New Horizons in Coatings and Thin Films
Room Town & Country B - Session F5-MoM

Machine Learning and Process Modeling for Coating Design and Production

Moderators: Adam Obrusnik, PlasmaSolve s.r.o., Czechia, **Ferenc Tasnadi**, Linköping University, Sweden, **Petr Zikán**, PlasmaSolve s.r.o., Czechia

10:00am **F5-MoM-1 Thin Film Process Modeling at Different Scales - from Kinetic Simulation to Digital Twin*, Andreas Pflug,*** Fraunhofer Institute for Surface Engineering and Thin Films IST, Germany **INVITED**

Modern products require coating stacks with increased complexity and precision as well as improved throughput, reproducibility and environmental footprint. Simulation is a valuable asset to reach these goals by modelling deposition reactor dynamics as well as thin film growth on atomistic level.

The various physical scales of thin film deposition can be addressed by either model-driven or data-driven codes. The first category is based on physically accurate models, that need only few unknown internal parameters but require high computational power. Examples are the Direct Simulation Monte Carlo (DSMC) and Particle-in-Cell Monte-Carlo (PIC-MC) methods for description of gas flow and plasma processes at low pressure and Molecular Dynamics (MD) or kinetic Monte Carlo (kMC) methods for modeling atomistic processes in thin film growth. Despite of their high computational demand, these methods are useful for getting insights into the functionality of novel deposition setups and plasma sources.

A complementary approach uses data-driven simulation codes, which are based on simplified, semi-empirical models or machine learning methods. On the one hand, they need a significant amount of internal data in order to be adjusted to represent specific process conditions, on the other hand they usually require only low computational power, which enables to do parameter optimization or use them as real-time capable digital twins for model-based in-situ process control.

This talk shows various examples for model-based simulation of PVD processes. Furthermore, it demonstrates how to use data obtained by physical modeling in order to create a digital twin for prediction of the coating uniformity on 3D substrates in a sputter reactor for optical coatings.

10:40am **F5-MoM-3 Coater-Scale Model of DC Magnetron Sputtering*, Andrej Roštek,*** Masaryk University / PlasmaSolve s.r.o., Czechia*; P. Zikán,* PlasmaSolve s.r.o., Czechia*; J. Tungli,* Masaryk University, Czechia*; A. Obrusník,* PlasmaSolve s.r.o., Czechia

Magnetron sputtering is a widely used technique for the deposition of metal and compound layers for numerous technical applications. However, optimizing a sputtering process is a challenging task, especially since each industrial customer has specific requirements and expectations.

In order to improve properties of deposited coatings it is essential to understand the physics influencing them. Since the physical processes in magnetron sputtering are complex, it is often necessary to employ computer simulations. There has been a lot of work done in this regard [1-3], however, the simulations typically focused only on one part of a sputtering process, such as target erosion, sputtered atom transport, or the discharge properties.

This contribution attempts to provide a bigger picture by creating a coater-scale model which is a combination of two sub-models: (1) The bulk plasma model, which is a fluid model describing the plasma between the target and the substrate. It mostly affects ion bombardment. (2) The cathode plasma model, which is a particle-based model where ions and electrons are traced in the electric and magnetic field in the close vicinity of the target where the plasma sheath resides. This model affects mostly the target erosion. Its implementation is similar to our previous model from [4].

Together, these two models provide insight into various phenomena such as ion flux distribution, which determines target erosion, and the magnitude of ion bombardment at the substrates, which is a key determiner of the coating performance properties (residual stress, hardness, composition). Moreover, parametric studies can be performed so that the influence of pressure, substrate bias voltage, position of the electrodes, and others can be studied.

This model will be validated against experimental data.

References:

[1] C. Feist, A. Plankensteiner, J. Winkler *Studying Target Erosion in Planar Sputtering Magnetrons Using a Discrete Model for Energetic Electrons*Proceedings of the Conference: COMSOL, 2013

[2] S. Mahieu et al. *Monte Carlo simulation of the transport of atoms in DC magnetron sputtering* Nucl. Instrum. Methods Phys. Res. B, 243 (2), 2006, 313-319

[3] E. Shidoji, N. Nakano, T. Makabe *Numerical simulation of the discharge in d.c. magnetron sputtering* Thin Solid Films, 351 (1–2), 1999, 37-41

[4] A. Rostek *Simulating ion flux to 3D parts in vacuum arc coating: Investigating effect of part size using novel particle-based model* Surf. Coat. Technol., 449, 2022, 128954

11:00am **F5-MoM-4 High-Throughput Simulations to Predict History Dependence of Feedback Control During Reactive Magnetron Sputtering*, Josja Van Bever*,** *K. Strijckmans, D. Depla,* Ghent University, Belgium

Feedback process control [1] of reactive sputtering is often required to achieve specific thin film properties. Although conceptually simple, it is far from trivial to make it reliable and reproducible. Two major problems can be identified.

First, depending on the initial state of the process two S-shaped process curves can be obtained under certain conditions [1]. Many suggestions have been made for the observation of this “*double hysteresis phenomenon*" such as target erosion, chamber heating, or anode effects. But even when these effects are excluded, the phenomenon can still be observed (figure 1) [2]. Hence it seems to be of a fundamental nature. Independently of the experimental observations, the simulation of the processes at the cathode facing the gas discharge led to the prediction of a double hysteresis [3].

Secondly, the *convergence of the feedback process* strongly depends on the history of the target process. Simulation of the transient target states may therefore also assists to improve this convergence.

In the first part of the presentation we present *high-throughput simulations* for double hysteresis behavior as a function of different process and material parameters [4, 5]. *New measures* are introduced that characterize the hysteresis with a single number and that vary in a continuous way as a function of these parameters. This allows us to *elucidate the nature of the double valued state during feedback control* and to explain for which materials and under which conditions this behavior is expected to occur (figures 2 and 3) [4].

In the second part we discuss the *application of this analysis* to feedback measurements of aluminum. A correct preparation of the target subsurface can speed up the feedback process and a *first direct proof of double hysteresis during feedback control* is delivered. Next, the measures from the high-throughput simulations are applied to investigate the role of diffusion [6] on the double valued nature of the process conditions achieved during feedback control.

Additional figures and references are found in the supplementary material.

11:20am **F5-MoM-5 Evatec Fabric – a Thin-Film Process and -Metrology Data Tracking System for Large-Scale, Automated Data Analysis in R&D Labs*, Clemens Nyffeler*,** *O. Rattunde, D. Jaeger, H. Zangerle, R. Gmuender,* Evatec AG, Switzerland

Managing data in an R&D lab is often tedious manual work and leads to heterogenous, incomplete data. To ensure reproducibility, information about experimental setups, process hardware, and -conditions, and sample pre-treatment, must be kept in addition to the primary results. Consolidating and harmonizing datasets for large-scale, overarching data science projects constitutes a substantial additional effort.

At Evatec we developed a system, designed to automate these things in the specific context of thin film process development and verification. Substrate information, hardware configuration, process log-data, and measurement results are linked together based on wafer-ID.

In contrast to traditional manufacturing execution systems (MES), the *Evatec Fabric* can dynamically reconstruct the chronology of events for each wafer without need to define a process flow in advance. This allows our scientists and engineers a wide degree of flexibility in carrying out their work.

A data-processing component, programmed in python, uses various algorithms, models, and data-fitting techniques to process the raw data, produced by process systems and metrology instruments. It extracts useful parameters and statistics that are stored in a highly structured and contextualized way, enabling data science and machine learning projects based on clean, homogenous data.

11:40am **F5-MoM-6 Predicting Reactive PVD Processes Using Global Process Modeling – a Physics-Based Alternative to Machine Learning**, ***Petr Zikán**, A. Obrusnik,* PlasmaSolve s.r.o., Czechia

Developing, transferring, or troubleshooting reactive PVD processes has always been a challenge. This can be partly attributed to the non-linear behavior of these processes. Additionally, the fundamental variables that drive the physics (e.g., plasma density and potential, the energy of sputtered and ionic species, …) are hard to measure, thus, often unknown in practice.

Another typical challenge is the number of consistent experiments available about the process. Experiments and their analysis are expensive and time-consuming. It is not uncommon that there are only a few (< 10) experiments available. This is the main limitation of machine-learning methods as these require large data sets (> 100).

In this contribution, we describe an alternative, physics-based approach that works well even with a low number of experiments. We illustrate that it is possible to formulate such a model for a whole coater that is either free of fitting parameters or contains only a few of them and they have a clear physical meaning. These models additionally contain coefficients, such as pumping speed, sputtering yields, or effective coating areas. These parameters are either known (pumping speed), can be obtained from the literature (sputtering yields), or can be pre-computed using 2D or 3D simulations (effective coating areas) for the coater and loading at hand.

Once created, such a model can reproduce the material composition across coaters and coater conditions with the accuracy of a few atomic percent. By correlating the process model outputs with literature data, the tool can also make predictions about the performance parameters of the coating (e.g., hardness). The approach will be illustrated in the case of nitride- or carbide-based ceramic coatings.

The specific global process model being discussed is not a simulation tool only but also an analytical tool in the sense that it works with a coater log at the input and combines machine log analytics with simulation data. As of submitting this abstract, the tool was already leveraged in five projects aimed either at process transfer between coaters (R&D scale) or achieving better process reproducibility (at MP-scale).

12:00pm **F5-MoM-7 Structure and Crystallographic Properties of Multi-Material Coatings Deposited in a Combinatorial Sputter Plant Compared to Simulations from the Machine Level to Microstructure**, ***David Böhm**,* TU Wien, Austria*; T. Schrefl,* Danube University Krems, Austria*; A. Eder,* MIBA High Tech Coatings GmbH, Austria*; C. Eisenmenger-Sittner,* TU Wien, Austria

Structure and crystallographic properties of multi-material thin films can be described with an interactive ray tracing software that simulates film deposition in arbitrary sputtering geometries, the so-called Virtual Machine (VM). Although based on a line-of-sight model, the VM also takes into account the decay of the flux density of the particles due to gas phase scattering. To further enhance the prediction capabilities of the VM a microstructure simulation package, based on rate equations and on the Potts Modell, was built.

At the machine level the VM recreates a real combinatorial DC-sputter plant from 3D models including the static arrangement of multiple targets, the substrate and eventual obstacles, as well as dynamics like e. g. rotating substrate holders. For the deposition process, individual sample points can be defined on the substrate to which the line-of-sight model is applied, taking kinematics into account. The resulting thickness and sequence of the layers is used to visualize the thickness-resolved composition. Post-processing the time dependent thickness and temperature data the crystallographic phases with their associated XRD patterns are calculated from a library of binary phase diagrams for the simulated film.

Applying the rate-equation model to a generated layer architecture the microstructure can be calculated. First it is decided whether Frank-van-der-Merwe (continuous layer) or Volmer-Weber growth (island layer) occurs. The distribution of islands follows a thermodynamic equilibrium approach, which considers the process of island formation while minimizing the free energy of the island surface. The crystallite structure of the matrix material surrounding the islands is calculated by a spatially scaled Potts Modell. The Monte Carlo simulator is initialized with a crystallite structure generated using the Voronoi construction of the crystallite density determined from empirical data using rate equations.

Since volume diffusion is not yet considered, only immiscible multilayer systems can be investigated at present. On the basis of examples, the above-mentioned comparisons are presented.

New Horizons in Coatings and Thin Films
Room Town & Country C - Session F3-TuA

2D Materials: Synthesis, Characterization, and Applications

Moderators: Ying-Hao Chu, National Tsing Hua University, Taiwan , **Chih-Yen Chen**, National Sun Yat-sen University, Taiwan , **Yi-Cheng Chen**, National Tsing Hua University, Taiwan

1:40pm **F3-TuA-1 Tellurene Electronics and Sensors*, Wenzhuo Wu,*** Purdue University, USA **INVITED**

Emerging technologies such as distributed computing and the internet of things (IoT) necessitate the implementation of high-speed, energy-efficient devices. Various technological paths are being actively pursued to synthesize and integrate high-performance channel materials for these applications. Specifically, 2D semiconductors have been intensely explored as promising channel materials for related ultra-scaled technologies. However, there has been a lack of synthetic strategies for the scalable, substrate-agnostic production of large-area, high-quality 2D crystals with a low thermal budget for back-end-of-line (BEOL) compatible applications. In this talk, I will discuss our recent progress in the scalable nanomanufacturing of tellurene, an emerging 2D multifunctional material pioneered by my group, for high-performance nanoelectronics and optoelectronics applications. Our results show that the air-stable tellurene exhibits a plethora of intriguing properties appealing for applications in electronics, optoelectronics, energy, sensors, and quantum devices.

