Kulczyk-Malecka@mmu.ac.uk),*** *S. Rowley-Neale, C. Banks, P. Kelly,* Manchester Metropolitan University, UK

Graphene is the most commonly studied 2D material due to its exceptional physical and chemical properties, originating from its atomic structure. However, the successful graphene applications are driven by the ability to synthesise it at high growth rates and low temperatures, which enable large-scale production on a variety of substrates. The synthesis of vertically standing graphene (VSG) is of particular interest due to its exposed sharp edges, non-stacking morphology and large surface-to-volume ratio, leading to advanced technological applications including sensors, flexible electronic devices and fuel cells. Plasma-enhanced chemical vapour deposition (PE-CVD) has emerged as a promising technique to synthesise graphene at lower temperatures. The plasma energy drives the CVD precursor decomposition and reaction kinetics, allowing better control over the deposition parameters that tailor graphene properties.

This study presents the growth of VSG on Si wafers in a single step process at relatively low temperatures (<300ºC). The samples were synthesised in a bespoke PE-CVD reactor, using a microwave (MW) source to decompose CH_4, H_2 and Ar gas mixtures, and drive the growth process without applying an additional heating source to the substrate. Deposition conditions, such as MW power, gas ratio, and substrate-to-plasma distance were studied to determine their significance on VSG growth, morphology and electrochemical performance. Samples were characterized by SEM, Raman and XPS, which confirmed the vertical nature and sp^2 hybridisation of the deposited graphene. Cyclic voltammetry (CV) was used to determine the intrinsic electrochemical properties of VSG, such as heterogeneous electron transfer coefficient (k^o) and the electroactive area (A_{active}). The VSG deposited in this study shows a large surface area, exposed sharp edges and non-stacking morphology. These characteristics are attractive for the development of energy generation and storage devices, such as fuel cells and super-capacitors.

F3-2 Better than Homoepitaxy? van der Waals Layer Assisted Growth of Thin Films, ***Koichi Tanaka (koichitanaka@ucla.edu),*** University of California Los Angeles, USA; *K. Hojo,* Nagoya University, Japan; *A. Deshpande, P. Arias, M. Liao, Y. Wang, H. Zaid, A. Aleman, M. Goorsky, S. Kodambaka,* University of California Los Angeles, USA

It is generally assumed, and often true, that homoepitaxy yields higher crystalline quality thin films than heteroepitaxy. Studies conducted nearly three decades ago have shown that layered materials, owing to weak van der Waals (vdW) bonding across the layers, can aid in heteroepitaxial growth of layered as well as non-layered materials. In the recent years, two-dimensional (2D) layered materials have been shown to promote 'remote epitaxy', where the 2D layer present at the substrate-film interface does not hinder the epitaxial registry between the film and the substrate. Here, we demonstrate that 2D hexagonal boron nitride (hBN, a = 0.250 nm and c = 0.667 nm) buffer layers improves the crystallinity of sputter-deposited thin films. We provide evidence for this phenomenon via heteroepitaxial growth of body centered cubic metal (Mo), hexagonal MoS_2, and trigonal Ta_2C thin films on hBN-covered $Al_2O_3(0001)$ substrates. Furthermore, our studies indicate that inserting hBN layers at regular intervals results in highly-0002-orientated growth and suppression of polycrystallinity in thicker Ta_2C films.

All our experiments are carried out in an ultra-high vacuum system equipped with facilities for direct current (dc) magnetron sputtering and chemical vapor deposition. hBN layers are grown on single-crystalline $Al_2O_3(0001)$ substrates via pyrolytic cracking of borazine. Mo and Ta_2C thin films are deposited, respectively, via sputtering of Mo and TaC targets in pure Ar discharges, while MoS_2 layers are grown by reactive sputtering of Mo target in Ar-H_2S gas mixtures. The as-deposited layers are characterized using x-ray diffraction (XRD), transmission electron microscopy (TEM), and x-ray photoelectron spectroscopy (XPS). We observe the growth of single-crystalline Mo(110), $MoS_2(0001)$, and $Ta_2C(0001)$ thin films with notable differences in all the layers deposited on hBN-covered Al_2O_3 (0001) compared to those grown on bare substrates: significantly stronger reflection intensities ω-2θ XRD scans with smaller full-width half maxima and observation of Laue oscillations around the primary peaks. Our results indicate that hBN layers enhance the crystallinity of sputter-deposited thin films.