2:20pm **F3-TuA-3 Phase/Structure-Engineered Two-Dimensional Layered Materials for Innovative Nanoelectronics*, Yu-Lun Chueh,*** National Tsing Hua University, Taiwan **INVITED**

Novel condensed matter systems can be understood as new compositions of elements or old materials in new forms. According to the definition, various new condensed matter systems have been developed or are under development in recent years. 2D layered materials, including graphene and transition metal dichalcogenides (TMDs) allow the scaling down to atomically thin thicknesses and possess unique physical properties under dimensionality confinement. The chemical vapor deposition (CVD) process is the most popular approach for all kinds of 2D materials due to its high yield and quality. Nevertheless, the need for high temperature and the relatively long process time within each cycle hinders commercial development in terms of production cost. However, the transfer procedure has become one of the major limitations of the overall performance. In my talk,an inductively coupled plasma (ICP) was used to synthesize Transition Metal Dichalcogenides (TMDs) through a plasma-assisted selenization process of metal oxide (MO_x) at a low temperature. Compared to other CVD processes, ICP facilitates the decomposition of the precursors at lower temperatures.We create the phase/structure-engineered-1T/2H 3D-hierarchical 2D materials derived from the MOx 3D-hierarchical nanostructures through a low-temperature plasma-assisted selenization process with controlled shapes grown by a glancing angle deposition system (GLAD). The applications, including (1) water splitting, (2) gas sensors, (3) batteries, and (4) resistive change memory, will be reported.

3:00pm **F3-TuA-5 Tellurene-Based Wearable Biosensor for Real-Time Longitudinal Monitoring of Neurotransmitters in Human Sweat*, Ruifang Zhang*, *W. Wu,*** Purdue University, USA

Metabolic biomarkers provide direct indicators of physical and mental health status. However, the state-of-the-art tools for monitoring metabolites in body fluids are expensive, time-consuming, and often require invasive procedures to collect the samples. Non-invasive wearable sensors for monitoring metabolites in sweat, the most accessible human secretion, are promising alternatives to costly diagnostic tools. Moreover, existing wearable sensors have limited sensitivity, selectivity, and lifetime for measuring disease-specific metabolic markers (e.g., neurotransmitters) from human sweat. Wearable sweat sensors that can monitor the dynamics of neurotransmitters directly from human sweat have yet to be developed. Here, the applicant reports a wearable biosensor based on tellurene that can enable, for the first time, the selective and sensitive longitudinal quantification of dopamine (DA) and norepinephrine (NE) concentrations in real human sweat. The applicant also evaluated and validated the concentrations of neurotransmitters in human sweat using high-performance liquid chromatography/mass spectrometry (HPLC/MS) for the first time. This research could create unprecedented diagnostic tools for improving the experience and outcomes of patient care. The development of non-invasive wearable sensors capable of longitudinal measurement of disease-specific metabolic markers from sweat will positively impact erroneous or delayed diagnoses, enable affordable and ubiquitous diagnostic tools, and foster data-driven precise mobile health monitoring with translational applications in patient care and beyond.

4:00pm **F3-TuA-8 A Two-Dimensional $Ti_3C_2T_x$ MXene/Mesochannel Ionic Diode Membrane for High-Performance Osmotic Energy Harvesting*, Wen-Hsin Hung,*** National Taiwan University of Science and Technology, Taiwan*; C. Chu,* Feng Chia University, Taiwan*; L. Yeh,* National Taiwan University of Science and Technology, Taiwan

Osmotic energy has attracted explosive attention in recent year because of its advantages of clean and sustainable. Osmotic energy can be harvested via the reverse electrodialysis technique and it can convert chemical potential stored in an ionic concentration gradient into an electrical energy by using an ion-selective membrane. The osmotic power generation, however, is still restrained due to the inherently limited ion flux in such a small nanochannel. Here, we report a subnano-on-meso architecture (named as MXene@MC), realized by deposition of an ultrathin layer of two-dimensional $Ti_3C_2T_x$ MXene on a single conical PET mesochannel (MC) (Fig. 1). The introduction of the asymmetries in pore geometry gives the MXene@MC outstanding ion current rectification property, which can amplify ionic current at a degree of up to 25.6 times (Fig. 2). We therefore probe the application of the subnano-on-meso ionic diode device in osmotic energy harvesting. The results show that a single MXene@MC can achieve a record osmotic power as high as 343 pW at a 1000-fold KCl gradient, exceeding all the state-of-the-art single-pore devices (Fig. 3).We expect that this study can provide an emerging platform towards high-performance osmotic energy generator.

4:20pm **F3-TuA-9 Discussion on the Growth Parameters and Oxygen Evolution Reaction Performance of Copper Sulfide*, Li-Wen Lin*, *C. Chen,*** Department of Materials and Optoelectronic Science, National Sun Yat-Sen University, Taiwan

With the advancement of science and technology, energy demand is increasing day by day. People began to look for alternative energy sources in order to solve the problem of insufficient energy. Hydrogen fuel cells have become one of the most notable research projects because of their environmentally friendly and renewable characteristics. One of the cleanest ways to generate hydrogen is through electrochemical water splitting, which can be divided into two parts: Hydrogen evolution reaction (HER) at cathode and oxygen evolution reaction (OER) at anode. Among them, OER is known to be more complicated and thus became the biggest hinder to water splitting.

In this work, Cu_2S microplates were successfully synthesized with non-toxic chemicals via a one-step solvothermal method. The as-prepared samples were then applied as working electrodes for OER electrochemical measurements. The results turned out that the as-prepared Cu_2S/CF electrodes have excellent OER performances with a low overpotential of 269.2 mV (at a current density of 10 mA cm^{-2}) and a Tafel slope of 102.1 mV dec^{-1}. These outstanding results indicated that Cu_2S microplates could be developed as excellent OER electrocatalysts.

4:40pm **F3-TuA-10 Cation and Anion Co-Doped Iron Oxide Toward Efficient Hydrogen Peroxide Formation and Electro-Fenton Degradation of Organic Pollutant*, Yemima Purba*, *J. Ting,*** National Cheng Kung University (NCKU) Tainan, Taiwan

Nowadays, electrochemical advanced oxidation processes, Fenton process, have attracted a lot of attention as compared to conventional degradation. Regarding the Fenton catalyst, iron oxide has been known as an efficient catalyst and demonstrated in degradation of organic pollutants. The metal doping into iron oxides has been shown to enhance the degradation rate due to rich redox reactions. However, there are only a few studies on the anion doping. It is known that anion doping is able to enhance the electrical conductivity of the oxide. In this study, novel cation and anion co-doped iron oxide has been firstly demonstrated for electron-Fenton catalyst. The synergistic effect of cation and anion doping is favorable to improve the selectivity of hydrogen peroxide, which thus can be utilized for electro-Fenton degradation of organic pollutants. The electro-Fenton degradation performance has been evaluated through degradation of tetracycline at different conditions. At the optimized condition, the obtained material generates hydrogen peroxide and tetracycline degradation efficiency of 98% within 2-h. This novel oxide catalyst can be regarded as a promising catalyst for wastewater treatment.

5:00pm **F3-TuA-11 Molten Salt Synthesis of Highly Dispersible Hexagonal Boron Nitride Nanosheets for Ultrafiltration***, **Neon Vicente III Rosell,*** National Cheng Kung University (NCKU), Taiwan, Philippines*; K. Chang,* National Cheng Kung University (NCKU), Taiwan

Hexagonal boron nitride (hBN) is a key material analogue for graphene. It is best known for its use by industry as a chemically-inert, refractory material for use in harsh environments. Conversely, it is this same robustness that make it difficult for researchers to synthesize hBN in the lab without the use of exotic setups and reagents. Molten salt synthesis affords researchers a facile method to synthesize quantitative amounts of hBN for research. In this research, hBN was synthesized in a LiCl-KCl molten salt eutectic at 900°C under nitrogen atmosphere. Boric acid and melamine were used as the boron and nitrogen source respectively. Recovery of bulk hBN from the cooled melt was done with washing with deionized water and centrifugation. The resulting powders were then subjected to materials characterizations such as XRD, FT-IR, Raman, and TEM-EELS that confirm the synthesis of hBN powders. The resulting powders has been shown to have high dispersibilty in water when subjected to exfoliation techniques such as ultrasonication. This hBN dispersion was then used as basis for an ultrafiltration membrane that demonstrates excellent separation efficiency for organic dyes (i.e. Rhodamine B, Methylene Blue, Methyl Orange). Regeneration of this ultrafiltration membrane has been demonstrated through the use of advanced oxidation processes where either exposure to hydrogen peroxide solutions, or decoration of P25 titania nanoparticles was used under xenon lamp illumination.

New Horizons in Coatings and Thin Films
Room Pacific E - Session F4-1-WeA

Boron-Containing Coatings I

Moderators: Marcus Hans, RWTH Aachen University, Germany, **Helmut Riedl**, TU Wien, Institute of Materials Science and Technology, Austria, **Johanna Rosén**, Linköping University, Sweden

2:00pm **F4-1-WeA-1 Improving the Oxidation Resistance of TiB_2 Coatings by TM-silicide Alloying (TM = Ti, Ta, Mo)***, Ahmed Bahr*[1]*, O. Beck, T. Glechner, A. Grimmer, T. Wojcik, P. Kutrowatz,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; J. Ramm, O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S. Kolozsvári, P. Polcik,* Plansee Composite Materials GmbH, Germany*; E. Ntemou, D. Primetzhofer,* Department of Physics and Astronomy, Uppsala University, Sweden*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

TiB_2 is considered a promising candidate among the family of transition metal diborides (TMB_2) to be applied in several high-performance applications under extreme conditions. In particular, the unique strength of TiB_2 is based on its high melting temperature (~3225 °C), high thermal shock resistance, and chemical inertness. However, the wide applicability of TiB_2 as a protective coating is still limited due to its poor high-temperature oxidation resistance by forming volatile, non-protective Ti- and B-based oxide scales. Si-alloying of TMB_2 provides a successful route to enhance the high-temperature oxidation resistance up to 1200 °C [1, 2]. Yet, the high Si content usually leads to the deterioration of the mechanical properties of these films [3].

Here, we investigated new alloying routes for sputtered TiB_2 coatings based on $TMSi_2$ secondary phases (TM = Ti, Ta, Mo) for achieving the challenging compromise between good mechanical properties and high oxidation resistance. We employed DC magnetron sputtering technique to synthesize TiB_2 alloyed coatings with different $TMSi_2$ phases from compound targets. The alloyed coatings were characterized in terms of chemical composition, phase constitution, and mechanical properties using high-resolution characterization techniques.Moreover, the oxidation kinetics within the alloyed Ti-(TM)-Si-B were studied at different temperature regimes up to 1400 °C, accompanied with detailed morphological characterization of oxide scales formed.

Keywords: Diborides; TiB_2; PVD; Protective Coatings; Oxidation; Mechanical Properties;

[1] T. Glechner, H.G. Oemer, T. Wojcik, M. Weiss, A. Limbeck, J. Ramm, P. Polcik, H. Riedl,Influence of Si on the oxidation behavior of TM-Si-B2±z coatings (TM = Ti, Cr, Hf, Ta, W), Surf. Coat. Technol., (2022) 128178.

[2] T. Glechner, A. Bahr, R. Hahn, T. Wojcik, M. Heller, A. Kirnbauer, J. Ramm, S. Kolozsvari, P. Felfer, H. Riedl,High temperature oxidation resistance of physical vapor deposited Hf-Si-B2±z thin films, Corrosion Science, 205 (2022) 110413.

[3] B. Grančič, M. Mikula, T. Roch, P. Zeman, L. Satrapinskyy, M. Gregor, T. Plecenik, E. Dobročka, Z. Hájovská, M. Mičušík, A. Šatka, M. Zahoran, A. Plecenik, P. Kúš,Effect of Si addition on mechanical properties and high temperature oxidation resistance of Ti–B–Si hard coatings, Surface and Coatings Technology, 240 (2014) 48-54.

2:20pm **F4-1-WeA-2 Quaternary CrTaBN: Experimental and Theoretical Insights Into a Novel Coating Material with Promising Mechanical Properties and Exceptional Thermal Stability***, **Christina Kainz**,* Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leoben, Austria*; M. Tkadletz,* Department of Materials Science, Montanuniversität Leoben, Austria*; L. Patterer, D. Bogdanovski,* Materials Chemistry, RWTH Aachen University, Germany*; H. Krüger,* Institute of Mineralogy and Petrography, University of Innsbruck, Austria*; A. Stark, N. Schell,* Institute of Materials Physics, Helmholtz-Zentrum Hereon, Germany*; I. Letofsky-Papst,* Institute for Electron Microscopy and Nanoanalysis and Center for Electron Microscopy, Austria*; M. Pohler, C. Czettl,* Ceratizit Austria GmbH, Austria*; J. Schneider,* Materials Chemistry, RWTH Aachen University, Germany*; C. Mitterer,* Department of Materials Science, Montanuniversität Leoben, Austria*; N. Schalk,* Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Austria **INVITED**

Owing to their combination of excellent thermal stability, outstanding oxidation resistance and beneficial mechanical properties, ternary CrTaN coatings have recently received increasing interest for use in demanding applications. Although the addition of B to ternary transition metal nitride coatings is an effective strategy to improve their mechanical properties and thermal stability, studies on quaternary CrTaBN coatings are not available in literature. The present work provides a comprehensive overview on the microstructure, phase composition and thermal stability of $Cr_{0.69}Ta_{0.20}B_{0.11}N$ coatings grown by cathodic arc evaporation. Lab–scale X–ray diffraction yielded only the fcc-$Cr_xTa_{1-x}N$ solid solution being present as crystalline phase of the coating. X–ray photoelectron spectroscopy, however, confirmed the presence of B–N bonds. A combination of atom probe tomography and transmission electron microscopy showed that B forms nanoscale segregations, which seem to be preferably located at the grain boundaries. The thermal stability of CrTaBN was investigated by complementary application of X-ray photoelectron spectroscopy, atom probe tomography and *in–situ* high–temperature synchrotron X-ray diffraction. Annealing the coating at 1000 °C provokes no change in the crystalline phase composition, but induces a reduction of the B content and the formation of B–metal bonds. These findings on phase composition and thermal stability of the coating were furthermore compared to density functional theory calculations. Finally, *in-situ* high–temperature synchrotron X-ray diffraction and nanoindentation confirmed that CrTaBN allows for an exceptional oxidation resistance up to 1100 °C with simultaneous high hardness (32±2 GPa). The thorough investigation of phase composition and microstructure of CrTaBN at ambient and elevated temperatures provides the basis for a fundamental understanding of this novel coating system.

3:00pm **F4-1-WeA-4 Transition Metal Diboride Superlattices: Combination of *Ab Initio* and Experimental Approach for Investigation of Ceramic Thin Films with Improved Ductility and Fracture Toughness***, **Tomáš Fiantok**,* Comenius University, Slovakia*; N. Koutná,* Linköping University, IFM, Sweden*; V. Šroba,* Comenius University, Slovakia*; M. Meindlhumer,* Austrian Academy of Sciences, Austria*; T. Roch, M. Truchlý, M. Vidiš, L. Satrapinskyy, M. Gocník,* Comenius University, Slovakia*; D. G. Sangiovanni,* Linköping University, IFM, Sweden*; M. Mikula,* Comenius University, Slovakia

Demanding high temperature mechanical applications create an opportunity to exploit the potential of transition metal diboride based thin films (TMB_2, TM = Sc, Ti, V, Cr, Y, Zr, Nb, Mo, Hf, Ta, W) due to their very high hardness and temperature stability. However, the industrial use of these materials is limited by their brittle behavior under high-temperature mechanical loads which results in the initiation and propagation of cracks leading to permanent failure.

One of the approaches to suppress the inherent brittleness of TM diboride films is the concept of superlattices (SL) – i.e., formation of alternating chemically and/or structurally modulated nanolayers. Such SL structures ensure efficient dissipation of accumulated energy in the vicinity of an already formed crack due to its deflection, blunting and stopping at the interface between the flexible and stiff layers.

In our work, using density functional theory (DFT) calculations, we predict the structural stability and theoretical ductility of 184 TMB_2 SL systems, where we search for suitable candidates exhibiting improved fracture toughness.

In the next step, we experimentally focus on the magnetron co-sputtered TiB_2 – TaB_2 films with different bi-layer period where we performed micromechanical bending tests on the film cantilevers which confirmed the

[1] **Graduate Student Award Finalist**

positive superlattice effect on improving the fracture resistance. In addition, for a more detailed explanation of the obtained results, the films are investigated using X-ray diffraction, and transmission electron microscopy. Mechanical properties (hardness and indentation modulus) are measured by nanoindentation techniques.

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The calculations were carried out using the resources by the Swedish National Infrastructure for Computing (SNIC)—partially funded by the Swedish Research Council through Grant Agreement (VR-2015-04630)—on the Clusters located at the National Supercomputer Centre (NSC) in Linköping"

3:20pm **F4-1-WeA-5 Tissue Phase Affected Fracture Toughness of Nano-Columnar TiB_{2+z} Thin Films***, **Anna Hirle**, C. Fuger, R. Hahn, T. Wojcik, P. Kutrowatz,* Christian Doppler Laboratory for Surface Engineering of High-performance Components, TU Wien, Austria*; M. Weiss,* Institute of Chemical Technologies and Analytics, TU Wien, A-1060 Vienna, Austria*; O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, 9496 Balzers, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, D-86983 Lechbruck am See, Germany*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of High-performance Components, TU Wien, Austria

Despite being intensively investigated and already established in industry as protective coatings for aluminium machining [1] or diffusion barriers [2], Titanium-Diboride (TiB_2) is still not fully understood. In particular, for the fracture behaviour and the corresponding material characteristic (intrinsic fracture toughness, K_{IC}) the literature presents only little descriptions. So far it is known that the mechanical properties (H and E) of TiB_2 are highly dependent on the crystal orientation [3] and the amount of tissue phase present [4], which in turn can be influenced by the choice of coating parameters. To figure out, if this also affects the fracture behaviour, we synthesized a broad stoichiometric variation from $TiB_{2.07}$ up to $TiB_{4.42}$ by DC magnetron sputtering and thoroughly determined their structural, morphological and mechanical properties. By using micro-mechanical test set-ups (in-situ microcantilever bending tests) the intrinsic fracture toughness was investigated in relation to the chemical and hence morphological variation. In addition, information about the stress states within the thin films were obtained by nanobeam (synchrotron) experiments. The presence of a B-rich tissue phase was confirmed by HR-TEM analysis, showing that the grain size is decreasing with increasing B content, which is accompanied by an increase in tissue phase fraction. The dominance of the tissue phase is progressing with increasing B, also forcing smaller column sizes (from ~10 to < 5 nm) [5]. A change in Boron content from $TiB_{2.22}$ to $TiB_{4.42}$ leads to a decrease in fracture toughness from 3.55 ± 0.16 MPa√m to 2.51 ± 0.14 MPa√m of these superhard films. In summary, this study underlines the influence of stoichiometry and the potential of tissue phase engineering on the mechanical properties of TiB_{2+z} based thin films.

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3:40pm **F4-1-WeA-6 Characterization of Ti-Al-La-B-N Hard Coating and Cutting Tool Application***, **Shin Takayama**, T. Ishigaki, M. Takahashi,* Mitsubishi Materials Corporation, Japan **INVITED**

Current machining applications require new developments in the field of hard coatings to achieve excellent precision and effective processes. TiAlN thin films are well established due to their good thermo-mechanical properties. Recently, we reported TiAlLaBN films by sputtering. In the report the addition of La into the TiAlN lattice was shown to increase film hardness and H/E which correlates with film toughness. The microstructure of the film composes fine grain crystals with a size of 5 nm. However, the relationship between the microstructure of the TiAlLaBN film and its mechanical properties is still unclear. It is necessary to understand the relationship to maximize the cutting performance. The microstructure of the film can be varied by changing the deposition rate. Increasing the deposition rate may change the crystal grain size, leading to coarse grain microstructure. In this study, we investigate the changes in microstructure and mechanical properties by changing the deposition rate in order to improve the cutting performance.

Two different deposition approaches of sputtering and CAE (Cathodic Arc Evaporation) were used for changing the deposition rate. Ti-Al alloy added with 2 mol% LaB_6 was used as metal target. So as to prepare the metal target including unstable La, it was stabilized by combining with boron to form the LaB_6 compound. The deposition rate in CAE was 144 nm/min which was faster than in sputtering, 104nm/min. From the cross-sectional SEM observation and TEM images, the TiAlLaBN film of 144 nm/min was found to be a fine columnar structure with a width of 10 nm and length of 30 nm. The film hardness H and H/E of the fine-grained TiAlLaBN were H=40.1 GPa and H/E=0.095, then those of columnar structure were H=35.3 GPa and H/E=0.096, where E is elastic modulus. Both increased compared to H=31.3 GPa and H/E=0.065 for conventional TiAlN by CAE. The hardness of the TiAlLaBN film with fine-grained structure was found to be larger than that of columnar structure, while film toughness H/E was almost the same regardless of their different structures.

Milling cutting performance of TiAlLaBN with columnar structure was evaluated on ductile cast iron that was widely used for automobile parts. The TiAlLaBN with columnar structure showed 1.25 times better performance than TiAlN by CAE. The observation of the cutting edges indicated that TiAlLaBN with columnar structure reduces crack damage on the rake face by 20%. This is because the addition of La improves the film toughness and oxidation resistance. TiAlLaBN coatings deposited by stabilization with boron is expected to be an important material for future cutting.

4:20pm **F4-1-WeA-8 Mechanical Properties and Thermal Stability of ZrBSiTaN Films***, **Kuo-Hong Yeh**,* National Taiwan Ocean University, Taiwan*; L. Chang,* Ming Chi University of Technology, Taiwan*; Y. Chen,* National Taiwan Ocean University, Taiwan

ZrBSiTaN films were fabricated on silicon and AISI 420 stainless steel substrates through direct current magnetron co-sputtering. ZrB_2, Ta, and Si targets were used. The power applied on the Si target and the nitrogen flow ratio of the reactive gas were the variables in the sputtering processes. The effects of Si and N contents on the mechanical properties and thermal stability of ZrBSiTaN films were investigated. The results indicated that all the as-deposited ZrBSiTaN films formed amorphous structures. The supplement of reactive gas with a nitrogen flow ratio of 0.4 resulted in that the ZrBSiTaN films exhibited a high N content of 60 at.%. The increase of Si content from 0 to 42 at.% in ZrBSiTa films decreased the hardness and Young's modulus values from 19.1 to 14.3 GPa and 264 to 242 GPa, respectively, whereas the increase of Si content from 0 to 21 at.% in ZrBSiTaN films increased the hardness and Young's modulus values from 11.5 to 14.0 GPa and 207 to 218 GPa, respectively. The amorphous BN and SiN_x phases played the vital role in the variations of structural and mechanical properties of ZrBSiTaN films. The thermal stability test was conducted at 800 °C for 10 min within purged Ar gas in a rapid thermal annealing furnace. The ZrBSiTa films oxidized with the residual oxygen in the vacuumed furnace, which was accompanied with the formation of ZrO_2, Ta_2O_5, and $TaSi_2$ phases, whereas the ZrBSiTaN films maintained amorphous structures. Further exploration on the oxidation behavior of ZrBSiTaN films will be studied.

4:40pm **F4-1-WeA-9 Formation of Orthorhombic MAB Phase $Mo_{1-x}Cr_xAlB$ Solid Solution Thin Films***, **Peter J. Poellmann**, D. Bogdanovski, S. Lellig, M. Hans,* Materials Chemistry, RWTH Aachen University, Germany*; P. Schweizer,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; D. Holzapfel, P. Zoell, S. Karimi Aghda,* Materials Chemistry, RWTH Aachen University, Germany*; D. Primetzhofer,* Uppsala University, Angstrom Laboratory, Sweden*; S. Kolozsvári, P. Polcik,* Plansee Composite Materials GmbH, Germany*; J. Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; J. Schneider,* Materials Chemistry, RWTH Aachen University, Germany

$Mo_{1-x}Cr_xAlB$ thin films were deposited by combinatorial magnetron sputtering at temperatures between 450 °C and 700 °C. Subsequent analysis by XRD, EDX, ERDA, and TEM revealed the compositional phase formation range to be between $0.38 \leq x \leq 0.76$ for orthorhombic MAB phase $Mo_{1-x}Cr_xAlB$, consistent with previous ab initio predictions, and can hence be rationalized by composition-induced changes in chemical bonding. For samples with lower x, the formation of Cr_2AlB_2, Cr_3AlB_4, and Cr_4AlB_6 side phases has been observed, again in accordance with theoretical and experimental literature data.

5:00pm **F4-1-WeA-10 Application of AlTiBN Coating for Cutting Tools for Exotic Materials Machining***, **Yuta Suzuki**, H. Kanaoka,* Sumitomo Electric Hardmetal Corporation, Japan

In recent years, the machining of difficult-to-cut materials, such as heat-resistant alloy and titanium alloy, has been increasing for aircraft, energy and medical markets. When cutting exotic alloys, the workpiece material is likely to adhere onto the cutting edge of a tool, resulting in a sudden fracture of the cutting edge of the tool. The tool life is significantly shorter than that of tools for cutting general steel. This study was intended to investigate the mechanical property and cutting performance of AlTiBN coating in order to solve the serious problems. AlTiBN coating was deposited on cemented carbide by arc ion plating method using nitrogen as reaction gas and Al-Ti-B alloys with B contents of 0, 2, 5 and 10 at. % were used as target materials. The mechanical properties of the coatings were measured by nano-indenter and the microstructure was evaluated by X-ray diffraction (XRD), Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM). The cutting performance was evaluated by milling test of Ni-based heat-resistant alloy, and then tool life and damage to the coating at the early stage of machining were evaluated.In conventional PVD coatings for cutting tools, Cr and Si has often been added to AlTiN in order to increase hardness and heat resistance, achieving high wear resistance. However, these methods increase hardness as well as Young’s modulus, which reduces toughness of coating. In heat-resistant alloy and Titanium alloy milling, coatings with a high Young’s modulus tends to develop internal cracks, leading to early destruction of the coatings. In this research, we developed an innovative coating with high hardness and low Young's modulus for difficult-to-cut materials milling. Optimizing B content of AlTiBN coating, we realized low Young's modulus of 504 GPa while maintaining high hardness of 38 GPa. This is probably because the pure AlTiN changed to a mixed crystal structure of cubic and hexagonal by the addition of B. When the cutting performance of this AlTiBN coating was evaluated in milling for Ni based super alloy, material equivalent to Inconel 718, it was found that internal cracks were suppressed at the initial stage of processing. As a result, cemented carbide tool with the AlTiBN coating achieved approximately 1.6 times longer tool life than that with B-free AlTiN coating. As described above, the AlTiBN film with high hardness and low Young's modulus has not only excellent wear resistance but also excellent toughness, so it is expected to contribute to the improvement of productivity in aircraft, energy and medical markets.