F3-3 Graphene Deposition on Copper Using Concentrated Solar-Thermal Heating, ***Abdalla Alghfeli (alghfeli@g.ucla.edu),*** *M. Abuseada, T. Fisher,* University of California at Los Angeles, USA

Manufacturing processes are often highly energy-intensive, even when the energy is primarily used for simple heating processes. This energy tends to derive from local utilities, which currently employ a blend of sources ranging from fossil fuels to renewable wind and solar photovoltaics, among others. When the end manufacturing need is thermal energy, direct solar-thermal capture provides a compelling option, but one that has rarely been employed to date. Here, we report a solar-thermal process using a simulated solar concentrator to demonstrate the ability of such a source to produce a high-value product, namely graphene on copper. Material deposition occurs at a surface and requires knowledge of material science, manufacturing, and heat transfer modeling. In this study, we employ a 10 kW_e concentrated solar source (solar simulator) capable of producing an adjustable high heat flux distribution (up to 4.5 MW/m^2, or 4,500 suns) in order to produce graphene rapidly on copper foil by chemical vapor deposition. The custom-built reactor consists of a xenon short arc lamp (that closely approximates the solar spectrum) placed at a truncated reflector’s first focal point to concentrate source radiation with a

Lorentzian-like heat flux distribution on the reflector's second focal point. Through the use of a controllable DC power supply and shutter, incident heat flux can be controlled and varied. Copper substrates are placed on a well-insulated mount that allows for varying the substrate's focal position, and hence heat flux distribution. We use the concentrated solar source to study the effect of heating and photocatalysis on the deposition product, and we begin to optimize the process by modeling substrate heat transfer processes that depend highly on optical and local thermal conditions. The process is monitored by optical emission spectroscopy, including an IR camera, pyrometer, and near-IR spectrometer, to determine appropriate gas recipes (flowrate and relative concentrations of methane and hydrogen) and other operating conditions, such as vacuum pressure, that yield high-quality product. The graphene produced through this process is further analyzed with scanning electron and Raman microscopy to assess the uniformity of graphene deposition as well as its quality, which is associated with the intensity ratio between Raman peaks of C-C in-plane vibrations and graphene lattice defects. Upon optimizing the operating conditions, graphene deposition will be extended to a larger and continuous scale through the use of a roll-to-roll solar chemical vapor deposition.

New Horizons in Coatings and Thin Films
Room On Demand - Session FP

New Horizons in Coatings and Thin Films (Symposium F) Poster Session

FP-1 Optical, Structural and Morphological Properties of NiO_X Thin Films Obtained by E-Beam*, Jhonathan Castillo* ***(jhonathan.castillo@uabc.edu.mx)*****,** Universidad Autónoma de Baja California, Colombia*; N. Nedev,* Universidad Autónoma de Baja California, Bulgaria*; B. Valdez,* Universidad Autónoma de Baja California, Mexico*; M. Bernechea,* University of Zaragoza, Spain*; M. Mendivil,* Centro de Investigación en Materiales Avanzados (CIMAV, Mexico*; M. Curiel,* Universidad Autónoma de Baja California, Mexico

Non stoichiometric nickel oxide (NiO_x) is a transparent conductive oxide (TCO) that has attracted a lot of attention because of its electrical and optical properties.Most of the available TCOs are n-type semiconductors, while NiO_x is a promising p-type candidate because of its excellent chemical stability and optical transparency. Some potential optoelectronic applications of NiO_x are as a p-type channel in transparent thin film transistors (TFTs) and as a hole transport layer in organic or quantum dot solar cells solar. In this work thin NiO_x films were obtained by thermal oxidation of ~20 nm thick Ni films deposited by electron beam evaporation. The films were deposited on glass substrates with size of 2.5×2.5 cm and n-type <100> silicon wafers. The oxidation process was carried out at 400, 500 and 600°C.

All samples were characterized by transmission electron microscopy, scanning electron microscopy, atomic force microscopy, X-ray photoelectron spectroscopy, UV-Vis spectroscopy, X-ray diffraction and diffuse reflectance spectroscopy. Results for the obtained NiO_x films will be presented and a discussion of their possible application in TFTs and in solar cells as hole transport layers will be given.