New Horizons in Coatings and Thin Films
Room Pacific E - Session F4-2-ThM

Boron-Containing Coatings II

Moderators: Marcus Hans, RWTH Aachen University, Germany, **Helmut Riedl**, TU Wien, Institute of Materials Science and Technology, Austria, **Johanna Rosén**, Linköping University, Sweden

8:40am **F4-2-ThM-3 Ternary Tungsten Boride Coatings with Improved Mechanical Properties Deposited by High-Power Pulsed Magnetron Sputtering from One Spark Plasma Sintered Target***, **Tomasz Mościcki**, R. Psiuk, J. Chrzanowska-Gizynska,* Institute of Fundamental Technological Research of Polish Academy of Science, Poland*; D. Garbiec,* Łukasiewicz Research Network – Poznań Institute of Technology, Poland **INVITED**

Today the deposition of protective coatings with magnetron sputtering is well known in scientific laboratories and in industry also. However, there is an increasing need to coat larger and heavier tools. Also, sometimes substrate materials shouldn't be deposited at temperature greater than 300˚C. This is a problem because some of novel materials like tungsten borides needs high substrate temperature (>400 ˚C) during deposition to obtain special mechanical properties. According to Thornton deposition model the deposition of films at lowered substrate temperature with exceptional mechanical properties (ZONE T) is possible by increasing of the energy of plasma. Such possibility gives a HIPIMS method. Additionally, this method allows to deposit defected by vacancies α-WB_2 structure which according to first-principles calculation possess exceptional mechanical properties.

In this presentation the influence of HIPIMS parameters like the pulse duration, frequency and power and also the bias voltage and substrate temperature on ternary tungsten borides films properties will be shown and discussed. The deposited at 350 ˚C coatings by High-Power Pulsed Magnetron Sputtering from one Spark Plasma Sintered W-Ti-B_{2-x} target are very hard (H>30 GPa) and possess high crack resistance. Additionally, they are thermally stable at temperature below 700 ˚C. The comparison between Titanium and Tantalum as a doping element will be presented also.

This work was financed by the National Centre for Research and Development (NCBR, Poland) under project no. TECHMATSTRATEGIII/0017/2019.

9:20am **F4-2-ThM-5 The Architectural Design of High-Temperature Protective Coatings: Improving the Oxidation Resistance of TMB_2 (TM = Hf, Ti, W) Thin Films***, **Sophie Richter**, T. Glechner, T. Wojcik,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; B. Widrig, O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S. Kolozsvári, P. Polcik,* Plansee Composite Materials GmbH, Germany*; J. Ramm,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; H. Riedl,* TU Wien, Institute of Materials Science and Technology, Austria

Transition metal (TM)-borides are well known for their high thermal stability, high melting points, and excellent mechanical properties such as high hardness and Young's modulus, making them suitable for a broad field of applications. However, TM-borides suffer from poor oxidation stability at high-temperature ranges. Therefore, improving the oxidation resistance is of great interest for coated high-performance components, where both – a combination of mechanical and oxidative resistance – are particularly desired.

Within this study an architectural approach to protect TMB_2 (TM = Hf, Ti, W) thin films from further oxidation is presented. For this purpose, different materials were investigated as protective layers on top of each boride system. The coatings have been deposited by PVD techniques. The phase formation, morphology, and mechanical properties (e.g., hardness and Young's modulus) of all as deposited thin films were determined using X-ray diffraction (XRD), scanning electron microscopy (SEM), and nanoindentation. Thermogravimetric analyses up to 1400 °C in synthetic air was utilized to investigate the barrier function of these coatings with respect to the underlying TMB_2 against oxidation. Subsequently, the long-term oxidation behavior of the synthesized films in ambient air at 1200 °C for 30 h was examined. In particular, the HfB_2 and TiB_2 systems were characterized by their oxidation resistance. High-resolution characterization techniques (i.e. TEM, HR-TEM, EDX) confirmed the good adhesion between the barrier top layers, as well as the unaffected diboride coatings and the sapphire substrates, respectively.

Keywords: Protective coatings; Oxidation resistance; High temperature; PVD; Borides;

9:40am **F4-2-ThM-6 Stoichiometry, Structure, and Mechanical Properties of Superhard Zirconium Diboride Films Prepared by the High-Power Impulse Magnetron Sputtering***, **Viktor Šroba**, K. Viskupová, T. Roch, L. Satrapinskyy, M. Truchlý, T. Fiantok,* Comenius University, Bratislava, Slovakia*; Š. Nagy,* Institute of Materials and Machine Mechanics SAS, Slovakia*; B. Grančič, P. Kúš, M. Mikula,* Comenius University, Bratislava, Slovakia

Diborides of refractory transition-metals (TMB_2) especially from IVB (ZrB_2, TiB_2) are thanks to their excellent mechanical properties like high hardness or wear resistance and high thermal stability, given by high melting temperatures (above 3000 °C), promising ceramic materials for applications in extreme environments. Magnetron sputtering of TM diboride films from compound target is accompanied by the different angular distribution of sputtered boron and metal atoms which leads to the growth of overstoichiometric films $TMB_{2+\Delta}$ (B/TM > 2), The films have a nanocomposite structure consisting of stoichiometric crystalline TMB_2 nanofilaments surrounded by an amorphous boron tissue phase. The presence and volume fraction of the boron tissue phase relative to the crystalline phase significantly determines the mechanical properties and affects behavior of the films during high-temperature exposure in a real environment. The progressive technology of high-power impulse magnetron sputtering (HiPIMS) using pulsed plasma discharges leads to the efficient ionization of the target atoms, whose flux and kinetic energy can then be controlled by appropriate synchronization with the pulsed negative substrate bias. In this way, a better control of the composition (B/TM) of the diboride films can be ensured, which then leads to the formation or absence of the boron tissue phase.

Here in this work, HiPIMS (Hipster 6, Sweden) with synchronized substrate bias is used to prepare ZrB_x films where changes in deposition parameters (pulse width, frequency, phase shift) on stoichiometry, formation of nanostructure and mechanical properties are investigated using X-ray diffraction, scanning and transmission electron microscopic and nanoindentation techniques. All ZrB_x films exhibit understoichiometric composition ratio of B/Zr which vary from 1.5 to 1.9. The films have a crystalline character identified as hexagonal α-ZrB_2. A deeper insight into nanostructure shows changes in nanocomposite character of the films. Hardness of ZrB_x films is up to ~ 45 GPa and indentation Young's modulus of ~ 430 GPa.

This work was supported by the Slovak Research and Development Agency (Grant No. APVV-21-0042) Scientific Grant Agency (Grant No. VEGA 1/0296/22), European Space Agency (ESA Contract No. ESA AO/1-10586/21/NL/SC), and Operational Program Integrated Infrastructure (Project No. ITMS 313011AUH4).

10:00am **F4-2-ThM-7 Exploring Phase Evolution and its Consequences on Mechanical Properties of a Novel HfB_2-AlB_2 Coating System***, **Samyukta Shrivastav**, D. Yun, K. Canova, J. Abelson, J. Krogstad,* University of Illinois at Urbana Champaign, USA

Thin films of ternary $Hf_xAl_{1-x}B_y$ were deposited using low temperature (200-300°C) chemical vapor deposition (CVD), using the precursors $Hf(BH_4)_4$ and AlH_3NMe_3.We hypothesized that the addition of Al would increase the oxidation resistance of HfB_y, which in the absence of Al oxidizes quickly at service temperatures of 700°C. One issue with aluminum alloying would be the formation of a soft phase that may deteriorate mechanical properties of the coating. Here, we report in detail on the phase and properties of $Hf_xAl_{1-x}B_y$ films. Due to the very low growth temperature, only ~ 0.09-0.1 on the homologous scale, it was not known whether the ternary films would be amorphous or crystalline, fully mixed or segregated, nonstoichiometric in B, or include elemental Al. We report that as-deposited $Hf_xAl_{1-x}B_y$ contains only metal diboride and that, remarkably, the films are nanocrystalline with grain sizes ~ 10 nm. This is in sharp contrast to as-deposited HfB_2, which is X-ray amorphous and has a metal sublattice density about half that of the crystalline phase. The concentration of aluminum is uniform throughout the coating thickness, indicating that the CVD reactions at the growth surface are kinetically in steady-state. We qualitatively evaluated the mechanical response using nanoindentation, to compare the effect of alloying on mechanical properties. AFM analysis of the indent on the as deposited $Hf_xAl_{1-x}B_y$ coatings shows elastic recovery, whereas HfB_2 exhibits considerable plastic response with outer pileup. These results show an improvement in mechanical response due to alloying, and negate the presence of a soft elemental Al phase.The improvement in mechanical properties could be due to the presence of an HfAlB ternary, which will be further explored using advanced chemical characterization techniques such as STEM-XEDS. We have also seen that the coatings form a uniform oxide at 700°C, and heat treatments do not seem to bring about any changes in microstructure and microscale phase segregations. We will also be showing our results for any nanoscale compositional fluctuations present due to heat treatments at 700°C, and the impact of such fluctuations and heat treatments on mechanical properties will also be demonstrated.

10:20am **F4-2-ThM-8 Challenges and Perspectives of Wear Resistant Boron-Containing Coatings***, **Jose L Endrino**,* Nano4energy SL, Spain*; J. Rao,* Cranfield University, UK*; T. Brzezinka,* Dell Technologies, UK*; A. Mendez, J. Santiago,* Nano4energy SL, Spain*; J. Molina,* Polythecnic University of Madrid, Spain **INVITED**

This invited talk will present two different cases studies related to the deposition of new generation of boron-containing coatings with highly ionized physical vapor deposition techniques such as filtered cathodic-arc evaporation and positive pulse high power impulse magnetron sputtering (HiPIMS). Although the deposition of boron-based compounds, brings in the prospect of hard coatings exhibiting very useful physical prospects, the brittle nature of borides, high melting points and characteristic compound formation introduces a unique set of challenges as well.

The first case study deals with the use of TiB2 for arc evaporation after first densifying its structure and adding non-metallic sinter additives such as C and TiSi2. Cylindrical cone-shaped cathode configuration is used and coating properties were compared to those obtained from monolithic TiB2 cathodes. Arc spots were found to stick at certain locations, leading to extensive local fracturing of the cathode. TiB2-C required the lowest current setting (40A) to trigger an arc and provided the best arc-spot stability and mobility. Carbon inclusions successfully prevented crack propagation, although they did not stop crack initiation, which resulted in high cathode flaking and poor target utilization. An appropriate distribution of magnetic fields from filtering and focusing coils was found to be essential for maintaining stable and mobile arc spots on TiB2-C and TiB2-TiSi2 cathodes.

The second case study deals with the optimization of nanostructured AlTiBN and AlCrBN coatings by tailoring metal ion fluxes and energies using HiPIMS with positive pulses. In this study, the formation of nanocrystalline grains embedded in an amorphous boron-rich phase provides enhanced toughness and wear resistance. Hardness up to 40 GPa were measured by nanoindentation techniques and high adhesion critical load values were obtained using nanoscratch testing.

11:00am **F4-2-ThM-10 TiB_X Thin Film Synthesis from an Industrial-Sized DC Vacuum Arc Source***, **Igor Zhirkov**, A. Petruhins, A. Shamshirgar,* Materials Design, Department of Physics, Chemistry and Biology (IFM), Linköping University, Sweden*; N. Hellgren,* Department of Computing, Mathematics, and Physics, Messiah University, USA*; S. Kolozsvári, P. Polcik,* PLANSEE Composite Materials GmbH, Germany*; J. Rosen,* Materials Design, Department of Physics, Chemistry and Biology (IFM), Linköping University, Sweden

Titanium diboride exhibits outstanding properties promising for the next generation of hard and wear resistant coatings. However, for efficient physical vapor deposition (PVD) through DC vacuum arc, the field is comparatively unexplored due to challenges associated with the materials synthesis process. It is well known that arc deposition allows synthesis of coatings with a deposition rate unreachable for any other PVD technique. This, in turn, can make DC arc deposition a preferred method for sustainable materials engineering, reducing the carbon footprint of the thin film industry. This motivates development and investigation of arc processes for TiB_2 synthesis. Furthermore, previously reported attempts of TiB_2 arc depositions from a TiB_2 cathode mentions process instability, cracking of the cathode, and intensive generation of macroparticles, which in turn limits an evaluation of the process efficiency. In this work, we show consistent analysis of the cathode surface, the plasma composition, the film composition (from XPS) and (micro-)structure (from SEM, XRD), as well analysis of collected macroparticles. The study is done with an industrial scale arc plasma source, Hauzer CARC+, which utilizes plane cathodes of 100 mm in diameter. The cathode weight loss, the amount of the generated droplets and the deposition rate is also measured as a function of process parameters (arc current and pressure). Furthermore, we also investigate tuning of the process efficiency by modifying the cathode composition. Plasma analysis shows average ion energies consistent with the velocity rule, around 115 and 25 eV for Ti and B, respectively. The plasma ion composition shows approximately 40 % Ti and 60 % B, while the deposited films are understoichiometric in B. The film hardness is found to be above 30 GPa for all shown samples. The deposition rate is around 100 nm/min, while the cathode weight loss is around 0.3 gram/min. Altogether, the results show potential for the use of cathodic arc as an efficient and useful method for synthesis of metal borides.

11:20am **F4-2-ThM-11 Oxidation Behavior of Stochiometric $Ti_{0.35}Al_{0.65}B_2$ Coatings***, **Sebastian Lellig**,* Materials Chemistry, RWTH Aachen University, Germany, and Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; A. Navidi Kashani,* Materials Chemistry, RWTH Aachen University, Germany*; P. Schweizer,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland, and Lawrence Berkeley Lab, USA*; M. Hans,* Materials Chemistry, RWTH Aachen University, Germany*; J. Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; J. Schneider,* Materials Chemistry, RWTH Aachen University, Germany

The oxidation resistance of stochiometric $Ti_{0.35}Al_{0.65}B_2$ coatings is investigated systematically in a TEM study at temperatures of 700 to 1000 °C and annealing times of 1, 4 and 8 h.
In the as deposited state, a native, amorphous aluminum oxide layer covers the surface as well as the grain boundaries of the lamellar structure. The oxidation behavior upon annealing is dominated by the formation of a partly amorphous and nanocrystalline aluminum oxide layer, whereby the crystallinity is increased with higher annealing temperatures. At higher temperatures, spinodal decomposition leads to the segregation of AlB_2 and TiB_2. Ti diffusion through AlB_2 regions is hindered due to the low solubility of Ti in AlB_2. Outdiffusion of Al from binary and ternary regions lead to a homogeneous concentration distribution over the whole film. Simultaneously, the diffusion of Al through the oxide layer is hindered by nanocrystalline and amorphous regions. At temperatures ≥ 920°C, it is evident that AlB_2 phase segregations decompose, whereby liquid Al is formed, leading to the disintegration of the film. It is reasonable to assume that the application temperature range of other AlB_2 segregation containing transition metal borides is restricted by the here identified decomposition process.

New Horizons in Coatings and Thin Films
Room Pacific E - Session F2-ThA

High Entropy and Other Multi-principal-element Materials

Moderators: Erik Lewin, Uppsala University, Sweden, **Jean-François Pierson**, IJL - Université de Lorraine, France

1:20pm **F2-ThA-1 Data Driven Methods Enable Rational Design of High Entropy Materials for Hydrogen Storage***, **Matthew Witman**, V. Stavila, M. Allendorf,* Sandia National Laboratories, USA **INVITED**

Data-driven modeling in recent years has ushered in a new paradigm for rapid discovery of useful materials across a plethora of domains in the physical and materials sciences. These methods become particularly invaluable when investigating applications of high-entropy materials, where the combinatorial growth of explorable chemical space makes brute-force experimentation or first-principles simulation intractable. To assess the primary figure(s) of merit for 10,000s of possible materials for a given application and down-select only top candidates for more rigorous examination, accurate and efficient machine learning and data-driven techniques are required. This talk will survey a variety of data-driven (high entropy) hydride discovery exemplars representing efforts between Sandia and a large international collaboration group. These range from traditional machine learning approaches for direct hydride thermodynamic property prediction to modern graph neural networks, trained as DFT surrogate models, that feed sampling-intensive first principles simulations. These modeling strategies can rapidly screen hydride thermodynamic properties and therefore experimentally target new materials or rationally tune existing ones for various hydrogen storage or compression use cases. Coupled with additional simple objectives (i.e., raw material costs), multi-dimensional Pareto optimal materials can therefore be identified, targeted, and synthesized.

2:00pm **F2-ThA-3 Effect of Mo Content on the Corrosion and Tribocorrosion Behavior of $(CoCrFeNi)_{100-x}Mo_x$ HEA Thin Films Deposited by HiPIMS***, **Alessandro Togni**, R. Tinazzi,* Department of Engineering "Enzo Ferrari", University of Modena and Reggio Emilia, Italy*; S. Deambrosis, E. Miorin, F. Montagner, C. Mortalò, V. Zin,* Institute of Condensed Matter Chemistry and Technologies for Energy, National Research Council, Italy*; G. Bolelli, L. Lusvarghi,* Department of Engineering "Enzo Ferrari", University of Modena and Reggio Emilia, Italy

Based on a multi-principal-element-design concept, high-entropy alloys (HEAs) feature enhanced mechanical strength, excellent thermal stability, and superior wear and corrosion resistance, making them promising candidates for applications in harsh environments. Moreover, the microstructure and properties of HEAs can be fine-tuned by changing their composition or by alloying them with additional elements, boosting their application potential even further. Therefore, HEA-based protective films with suitably designed compositions could improve the wear and corrosion resistance of low-cost substrate materials under various service conditions. In this work, $(CoCrFeNi)_{100-x}Mo_x$ HEA thin films were deposited on Si and AISI 304 stainless steel substrates by high-power impulse magnetron sputtering (HiPIMS) using pure Mo and equiatomic CoCrFeNi targets. The effect of Mo content on the microstructure, mechanical properties, and corrosion and tribocorrosion behavior of the films was investigated by adjusting the Mo target-to-substrate distance. Higher amounts of Mo favored the formation of a dense microstructure, resulting in higher hardness values. The potentiodynamic polarization curves revealed that the corrosion resistance of the films in 3.5 wt.% NaCl solution is not significantly affected by Mo concentration. Differences were found, however, in terms of tribocorrosion behavior. With increasing Mo content up to 12 at.%, the wear rate of the films gradually decreased. Above this value, further Mo addition resulted in increased material loss. The obtained results aim to contribute to a comprehensive understanding of the corrosion and tribocorrosion behavior of HEA thin films in artificial seawater to broaden their application in marine engineering.

2:20pm **F2-ThA-4 Corrosion Behavior of Sputter-Deposited CoCrNiFeAl High Entropy Alloy***, A. Korra,* University of Tennessee at Chattanooga, USA*; H. Raji,* Florida Institute of Technology, USA*; **Hamdy Ibrahim**,* University of Tennessee at Chattanooga, USA*; S. Saedi,* Florida Institute of Technology, USA

Multicomponent or High-entropy alloys (HEA) are the new generation of alloys with exceptional properties such as high strength and hardness, excellent thermal stability at high temperatures, and remarkably good fatigue. Recently HEA thin films have attracted significant attention due to their superior corrosion resistance and emerged as potential candidates to meet demanding requirements for selected extreme applications, particularly in the nuclear, turbine, and aerospace industries. Prominent advantages of HEAs are primarily derived from their ability to stabilize as a single-phase crystalline structure when specific alloy design criteria are met. HEA thin films have been fabricated using a wide range of technologies including laser cladding, arc cladding, electrodeposition [https://www.sciencedirect.com/topics/materials-science/electrodeposition], and spraying. However, magnetron sputtering is one of the most desirable fabrication methods due to lower growth temperatures, precise control, good film-forming ability, high efficiency, and good film adhesion. In this work, CoCrNiFeAl (at.%) was deposited by Radio Frequency (RF) magnetron sputtering to evaluate its corrosion behavior. While homogenization is a common post-processing treatment in metallurgy, the process for HEA can be entirely different from regular alloys due to the slow/sluggish diffusion and phase transformation rate in HEAs. To understand the effects of homogenization on the sputter target deposited HEAs, heat treatments in the range of 800-1100 °C were performed and the microstructure, phase stability, hardness, and corrosion behavior were investigated. While the results obtained from both Calphad modeling and experiments showed that homogenization is a strong mechanism for improving the corrosion resistance in HEA composition, it was also concluded that hominization temperature can play an important role in the formation of phases that can significantly deteriorate the corrosion resistance. The conclusion was drawn from the fact that lower homogenization temperatures led to the formation of an undesirable sigma phase in the microstructure that was decomposed to a secondary BCC single phase in the alloys treated at higher temperature ranges.

2:40pm **F2-ThA-5 Mechanical Properties of Low Density Ternary Titanium-rich Medium-entropy Alloy with Heterogeneous Structure***, **Che-Wei Chang**,* Department of Materials and Optoelectronic Science, National Sun Yat-sen University, Taiwan*; P. Chen, S. Jang,* Institute of Material Science and Engineering, National Central University, Taiwan*; C. Chen,* Department of Materials and Optoelectronic Science, National Sun Yat-sen University, Taiwan

At present, global warming is becoming more and more serious. We plan to reduce the weight of the material to reduce energy loss during transportation. Therefore, we expect the medium entropy alloy to have good mechanical properties, and it can also have low density characteristics, so we choose alloys to carry out. In follow-up studies, the mechanical properties of alloys have always been an important issue for researchers. It is well known that the strength and ductility of alloys compete with each other. It has been pointed out that the heterostructure allows alloys to exhibit good strength and ductility simultaneously. Therefore, we attach our alloys to rolling and annealing and expect to obtain a heterostructure. X-ray diffractometer (XRD) and electron backscatter diffractometer (EBSD) was used to observe the changes in crystal structure and microstructure of the alloy under different annealing time. Finally, we perform tensile tests to obtain the mechanical properties of the alloys and compare the microstructural evolution between them.

3:00pm **F2-ThA-6 Charge Transfer Effects in Multicomponent Materials – Shown by Ab-Initio Calculations and X-Ray Photoelectron Spectroscopy XPS***, **Barbara Osinger**,* Uppsala University, Angstrom Laboratory, Sweden*; L. Casillas-Trujillo,* Linköping University, Sweden*; R. Lindblad,* Uppsala University, Angstrom Laboratory, Sweden*; B. Alling,* Linköping University, Sweden*; U. Jansson,* Uppsala University, Angstrom Laboratory, Sweden*; I. Abrikosov,* Linköping University, Sweden*; E. Lewin,* Uppsala University, Angstrom Laboratory, Sweden

Multicomponent materials have opened a vast landscape for complex compositions and interesting properties. They exhibit complex bonding, due to their diverse chemical environment, as a result of the extensive alloying, typically involving 5 or more elements. Ab-initio calculations, using density functional theory (DFT) and X-ray photoelectron spectroscopy (XPS), were used to investigate the electronic structure of multicomponent thin films based on the HfNbTiVZr system. The charge transfer was evaluated theoretically using relaxed, non-relaxed, as well as elemental reference structures using a fixed sphere size model to quantify the charge transfer. High-resolution XPS spectra were obtained from HfNbTiVZr and (HfNbTiVZr)C magnetron sputtered thin films.

The HfNbTiVZr alloy shows core level binding energy shifts and peak broadening, compared with metal references, which are in good agreement with shifts calculated from DFT simulations, where charge transfer between the metal atoms is observed. The charge transfer follows the general electronegativity trend, and results in a reduced atomic size mismatch and lattice distortion δ, compared with estimates based on tabulated atomic radii. Similarly, the (HfNbTiVZr)C carbide films exhibit core level binding energy shifts and broadening effects, as a result of their complex chemical environment.

This study demonstrates the importance of chemical bonding and environment when discussing multicomponent materials. Moving beyond the concept of an ideal solid solution and considering the bonding in more detail opens up a deeper understanding and the possibility of tuning the electronic structure. This would be especially interesting for the design of multicomponent materials, as many desirable properties are a result of their bond character.

3:20pm **F2-ThA-7 Toughness Estimation of High Entropy Nitride Coatings by Tensile Testing**, ***Martin Kuczyk**, T. Krülle,* Technische Universität Dresden, Germany; *M. Zawischa, M. Leonhardt, O. Zimmer, J. Kaspar,* Fraunhofer IWS, Germany; *C. Leyens, M. Zimmermann,* Technische Universität Dresden, Germany

High Entropy Nitrides (HEN) are an interesting material system intended for sophisticated wear and high-temperature applications. Being closely linked to the group of so-called high entropy alloys, which were discovered independently by Cantor and Yeh in the early 2000s [1,2], they consist of five or more nitride-forming constituents in a near equimolar ratio as well as 50 at% nitrogen forming single-phased fcc microstructures. Multiple works have shown that through the use of HEN superior hardness close to or in some cases well into the superhard range (H > 40 GPa) can be achieved while also maintaining high thermal stability [3,4].