Keywords: NiO_x, e-beam, thin films

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FP-2 Characterization and Photoluminescence of Al- and Ga-doped V_2O_5 Nanostructures Synthesized by Thermally Activated Process*, Chih-Chiang* ***Wang (twinbads@yahoo.com.tw)*****,** National Chung Hsing University, Taiwan*; C. Lu,* Chinese Culture University, Taiwan*; F. Shieu,* National Chung Hsing University, Taiwan*; H. Shih,* Chinese Culture University, Taiwan

V_2O_5 has an orthorhombic crystal structure, and narrow direct and indirect bandgaps of 2.4 and 2.0 eV. Its optoelectronic properties can be modified by adding various dopants, such as Ga, Al, and Nd, due to the formation of the defect-levels. The applications of V_2O_5 are widely used in gas sensors, catalysts, and electrochromic devices. In this study, Al- and Ga-doped V_2O_5 nanostructures were fabricated by the thermally activated process at 850°C via the V-S mechanism. The Raman and XRD patterns have showed the typical V_2O_5 orthorhombic crystal structures of Al- and Ga-doped V_2O_5. The variations of c/a and c/b ratios estimated from the XRD patterns confirmed the substitutions of the Al^{3+} and Ga^{3+} into the V^{5+} lattice sites. HRTEM images showed that the growth direction of Al- and Ga-doped V_2O_5 nanostructures were along the [110] direction. The XPS results for the Al-doped V_2O_5, metallic Al was formed inside the nanostructure and the amorphous Al-O and Al-OH phases were generated on the nanostructure surface; for the Ga-doped V_2O_5, Ga-O phase was formed in the V_2O_5 nanostructures. PL spectra showed the increasing intensities in blue (1.94 eV) and green (1.77 eV) emissions of the V_2O_5 nanostructures while the Ga dopant was in 0.5 wt.%, which can be contributed to the formation of and -defects; the Al dopant showed a decreasing intensities in blue (1.94 eV) and green (1.77 eV) emissions of the V_2O_5 while the adding of Al, which can be attributed to the formation of the metallic Al inside the V_2O_5 nanostructures. This study showed that the photoluminescence properties of V_2O_5 nanostructures can be modified by the dopants of Al and Ga. The Al dopants revealed a significantly suppressing effect while starting the addition of Al, and the Ga showed an enhancing effect while the Ga contents were in 0.5 wt.%.

FP-3 On the Grain Size Dependence on Film Thickness*, Dulmaa Altangerel* ***(dulmaa.altangerel@ugent.be)****, R. Dedoncker, F. Cougnon, D. Depla,* Ghent University, Belgium

A meta-analysis of published data in combination with measurements on Al, Cu, CuO, CrCoFeMnNi, $Ni_{90}Cr_{10}$, TiN, and V sputter deposited thin films, permits to demonstrate that the grain size-thickness correlation can be described by a power law. The exponent depends on the homologous temperature which is defined as the ratio between the deposition and the melting temperature of the studied material. The exponent is close to 0.4 at a homologous temperature between approximately 0.15 and 0.3. Theoretical film growth models that depict an evolutionary overgrowth mechanism obtain the same exponent. Above a homologous temperature of approximately 0.3, a slightly higher exponent is observed which agrees with the general idea that at higher homologous temperatures the grain size is also influenced by restructuring mechanisms occurring during film growth. The exponent becomes substantially lower at low homologous temperatures (<0.15). From a theoretical point of view its value should be close to zero. The aforementioned boundaries of the homologous temperatures corresponds with those observed in published structure zone models which describe the microstructure of physical vapor deposited thin films. The good agreement suggests that the underlying reason for the observed boundaries is the atom mobility. This hypothesis was further investigated by a study on the influence of intentionally added impurities on the power law behavior for Al and Cu thin films. A decrease of the grain size is observed for both materials when the impurity-to-metal flux ratio is increased. No change of the exponent is observed for Al, while for Cu the exponent becomes equal to zero at sufficiently high impurity-to-metal flux ratios.

FP-4 Structural and Photoluminescence Properties of ZnO Nanorods Grown on Various TCO Seed Layers by Chemical Bath Deposition*,* ***Tomoaki Terasako (terasako.tomoaki.mz@ehime-u.ac.jp)****, K. Hamamoto,* Ehime University, Japan*; M. Yagi,* National Institute of Technology (KOSEN), Kagawa College, Japan*; Y. Furubayashi, T. Yamamoto,* Research Institute, Kochi University of Technology, Japan

Zinc oxide (ZnO) with a wide band gap (E_g) of ~3.37 eV and a large exciton binding energy of ~60 meV has received much attention because of its wide range of applications. The use of quasi-one-dimensional (1D) nanostructures, such as nanowires, nanorods (NRs) and nanobelts, in ZnO based gas-sensing devices and photodetectors is expected to be effective for achieving higher performance. Among various methods for preparing the 1D-ZnO nanostructures, we have paid our attention to chemical bath deposition (CBD) because this is usually performed at low temperatures (<100 °C), which allows us to use polymers as substrate materials. In this paper, the influences of the difference in seed layer on the structutral and photoluminescence properties will be discussed.