For the possible use as protective tool coatings, not only hardness and thermal stability are important factors but also toughness. A method that might be suitable for high throughput screening of coating toughness is tensile testing of coated substrates. The description of critical strains at which first cracks in the coating appear as well as the development of the crack density with increasing applied strain can be used to reasonably estimate coating toughness values.

In this work, three HEN coatings are compared to (AlTi)N via tensile testing. The three coatings are (AlCrTaTiZr)N, (AlCrNbSiTIV)N and (HfNbTaTiVZr)N and were chosen based on previous works of the author [4]. The applicability of that method for the screening of coating toughness is discussed by comparing the results with other more established methods for the estimation of fracture toughness such as micro-beam bending.

It could be shown that tensile testing is a feasible method for high throughput screening of coating toughness.

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3:40pm **F2-ThA-8 Synthesis and Characterisation of (Gd,Hf,Sc,Ti,Zr)-Oxide Coatings**, ***Alexander Kirnbauer**, E. Peck, M. Derflinger,* TU Wien, Institute of Materials Science and Technology, Austria; *P. Polcik,* Plansee Composite Materials GmbH, Germany; *P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

High-entropy alloys (HEAs) and high-entropy metal-sublattice ceramics (HESCs) have recently gained particular attraction in the field of materials research due to their promising properties, such as high hardness, high strength, and thermal stability. Especially oxides are of great interest as they can serve as oxidation protection coatings at high temperatures. A very common oxidation-protection coating is α-Al_2O_3, usually synthesised by chemical vapour deposition as very high temperatures are required to form the stable α form. Another interesting oxide for use at high temperatures is HfO_2 as it exhibits the highest melting point within the group of oxides besides Thorium oxide. As HfO_2 crystallises, similar to ZrO_2, in three different crystal structures, the desired cubic high-temperature modification is hard to stabilise. Within this work we report on the phase formation and mechanical properties of (Gd,Hf,Sc,Ti,Zr) oxide coatings. High-entropy metal sublattice oxides were synthesised using reactive magnetron sputtering utilising a single equiatomic target consisting of Gd, Hf, Sc, Ti, and Zr. For synthesis of oxide coatings different $O_2/(Ar+O_2)$ flow ratios were used to investigate the influence of reactive gas flow on the structure and mechanical properties. X-ray diffraction analysis show that the coatings crystallise in a single-phase fcc structure. Nanoindentation measurements revealed hardness values of ~20 GPa and an indentation modulus of ~ 250 GPa. Furthermore, transmission electron microscopy investigations were done to get more detailed information about the growth morphology and crystal structure of the oxide coatings. To investigate the structural stability at elevated temperatures, vacuum annealing treatments and subsequent XRD and nanoindentation measurements were done.

4:00pm **F2-ThA-9 Characterization and Surface Properties of Magnetron Sputtered Cr-Co-Nb-B Thin Film Metallic Glass**, ***Pak Man Yiu**,* Ming Chi University of Technology, Taiwan; *N. Bönninghoff, J. Chu,* National Taiwan University of Science and Technology, Taiwan

In this work, the microstructure, surface properties and thermal stability of a Cr-Co-Nb-B thin film metallic glass (TFMG) fabricated by DC-magnetron sputtering were investigated. Its glass transition (Tg) and crystallization (Tx) temperatures were determined to be 530 ◦C and 615 ◦C respectively. Also, Cr-Co-Nb-B TFMG shows significantly higher hardness but lower coefficient of friction (CoF) than that of PVD pure Cr. In a contact angle analysis, it also showed very low surface energy, in which eventually lead to less adhesion when a drop of low density polyethylene (LDPE) was molten on its surface. Results suggested that our TFMG has great potential as a non-stick, wear resistant coating.

4:20pm **F2-ThA-10 Functional Materials for Energy Applications**, ***Susan Sinnott**,* Pennsylvania State University, USA **INVITED**

The development of new functional materials for use as battery electrodes, for catalysis, and for electronic devices is an ongoing area of research. Structure-property relationships are determined using a combination of experimental characterization and high-fidelity computational methods. Here, first-principles density functional theory (DFT) calculations are used to investigate functional two-dimensional inorganic materials and high-entropy oxides (HEOs). Two-dimensional materials have properties that strongly depend on composition, defects, and surface structure. This presentation will focus on two-dimensional metal dichalcogenides and metal dichalcogenide/metal carbide heterostructures that have unique properties related to electron confinement within these layered materials. The computational predictions are compared to experimental data to advance design of two-dimensional materials for electronic devices. Similarly, the controlled synthesis of functional HEOs are being investigated, including J14 [(Mg, Co, Cu, Ni, Zn)0.2O] and F1 [Ce, La, Pr, Sm, Y)0.2O2-δ] where δ indicates oxygen vacancies. In this case, DFT calculations are being employed to help explain recent findings of structural dependencies on growth conditions for J14 and to reveal structure-transport composition trends in F1, a leading high-ion conductor. The synergies between experimental synthesis, characterization, and modeling is a focus of the presentation.

New Horizons in Coatings and Thin Films
Room Golden State Ballroom - Session FP-ThP

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

FP-ThP-1 Fabrication of Chemical Bath Deposited ZnO Nanorods Layer Based Ultraviolet Light Detectors and Their Device Properties: Influences of Solution Concentration and Thermal Annealing*, **Tomoaki Terasako**, T. Fujikawa, K. Hirota, K. Kobayashi,* Graduate School of Science and Engineering, Ehime University, Japan*; M. Yagi,* National Institute of Technology, Kagawa College, Japan*; T. Yamamoto,* Materials Design Center, Research Institute, Kochi University of Technology, Japan

Zinc oxide (ZnO) has a bandgap energy of ~3.37 eV which enable to realize ultraviolet (UV) light detectors. In addition, the enhancement of specific surface area by nanosizing the ZnO crystallites is expected to improve the performances of the ZnO based UV light detectors. Among the various techniques for preparing ZnO nanorods (NRs), we have paid attention to chemical bath deposition (CBD) because of its simple procedure, cost-effectiveness and low deposition temperature.

The UV light detectors studied in this paper have a structure of PEDOT:PSS/ZnO NRs/ZnO:Ga(GZO) Schottky junction. To clarify influences of the morphologies and surface states of the NRs on the performance of UV light detecting, the PEDT:PSS/ZnO NRs/GZO Schottky junction UV light detectors with the ZnO NRs layers grown from the CBD solutions with the different concentrations and those annealed under the different conditions are fabricated and characterized.

The GZO seed layers were deposited on alkali-free glass substrates by ion-plating with a DC arc discharge. The ZnO NRs layers were grown by CBD using the mixed aqueous solutions of zinc nitrate hexahydrate (ZnNit) and hexamethylenetetramine (HMT) with the different concentration ratios of HMT to ZnNit ([HMT]/[ZnNit]). The [HMT]/[ZnNit] value was changed in the range of 0.24-3.78. The bath temperature and growth time were ~86°C and 60 min, respectively. Thermal annealing was done to some of the NRs layers in the air. The annealing temperature and time were changed in the ranges of 150-450 °C and 20-60 min, respectively. The PEDOT:PSS layer was spin-coated on the surface of the NRs layer, followed by thermal annealing.

Values of diode ideal factors (n), rectification ratios (I_F/I_R) and potential barrier heights at the PEDOT:PSS/ZnO NRs heterointerfaces (Φ_b) were determined from the voltage-current characteristics taken in a dark. The n values smaller than 2 were obtained in the [HMT]/[ZnNit] range of 0.94-2.83. Both the I_F/I_R and Φ_b increased with increasing [HMT]/[ZnNit]. The UV light detector with the NRs layer grown from the CBD solution with [HMT]/[ZnNit]=0.94 exhibited the maximum ratio of photocurrent (PC) to dark current of 92.6. PC spectra were composed of bands with peaks at ~360 and ~380 nm. The intensity ratio of the 360 nm peak to the 380 nm peak (I_{360nm}/I_{380nm}) showed a maximum at [HMT]/[ZnNit]=0.94. The I_{360nm}/I_{380nm} value decreased along with the change in [HMT]/[ZnNit] from 0.94 towards both the lower and higher sides. The increase in annealing temperature led to the decrease in forward current, resulting in the decrease in I_F/I_R.

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FP-ThP-2 Advances in Nanosynthesis by Atmospheric Pulsed Arc Discharges*, **Carles Corbella**, S. Portal,* George Washington University, USA*; M. Kundrapu,* Tech-X Corporation, USA*; M. Keidar,* George Washington University, USA

Arc discharges sustained at atmospheric pressure are one type of thermal plasma commonly used in welding, material processing, and more recently, in the synthesis of nanomaterials like graphene, carbon nanotubes, and monolayers of transition metal dichalcogenides. Atmospheric arc plasma fed with periodic power pulses constitutes an excellent way to merge all virtues in one plasma nanosynthesis method, namely competitive deposition rates, lower thermal loads, better utilization of the ablated material, economical use of supplied power, and improved stability of discharges. In contrast with standard glow discharge technologies optimized to obtain nanocomposite materials, anodic arc discharges excited with pulsed power show the unique capability of producing high-purity, stand-alone nanomaterials outside of any supporting host matrices. Here, we review recent efforts to implement pulsed anodic arc discharges for nanosynthesis in four distinct directions: (1) tuning the growth and properties of fullerenes and single- and double-wall carbon nanotubes; (2) localized deposition of nanomaterials on substrates with high spatial resolution; (3) synthesis of heterogeneous nanostructures, especially core-shell nanoparticles, by pulsed plasmas in liquids, and (4) design of pulse waveforms able to generate repetitive and stable arc discharges with minimal production of undesired byproducts, like powder macroparticles. Advanced plasma diagnostics and modeling have been introduced to study the kinetics of nanoparticle growth with spatial-temporal resolution, and the outcome of this research constitutes the forefront of atmospheric arc physics nowadays. Future work requires a deeper understanding of the plasma species transport and its connection with pulse parameters and basic structural information of the grown nanomaterials, such as diameter of nanotubes and thickness of atomic multilayer stacks. A crucial milestone consists of decoding the synthesis-structure-properties sequence involving arc discharges, whose correlations should be developed from a neural network approach. In conclusion, the inherent flexibility of pulsed arc processes by modulating current and voltage waveforms is widely beneficial for the engineering of nanostructured materials with tailored properties attractive for electronic, photonic, and biomedical applications.

FP-ThP-3 Structure, Mechanical Properties, and Thermal Stability of (Gd,Hf,Sc,Ti,Zr)-Nitride Thin Films*, **Alexander Kirnbauer**, M. Derflinger,* TU Wien, Institute of Materials Science and Technology, Austria*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

In recent years the exploration of so-called high-entropy alloys (HEAs) and high-entropy metal-sublattice ceramics (HESCs) is in the focus of many research groups. Their unique properties, attributed to the high entropy (> 1.5R) on the metal sublattice, make them interesting for many applications. These materials combine high-hardness and toughness with increased thermal stability as, due to sluggish diffusion, softening processes are slowed down. In a previous study on (Hf,Ta,Ti,V,Zr) nitride we could show that thin films based on the high-entropy concept exhibit outstanding thermal stability as the coatings are single-phased and the elements are randomly distributed up to an annealing temperature of 1300 °C [1]. At higher temperatures the coating decomposes due to nitrogen loss. To overcome the problem of nitrogen loss Ta and V which form a Me_2N solid solution are exchanged by Gd and Sc which do not exhibit a Me_2N phase. For the synthesis of (Gd,Hf,Sc,Ti,Zr) nitride thin films reactive magnetron sputtering was used. We investigated the influence of nitrogen partial pressure as well as substrate temperature on the phase formation and mechanical properties. Therefore, X-ray diffraction and nanoindentation measurements were carried out. The results show that with low nitrogen partial pressure the coatings are partly amorphous while with increasing nitrogen flow the coatings crystallise in a single-phase fcc structure. With increasing substrate temperature, the hardness increases from 23 to 32 GPa. Additionally, to a variation of the deposition parameters, differential scanning calorimetry (DSC) measurements were carried out to investigate the thermal stability and evaluate temperature ranges where phase changes occur. Furthermore, the coating which exhibits the highest hardness was vacuum annealed up to 1200 °C to investigate the change of the mechanical properties upon annealing. The results show that the coatings stay single-phased up to 1000 °C, whereas at higher temperatures phase separation occurs. The hardness thereby decreases from ~32 to 22 GPa.

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FP-ThP-4 Demystifying the Entropy Forming Ability – The Role of Atomic Size Effects*, **Andreas Kretschmer**, P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

The desire for rapid materials discovery calls for efficient procedures to explore unknown compositions. This task is especially daunting in the field of high-entropy materials due to the sheer number of possible element combinations to explore. One such procedure has been proposed by Sarker et al. [1], who formulated the so-called entropy forming ability (EFA), using AFLOW-POCC calculations [2], and demonstrated its use on 10 different high-entropy carbides. The tendency to form a single-phase compound was correctly predicted by the magnitude of the EFA.

However, this abstract descriptor lacks a physical explanation, which we have now uncovered by our own simulations. We quantified the lattice distortion in the same carbides as treated in [1], using 10 individual special quasi-random structure (SQS) cells with 64 atoms per carbide, and then calculated the radial distribution function (developed in [3]) of the first coordination sphere. Hereby, we see a strong correlation between the lattice distortion and low EFA values, signifying multi-phase structures. We confirmed this relationship on solid solution carbides with 2, 3, and 4 metals, by calculating both the POCC-derived EFA and the SQS-derived lattice distortion.

Due to the causal relationship of large atomic size mismatch and large lattice distortion we can conclude that the EFA descriptor effectively screens for compositions with low atomic size mismatch, which is already well-known as the Hume-Rothery rules of solid solutions.

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FP-ThP-5 High-Temperature Oxidation Resistance of CrB_2 Coatings Alloyed by Transition Metal Disilicide Phases*, **Ahmed Bahr**, T. Glechner, T. Wojcik, P. Kutrowatz,*
Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; J. Ramm, O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S. Kolozsvári, P. Polcik,* Plansee Composite Materials GmbH, Germany*; E. Ntemou, D. Primetzhofer,* Department of Physics and Astronomy, Uppsala University, Sweden*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

Transition metal diborides (TMB_2) are a promising family of materials to be applied as protective coatings in several high-performance applications owing to their high melting point, chemical inertness and outstanding mechanical properties [1]. Among them, CrB_2 exhibits attractive aggregate of properties as good wear resistance, high thermal conductivity and corrosion resistance. However, it suffers rapid oxidation above 600 °C by forming non-protective scales [2].

In this study, we explored the alloying of CrB_2 with secondary TM-silicide phases (TM = Cr, Mo) and investigated the role of the $TMSi_2$ alloying phases on the phase formation, oxidation behavior and mechanical properties of these coatings. We employed direct current magnetron sputtering (DCMS) technique to synthesize alloyed Cr-(TM)-Si-B coatings from compound targets of CrB_2/$MoSi_2$ and CrB_2/$CrSi_2$ providing different compositions. The oxidation kinetics of these coatings have been investigated up to 1400 °C. The alloyedcoatings were analyzed in terms of phase formation and stability, chemical composition, as well as mechanical properties using diverse high-resoultion characterization techniques.

Keywords: CrB_2; Sputtering; Protective Coatings; Oxidation; Phase Stability; Mechanical Properties;

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FP-ThP-6 The Photodetection of the in-, Sn-, and Te-Doped Bi_2Se_3 Nanoplatelets*, **Chih-Chiang Wang**,*
National Chin-Yi University of Technology, Taiwan*; H. Shih,* Chinese Culture University, Taiwan*; F. Shieu,* National Chung Hsing University, Taiwan*; A. Lo,* National Chin-Yi University of Technology, Taiwan

The compound Bi_2Se_3 has a narrow band gap of 0.35eV with a rhombohedral crystal structure and is a unique material with the gapless surface-state and the insulating bulk. It is a potential material in the application of photodetection, FET, quantum computation, etc. Bi_2Se_3 has the layered structure composing of 5-atomic layers of Se^1-Bi-Se^2-Bi-Se^1 known as a quintuple layer (QL) with a thickness of around 1 nm. The main bonding type inside the QL is the covalent bonds, and the van der Waals force dominates the bonding between the QLs.

In this investigation, the pure Bi_2Se_3, and In-, Sn-, and Te-doped Bi_2Se_3 nanoplatelets (NPs) were synthesized by the thermal CVD process using horizontal quartz tube at 600℃ under the pressure of 2×10^{-2} Torr, using sapphire as the substrate. The FESEM images show the hexagonal-like morphologies of the NPs. The results of XRD, HRTEM, Raman, and XPS confirm the typical rhombohedral Bi_2Se_3. The photodetection of the pristine Bi_2Se_3NPs shows that the photocurrent and the ratio of photocurrent/dark-current under UV- and under red-light are of the 4×10^{-11} and 23.8×10^{-14}A and 7.7 and 1, respectively, while the co-dopants of In and Sn enhance the photocurrent as well as the ratio of photocurrent/dark-current of the Bi_2Se_3 NPs under UV- and under red-light up to 52×10^{-11} and 3.5×10^{-11}A and 30.7 and 52.2, respectively. The proposed factors can be summarized as the following: (1) formation of the donor defects (In^{3+}_{V0}) and (Sn^{4+}_{Bi3+}), the acceptor defects (V^0_{Bi3+}) and (Sn^{2+}_{Bi3+}), and the neutral defect (In^{3+}_{Bi3+}), (2) the reduced optical band gap of the doped Bi_2Se_3 NPs, and (3) the similar melting point of the powder precursors.

FP-ThP-7 Metallic Zn and Mg Nanowire Coatings by Conventional Reactive DC Sputter Deposition*, J. Zawadzki, **Michał, Adam Borysiewicz**, M. Wzorek,*
Łukasiewicz Research Network - Institute of Microelectronics and Photonics, Poland

Metal nanowires owing to their enormous surface-to-volume ratio as well as one-dimensional structure, possess outstanding chemical and physical properties in comparison to bulk materials and are interesting for a broad range of absorbing applications. Magnesium nanowires exhibit a high hydrogen absorption capacity (7.6 wt.%), which determines their potential application in hydrogen storage [1]. Along with zinc nanowires, they are successfully used in energy storage devices such as Mg/air batteries [2] andZn/air batteries [3], respectively. Moreover, zinc nanowires are used as a precursor for obtaining Zn-based semiconductors such as ZnO [4,5], ZnS [5], ZnTe [6], ZnSe [5], which are applied widely in optoelectronics, photonics, and sensing.

Despite of a great effort of scientific groups all over the world, the synthesis of nanowires is still a low-scale process related mostly to solution-based synthesis, or chemical vapor transport processes. The methods of physical vapor deposition (PVD) are an excellent instance of bottom-up techniques not requiring chemical solvents, thereby being eco-friendly and yielding more pure nanostructures. The majority of Zn, Mg nanowire synthesis by PVD methods is based on evaporation techniques [7,8,9,10], while the use of the magnetron sputtering technique [11] remains seldom studied.

On the basis of previous works done by our group on the growth of porous Zn films by reactive magnetron sputtering [12,13], we here demonstrate a catalyst-free method of metallic Zn and Mg nanowire growth using conventional geometries of the reactor chamber (not glancing angle) and cathode. We discuss the synergistic effect of oxygen controlling the morphology of the wires and substrate heating for mass transport for nanowire formation usingbothZn and Mg [see Fig. 1,2]. We discuss the different results for both elements. We comment on the structural and chemical properties of the material and apply high-temperature oxidation to convert them into metal-oxide nanowires. The proposed approach is a big step to achieve a universal method for high-purity, ligand-free metallic nanowires using magnetron sputtering deposition, paving the way for their widespread applications.

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[13] 10.12693/APhysPolA.125.1144

FP-ThP-8 Synthesis and Electrical Properties of Gasb Nanowires*, Tzai-Wei Chen, C. Wang,* National Taiwan University of Science and Technology, Taiwan

In this work, we used anodic aluminum oxide (AAO) template-assisted vacuum die-casting method to prepare GaSb nanowires. Due to their good stoichiometric controllability, low cost and good stability. We can control chemical composition of nanowires easily by modifying composition of bulk. At first, a mixture of gallium ingot (99.99 % purity) and antimony ingot (99.99 %) with an appropriate amount of atomic ratio was entered into quartz tube. Using single zone furnace to heat up to 950 °C and keep for 2 hr then quench into water. GaSb nanowires were synthesized with AAO (annealing at 550 °C for 1hr and non-annealing) template-assisted by vacuum die-casting method. Dissolving time of annealing (400 °C for 24 hr) and non-annealing GaSb nanowires were discussed, respectively. We used different etching solutions (H_2CrO_7 and NaOH solution) to dissolve single and two flakes AAO templates, respectively. The results show that excessive dissolving time and concentration of etching solution cause the nanowires to be damaged or even disappear. The as-fabricated photodetectors via EBL process with 250 nm of Ni as electrode. At 1.0 V bias, the responsivity, EQE and detectivity were calculated to be 7.085 × 10^3 A/W, 1.352 × 10^6 % and 6.384 × 10^{12} Jones, and 2.292 × 10^3 A/W, 3.42 × 10^5 % and 1.713 × 10^{11} Jones under 650 and 780 nm laser illuminated, respectively.

FP-ThP-9 Spacing-controllable core@shell TiO_2@Ru/RuOx Nanotube Array for Biocompatible Stimulating Electrode Applications*, Jia-Jun Li,* National Taipei University of Technology, Taiwan

Recently, implantable bio-electronic devices have attracted considerable attention owing to their promising potential in monitoring and regulating malfunctioned neural systems and internal organs. In operation, these devices require a bio-compatible interface to facilitate the electrical signal communication between inorganic Si-based circuits and neurons/cells in an aqueous environment. A critical parameter for a bio-electrode is its “charge storage capacity” (CSC). A larger CSC is desirable for electrode miniaturization and sufficient neurostimulation.

We develop a chemical bath for a conformal Ru/RuOx deposition with a thickness of ~15 nm on TiO_2 nanotubes with a length of ~800 nm. In addition, we develop an anodization process that can control the spacing of the TiO_2 nanotube array. These Ru/RuOx nanotube arrays undergo electrochemical analysis in charge storage capacity (CSC), charge injection capability (CIC), and electrochemical impedance to evaluate their potential as neurostimulation electrodes for bioelectronics. Images from electron microscopes confirm the formation of uniform Ru/RuOx on both nanotubes' internal and external surfaces. An X-ray diffraction pattern indicates a good crystallinity of the Ru/RuOx nanotube array. In addition, the cycling lifetime of Ru/RuOx nanotube arrays is evaluated by performing CV scans for 1,000 cycles with a scan rate of 0.1 V/s. The Ru/RuOx nanotube arrays reveal large CSC values and low electrochemical impedances, which are attributed to hollow tubular nanostructure with Ru/RuOx deposition.Additionally, the Ru/RuOx-coated TiO_2 nanotube array exhibits stability, durability, and good biocompatibility.

FP-ThP-10 Nickel Sulfide on Organic Framework for Efficient Hydrogen Evolution Reaction*, Yu-An Ji,* Department of Materials and Optoelectronic Science, National Sun Yat-Sen University, Taiwan*; T. Chang, C. Kung,* Department of Chemical Engineering, National Cheng Kung University, Taiwan*; C. Chen,* Department of Materials and Optoelectronic Science, National Sun Yat-Sen University, Taiwan

Hydrogen is eco-friendly and high-efficient energy. Choosing the electrocatalysts for hydrogen evolution reaction (HER) is an essential challenge to water splitting. And then transition metal chalcogenides (TMCs) are easy to prepare and cheap, so this works chemical vapor deposition (CVD) to sulfurize nickel-based metal-organic framework (MOF). The Scanning Electron Microscope (SEM) results of α-NiS-MOF indicate that the extensions on the branch can increase surface area. Experimentally, the electrochemical measurement results reveal that MOF after sulfidation has enhanced HER electrocatalytic performance in 1 M KOH (overpotential is 76.7 mV and 210 mV at the current density of -10 mA/cm^2 and -100 mA/cm^2), and widely improve electrochemical surface area (electrical double-layer capacitance is 0.8336 F/cm^2) compared to nickel foam after sulfidation. At the same time, X-ray photoelectron spectroscopy (XPS) was used to observe the chemical state changes of the surface elements of the electrocatalyst before and after the hydrogen evolution reaction. As a result, this work demonstrates a facile synthesis to optimize nickel sulfide electrocatalysts to improve their electrocatalytic performance for practical applications in future energy devices.

FP-ThP-11 Research of The Growth Mechanism of Solvothermally Synthesized Sb_2Te_3 Nanosheets*, Yen-Jen Lin,* *C. Chen,* Department of Materials and Optoelectronic Science, National Sun Yat-Sen University, Taiwan

Sb_2Te_3 is one of the topological insulated (TI) materials. Owing to the strong electron spin-orbital coupling, TI materials have conductive surfaces, and the inside parts are insulated. One of the most critical factors in showing the topological insulating property is the thickness of the materials. In this work, we successfully synthesized Sb_2Te_3 nanosheets by solvothermal method. Inspecting the growth process using scanning electron microscopy showed that we obtained Te nanowire initially. Te nanowire then turned into Sb_2Te_3-Te hierarchical nanostructure with increasing of time and finally into Sb_2Te_3 nanosheets. We can suggest the growth mechanism of Sb_2Te_3 nanosheets from the results. We also found that the absorption range in UV-Vis was different by the difference of experimental products. It has become a convenient method to identify the section of the as-prepared products. Furthermore, we also found that by tuning the concentration of NaOH or increasing temperature, we can successfully synthesize nanosheets with a radius and thickness of 1.5 µm and 9.8 nm, respectively. Being able to well-control the thickness of Sb_2Te_3 nanosheets is very helpful for the subsequent component fabrication.