The ZnO NRs layers were grown on ion-plated ZnO:Ga (IP-GZO), SnO_2:F (FTO) and In_2O_3:Sn (ITO) seed layers, by CBD using the mixed aqueous solutions of $Zn(NH_3)_2 \cdot 6H_2O$ (ZnNit) and $C_6H_{12}N_4$ (HMT). Both the concentrations of ZnNit and of HMT were varied in the range of 0.025-0.075 M. Bath temperature was kept at ~86 °C. Growth time was varied in the range from 30 to 180 min.

SEM observations revealed that the vertically aligned NRs were successfully grown on the IP-GZO seed layers. After the growth time of 60 min, their average diameter and length tended to be saturated at 80 and 600 nm, respectively. On the other hand, on the FTO and ITO seed layers, many NRs were inclined with respect to the the seed layer surface. Both the average widths and lengths of the NRs grown on the FTO and ITO seed layers were lager than those on the IP-GZO seed layers and became lager with the growth time.

All the photoluminescence (PL) spectra were composed of a near-band-edge (NBE) emmission at ~380 nm and an orange band (OB) emission at ~600 nm. Regardless of the difference in seed layer, PL intensity ratio of the NBE emission to the OB emissin (I_{NBE}/I_{OB}) became larger with the increase in the average width of the NRs. There is a possibility that the reduction of the band bending formed at the NR surafce contributes to the increse in I_{NBE}/I_{OB} with increasing the average width of the NRs [1,2].

This work was supported by JSPS KAKENHI Grant Number JP17K04989.

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FP-5 Superior Hydrophilicity in a Magnetron Sputtered Fe-Cr-Ni Thin Film With Nano-Pyramid Surface Structure*, **Pak Man Yiu (pmyiu@mail.ntust.edu.tw)**, J. You, S. Wang, J. Chu,* National Taiwan University of Science and Technology, Taiwan

In this study we sputter deposited a Fe-Cr-Ni alloy film using SUS316 stainless steel as the target material. We deposited the film across a range of argon working pressure from 3 mTorr to 12 mTorr, and thickness ranged from ~200 nm to 1200 nm. Water contact angle of each specimen was measured. We found that the film surface showed a gradual transition from hydrophobic to hydrophilic behavior as the working pressure increased. At 12 mTorr / 1200 nm thickness the water contact angle measured was as low as ~20 degrees. We investigated the surface morphology with AFM and SEM, the images revealed that the specimens with high hydrophilicity possess a nano-pyramid structure, consisted of fibrous grains with a pyramid-like tip.

FP-6 Synergistic Effect of Ultra-thin Ag Film Coupled ITO Sandwich Structures*, **Ying-Jie Gao (www25635179@gmail.com)**, H. Song, W. Wu,* Da-Yeh University, Taiwan

With the fast developments in modern optoelectronic devices including organic light emitting diodes (OLEDs), light-emitting diodes (LEDs), solar cells, and touch screens, the demand of flexible transparent conductive oxide (TCO) is increased. Tin-doped indium oxide (ITO) is most widely adopted because of its high optical transparency and electrical conductivity. For TCO on flexible electronic device, manufacturing challenges such as processing temperature, annealing temperature, total film thickness, and film stress become crucial.

High-power impulse magnetron sputtering, (HiPIMS) technology exhibits a high plasma density and target ionization rate through a duty cycle of less than 5 % and high peak power. Compared with traditional magnetron sputtering technology, the HiPIMS-deposited film has a higher density, adhesion, flatness, and processing temperature below 100 °C. HiPIMS has several advantages for the deposition of TCO structures on polyethylene terephthalate, (PET) and polyethylene naphthalate, (PEN) substrates because of the low heat resistance of the flexible substrate. Due to ITO alone can not fully meet the demand for flexible electronic devices, various materials or structure design have been developed. Among them, the sheet resistance was effectively reduced by stacking the oxide and ultrathin metal film to form a sandwich structure of oxide/metal/oxide (OMO). The ultrathin metal film provides a continuous electronic conduction and the upper and lower oxide layer provide anti-reflection effect and increases transmittance.

In this study, sandwich ITO/Ag/ITO structure have been prepared onto 1.2 mm thick soda lime glass, (SLG) substrates, flexible polymer substrates including PET and PEN using HiPIMS technology after investigating the single layer of Ag and ITO. Through the optical simulation and the thickness optimization, the synergistic effect of ultra-thin Ag film Coupled ITO sandwich structures was studied. The flexible sandwich ITO/Ag/ITO structure in our study gives a sheet resistance of less than 10 Ω/sq, a resistivity of less than 10^{-5} Ω·cm, and an average visible light transmittance of more than 80 %.

Keyword：ITO、HiPIMS、TCO、OMO

FP-7 Development of Hydrogen Barrier Coatings based on Tungsten-doped Alloys*, **Issam Lakdhar (issam.lakdhar@utt.fr)**, A. Alhussein,* Université de Technologie de Troyes (UTT), France*; J. Creus,* LASIE, CNRS-Université de La Rochelle, France

Hydrogen energy, classified as one of the cleanest energy sources, developed in the industrial countries around the world presents a substitution for oil and other fuels [1]. However, the transport and the storage of the smallest chemical element at ambient conditions still a crucial issue because hydrogen can dissolve then permeate in any metallic material and cause its embrittlement and failure (pipelines, tanks). The coating barriers are an effective and practical option to reduce hydrogen permeation. In general, two crucial parameters govern the process of hydrogen permeability: the diffusion coefficient and solubility. Some bulk materials have a low hydrogen permeability in particular W, Mo, Ti, Ni and ceramics [2].

This work focuses on the development of hydrogen barriers based on tungsten-alloy thin films (ternary alloys Al-Ti-W/Ti-W-N) and alternative multilayers (Al-Ti-W/Ti-N-W) elaborated with physical vapor deposition technology in presence of plasma environment. According to some specifications, protective coatings must be dense and without defects. The optimization of elaboration parameters was necessary to obtain good films. Many characterizations were carried out (SEM, XRD, Scratch and Nano-indentation…). The coating efficiency was evaluated under hydrogen by chemical and electrochemical charging and the hydrogen quantity absorbed was determined with analytical and experimental methods (Thermal-Desorption Spectroscopy (TDS).

The mechanical characterizations (tensile and fatigue tests) are performed to evaluated the real behavior of a coated structure under hydrogen[3]. The coating performance as a barrier will be compared with other films reported in the literature and should allow us to continue our development for advanced coatings to increase the life duration of structures under hydrogen.

Keywords: Thin films, Barrier coatings, Hydrogen industry, PVD plasma technology, Electrochemical and mechanical properties.

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FP-8 Structure and Mechanical Properties of ZrB_{2+x} and $ZrAlB_{2+x}$ Hard Coatings*, **Tomáš Fiantok (tomasfiantok1@gmail.com)**, T. Roch, M. Truchlý,* Comenius University in Bratislava, Slovakia*; P. Švec,* Slovak Academy of Sciences, Slovakia*; M. Zahoran, M. Mikula,* Comenius University in Bratislava, Slovakia

Transition metal diborides (TMB_2) of the IVB to VIB group are in the form of films, attractive for use in the mechanical engineering industry due to their high temperature stability, excellent mechanical properties, in particular high hardness, and wear resistance. Here, we present two approaches to influencing stoichiometry, structure and mechanical properties of the perspective ZrB_{2+x}. In the first approach, we focus our efforts on investigating the effect of the amount of Ar particles and their energy on the sputtering of a stoichiometric ZrB_2 target resulting in a change in the character of the growing films. Using High Target Utilization Sputtering (HiTUS), where it is possible to influence the energy of target bombarding Ar particles (target voltage) at their constant amount (constant target current), we have grown nanocrystalline ZrB_{2+x} films over a wide concentration range (x ~ 2.4 ÷ 3.2). The highest hardness of 44.6 ± 2.0 GPa and the lowest hardness of 35.9 ± 1.0 GPa were achieved for $ZrB_{2.39}$ and $ZrB_{3.2}$, respectively. The films have a brittle character, expressed by the high Young's modulus, with the highest value of 446.0 ± 11.6 GPa for $ZrB_{2.39}$.

In the second approach we focused on investigating thermally-induced changes in the structure and mechanical properties of ZrB_{2+x} films alloyed with aluminium. The ternary system Zr-Al-B_{2+x} was prepared by magnetron sputtering of sintered $ZrAlB_2$ target with aluminium content 10 at.%. The idea is based on the theoretical prediction of B. Alling et al. [1] who, based on the different bulk moduli and volume misfits of the binary constituents ZrB_2 and AlB_2, predict that Zr-Al-B_2 is a metastable system with a tendency to spinodal decomposition during annealing. This phase separation can be accompanied by age hardening, similar to the known Ti-Al-N system. Here, we have grown Zr-Al-B_{2+x} films containing approximately 5 at.% Al, where the B/Zr ratio is approx. 2.6. The films have a hexagonal highly orientated (0001) structure. The addition of aluminium to the films reduces the hardness to 28.8 ± 1.0 and the Young's modulus to 335.6 ± 6.4 GPa. Subsequently, the annealed Zr-Al-B_{2+x} films are investigated by wave-dispersive x-ray spectroscopy (WDS), x-ray diffraction (XRD), transmission electron microscopy (TEM) and nanoindentation measurements. The experiments are supported by density functional theory (DFT) calculations.

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FP-10 Fabrication of Nanocomposite Thin Films of Metallic Nano Particles in Amorphous Carbon*, **Stephen Muhl (muhl@unam.mx)**, F. Maya,* Universidad Nacional Autónoma de México, México*; S. Rodil,* Universidad Nacional Autónoma de México, México*; R. Calderon,* Universidad Nacional Autónoma de México, México*; A. Perez,* Unidad de Investigación y Desarrollo Tecnológico (UIDT-CCADET), Hospital General de México, México

A new planar hollow cathode design based on a combination of a toroidal electrode and the gas flow sputtering source has been developed; the Toroidal Planar Hollow Cathode (TPHC). Here a resonant discharge occurs between the upper and lower electrode surfaces and the only way that electrons can leave the discharge is via the upper or lower aperture in these electrodes. We have used the system to deposit bismuth and aluminium based thin films and nanoparticles as a function of the experimental parameters. The cathode can be operated from 1 few militorr up to >5 torr. The deposition rate is mainly dependent on the plasma power and gas pressure, and to some extent on the gas flow. The size of the nanoparticles mainly depends on the gas pressure and plasma power. Nanocomposite coatings have been made by using the plasma plume at the exit of the TPHC to remotely decompose acetylene or methane and deposit a combination of the nanoparticles and an a-C:H film. We report that the distribution of the nanoparticles is uniform throughout the thickness of the deposit, and the density of nanoparticles in the nanocomposite can be easily controlled.

FP-11 Growth and Characterization of Ga_2O_3/Ag-Cu /Ga_2O_3 Multilayers by High Power Impulse Magnetron Sputtering*, **Shih-Hsin Lin (jimmylin344@gmail.com)**, W. Wu, D. Wuu, J. Chiang, H. Sung,* Da-Yeh University, Taiwan

High-energy ultraviolet radiation (λ <300 nm) is widely used for surface sterilization of surface, static water, and flowing water. In the past, mercury lamps have always been the only choice for ultraviolet radiation sources, but due to the "Minamata Convention on Mercury", it will be restricted internationally in the future. Therefore, ultraviolet radiation emitting device have become the most potential substitute. The UV device must use transparent conductive electrode materials to prevent electrodes from covered light-emitting elements. However, the most commonly used indium tin oxide (ITO) has a very serious absorption problem at UV. Therefore, reducing the Ultraviolet radiation-absorbing transparent conductive oxide (Transparent Conductive Oxide, TCO) is one of the key technologies to effectively improve component efficiency. Gallium oxide (Ga_2O_3) has a very wide band gap (4.87 eV) and has excellent transmittance in the shorter wavelength UVC (100~280 nm). However, the wide band gap also led to electrical performance almost insulating in Ga_2O_3. According to many literature studies, sheet resistance could be effectively reduced by using a multilayer OMO (Oxide/Metal/Oxide) stacking method. Moreover, an ultrathin metal film has a certain degree of transmittance in UV and visible spectrum. Therefore, developing Ga_2O_3/Metal/ Ga_2O_3 nano-multilayer film structure as the TCO electrode for the UVC element is necessary.

In this work, the use of HiPIMS co-sputter deposition of Ag-Cu alloy structure reduce the island growth of pure metal thin films and further improve the performance of OMO multilayer film. The dense and continuous ultra-thin metal film improves the optical and electrical properties of the overall structure of the OMO. By fixing the power of Ag and adjusting the current of Cu, various composition of Ag-Cu film was deposit for investigating the influence of the concentration of Cu on the sheet resistance and optical transmittance continuity of the ulta-thin metal film.

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