FP-ThP-12 Exploring Zn-Sn-O (ZTO) Composition Spreads with Combinatorial Sputtering*, Siang-Yun Li,* *Y. Shen, K. Chang, W. Wu, J. Ting,* National Cheng Kung University, Taiwan

Transparent conducting oxide (TCO) films are extensively applied as electrodes in the fields of solar cells and displays, due to their high transparency and excellent conductivity. Multicomponent oxides such as Zn-Sn-O (ZTO) have attracted much attention resulting from no expensive elements, i.e. indium (In), involved. In addition, thermal stability and mechanical strength of ZTO could be tailored as well by varying its stoichiometry. However, making different ratios of Zn/Sn compounds systematically is not trivial.

Combinatorial methodology has been proven its validity in such an application. This approach allows Zn/Sn continuously changing across the single sample area and a feasible intimate mix of Zn and Sn. Therefore, a single ZTO composition spread sample essentially includes a full spectrum of properties to be investigated. A Zn-Sn-O (ZTO) composition spread, consisting of thickness wedges of SnO and ZnO, was prepared using a state-of-the-art combinatorial sputtering system, equipped with a moving shutter and two RF guns for the targets of Zn and Sn, respectively. The thickness gradient was determined using SEM, α-step and SIMS. It was found a smooth thickness variation across the sample area for both ZnO and SnO with the coefficient of determination (R2) ≅ 0.99, indicating a good control of the ZTO composition spread. Structure evolution was characterized using XRD. We found in-situ 500 ºC annealing resulted in crystallization of the samples, where ZnO, Zn2SnO4, ZnSnO3, and SnO2 phases were observed, depending upon the ZnO/SnO ratios on the ZTO composition spread. The resistivity was characterized using a four-point probe on different substrates, which revealed lower resistivity near ZnO-rich. Morphology and optical characteristics were studied as well using AFM, SEM and UV-Vis spectrometry. A clear variation trend of both properties was observed. A systematic study of physical properties of ZTO has been successfully demonstrated.

FP-ThP-13 On the Stability of Nanostructured Ti-Cr-Zr Multilayers*, J. Nascimento Pereira,* São Carlos School of Engineering (EESC), University of São Paulo (USP), Brazil*; V. Ott, M. Stüber, C. Greiner,* Institute for Applied Materials (IAM), Karlsruhe Institute of Technology (KIT), Germany***; Haroldo Cavalcanti Pinto,*** São Carlos School of Engineering (EESC), University of São Paulo (USP), Brazil

Nanocrystalline materials have attractive mechanical, electrical, magnetic, and optical properties due to their high density of interfaces. It is well established that many of the beneficial physical and mechanical properties of nanostructured materials, such as outstanding strength, are due to their nanometric grain size (and subsequently large proportion of interfaces). However, these systems present an energy instability due to the large grain boundary volume fraction that raises the overall energy causing grain growth that negatively impacts even at low temperatures. One method of stabilizing grain boundaries is by solute segregation, in which alloying elements are added to diffuse to the grain boundary modifying its structure, energy, and chemistry. Thus, nanolayers of pure Ti, Zr, and Cr were sequentially deposited by magnetron sputtering. Three different stacking sequences (TiCrZr, ZrCrTi, and ZrTiCr) and three different layer periodicities (2, 5, and 10 nm) were chosen to be studied. The samples were heat treated at 475 and 1100 ºC under vacuum (pressure ≈ $2x10^{-4}$ Pa) in order to diffuse the elements. It was observed that complexions structures form during this treatment. This structure acts by preventing boundary movement or grain growth, stabilizing nanocrystalline grains and retaining the properties desired. X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) were performed to analyze the coatings. The next step will be to proceed with the characterization of the coatings. X-ray photoelectron spectroscopy (XPS), Transmission electron microscopy (TEM), X-ray residual stress, and X-ray texture analysis will be done. The objective is to characterize and understand the effect of the heat treatment on the nanolayers, as well as, to observe the formation of complexion structures.

FP-ThP-14 High-Precision Feedback Control Measurements of the Aluminum-Oxygen Double Hysteresis Curve in Reactive Magnetron Sputtering*,* ***Josja Van Bever****, K. Strijckmans, D. Depla,* Ghent University, Belgium

Feedback process control [1] of reactive sputtering can be used to achieve specific thin film properties. Although conceptually simple, it is far from trivial to make it reliable and reproducible.

Depending on the initial state of the process two S-shaped process curves can be obtained under certain conditions [1]. It is shown in our most recent work [2-4] that this phenomenon, which is termed *double hysteresis*, is related to implanted oxygen ions that are eroded from the target surface before having reacted with the target metal. While the two S-shaped curves can be clearly observed using *IV-characteristics* [5], no accurate measurements of the states with *feedback control* have been obtained yet.

Feedback measurements of double hysteresis curves are however of great use. First, such measurements deliver a *direct proof* of the phenomenon. When using IV-characteristics, a much broader data set must be obtained [5]. Therefore, the double hysteresis curves cannot be obtained as a function of erosion time or process parameters that are known to influence double hysteresis [2-4]. *With feedback control, the complete double hysteresis curve can be characterized with one target and within a limited amount of erosion.* Finally, good control of discharge voltage and/or oxygen pressure is required to investigate properties of films deposited within the meta-stable region. This is only feasible with feedback control.

In this poster we present high-precision feedback measurements of double hysteresis curves of the aluminum-oxygen system. We address problems encountered during such measurements, ranging from controlling instabilities and relaxation of the sputtering system to accurately switching between different types of feedback. The sampling of totally new target states is discussed. *A new measurement protocol is introduced and implemented in the software package “RSDmeasure”*. We use the developed protocol to obtain the first direct proof of double hysteresis during reactive magnetron sputtering and the *first complete characterization of double hysteresis curves as a function of process parameters* that are of interest to manipulate the reactive sputtering process.

Additional figures and references are found in the supplementary material.

FP-ThP-15 Impact on Phase Interactions between Metal-Covalent Organic Frameworks and Piezoelectric Polymers*,* ***Hsin Hui Lin****, K. Lin, J. Ruan,* National Cheng Kung University (NCKU), Taiwan

The covalent organic frameworks (COFs), as a kind of newly emerging coordination polymer and 2D molecules also, have widely attracted research interests due to their designable molecular structures, adjustable energy bandgaps, and outstanding thermal stability. With covalent bonding among selected organic monomers, porous reticular planar molecular layers are able to form and stack through π-π interactions, which capably yields abundant reachable reactions sites and molecular features required for gas storage and separation, energy storage, optoelectronic device, and especially in the fields of catalysts. Interestingly, with the presence of remained lone pair electrons within monomers or selected ionic linkers, the growth of metal coordination COFs (M-COFs) is achievable. With the presence of metal ions, the self-exfoliated M-COFs is promoted as π-π interactions among layers are weaker, resulting in larger surface areas and molecular contacts. Furthermore, the coordinated metal ions are also able to serve as the electron acceptor to facilitate the charge separation within each molecular layer, and therefore active sites for catalysis reactions.

In this research, two COFs with disparate designs of molecular structures and corresponding M-COFs have been successfully synthesized. Upon the growth of ferroelectric lamellae on the surface of M-COF, enhanced piezo-responses have been measured, and metal coordination further promotes reachable piezoelectric constants. The involved mutual polarization between deposited COFs and PVDF-TrFE lamellar crystals has been experimentally acknowledged as a kind of phase interactions. The phase interactions are expected to serve as a new factor for the contribution of hybrid crystalline materials and possible solution to overcome the current bottlenecks of materials application. Understanding possible influences of selected compositions of interacting phases should further help to unveil mechanisms and routes to optimize phase interactions, which is promising to significantly enhance water splitting reactions and the efficiency of piezoelectric nanogenerators.

FP-ThP-16 Synthesis and Characterization of Titanium Thin Films by Magnetron Sputtering and the Effect of the Addition of a Graphite Anode*,* *D. Jacobo Mora, M. Martinez Fuentes,* ***Stephen Muhl****,* Universidad Nacional Autónoma de México

Titanium (Ti) thin films were deposited onto glass substrates using two different setups: normal DC magnetron sputtering [MS] and by MS assisted by a secondary graphite anode discharge. The films were analysed as a function of the argon gas pressure, the MS power and voltage applied to the anode. The properties of the films, film thickness, adhesion and hardness were studied as a function of the experimental paraments used for the deposition. Lastly, optical emission spectroscopy (OES) was used analyse the two types of discharge.

This work was supported by: PAPIIT-IG101220, M Martinez would like to thank CONACYT (Mexico) for his postdoctoral fellowship.

Keywords: Magnetron sputtering; Optical emission spectroscopy; Deposition rate; Adhesion.

FP-ThP-17 Developing Materials for Future Generation Nuclear Reactors*,* ***Vladimir Vishnyakov****,* Huddersfield University, UK

Nuclear reactors have a very extended list of material requirements. Long-term environmental concerns related to decommissioning add to the list of requirements and limit the score of chemical elements which can be utilised. Stringent safety obligations necessitate treating almost any modification of material properties in service as damage. Self-healing in broad sense materials need to be well understood and crafted to enable safe future nuclear reactor operation. The self-healing relies on repair mechanisms when the material preserves its properties under severe conditions and radiation damage. Atomic level processes such as point defect recombination, defect diffusion, defect sinks and process activation energies need to be well understood. Self-healing processes in materials for nuclear energy generation will be examined on the developed solutions in thin film High Entropy Alloys, High Entropy Ceramics and MAX phases. Empirical suggestions for future development of nuclear reactor alloys will be discussed.

FP-ThP-18 Influence of Al Incorporation and N Stoichiometry on the Thermal Stability of (Ti,V,Zr,Nb,Hf,Ta)N Thin Films*,* ***Deborah Neuß****, M. Hans, G. Fidanboy, H. Lasfargues, C. Azina, S. Mráz,* RWTH Aachen University, Germany*; S. Kolozsvári, P. Polcik,* Plansee Composite Materials GmbH, Germany*; D. Primetzhofer,* Uppsala University, Angstrom Laboratory, Sweden*; J. Schneider,* RWTH Aachen University, Germany

Recently, the concept of high entropy alloys has been transferred to ceramic thin films such as transition metal aluminum nitrides. In the present work $(Ti,V,Zr,Nb,Hf,Ta)_{1-y}N_y$ (TMN) and $((Ti,V,Zr,Nb,Hf,Ta)_{1-x}Al_x)_{1-y}N_y$ (TM,AlN) films were grown by reactive sputtering using a hybrid co-deposition geometry. The thermal stability was studied through vacuum annealing in a temperature range from 700 to 1300 °C and subsequently the films were analyzed regarding chemical composition, phase formation as well as mechanical properties.Configurational entropy contributions on the metal sublattice exceed 1.5R for all configurations, increasing in TMN as well as (TM,Al)N from overstoichiometric to understoichiometric compositions: from 1.57R up to 1.79R in case of TMN films as well as from 1.69R to 1.86R for (TM,Al)N films. Spatially-resolved compositional analysis at the nanometer scale has been carried out using atom probe tomography (APT). In case of (TM,Al)N films a dual-phase structure is readily observed in the as deposited state as aluminum decorates the grain boundaries and the formation of Al-rich regions is enhanced after vacuum annealing at 700 °C. Thus, surface diffusion, as driving force for Al segregation dominates the phase formation regardless of the higher configurational entropy compared to TMN. Contrary, in the as deposited state of TMN, all metals are equally distributed and no segregation is observed. The onset of thermal decomposition for TMN films occurs after annealing at 1100 °C independent of the N content and the formation of V-rich clusters is observed. Thus, it is noteworthy that despite the similar values computed for the metal sublattice configurational entropy for TMN and TMAlN films significant differences in decomposition behavior and hence thermal stability are observed. Nanoindentation of as deposited TMN revealed the elastic modulus increasing with N-content from 329 ± 10 GPa (41 at.% N) to 420 ± 9 GPa (56 at.% N). Despite the presence of a secondary Al-rich phase at the grain boundaries, the elastic modulus of (TM,Al)N films increases from 354 ± 21 GPa (45at.% N) to 395 ± 8 GPa (56 at.% N).

FP-ThP-19 Effect of Surface Treatment on the Bifunctional Performance of Core-Shelled High Entropy Spinel Oxides*, **Yi- Ting Jhuo**,* National Cheng Kung University (NCKU), Taiwan*; T. Nguyen,* National Cheng Kung University (NCKU), Taiwan, Viet Nam*; J. Ting,* National Cheng Kung University (NCKU), Taiwan

Several high entropy spinel oxides were prepared using microwave hydrothermal method and used as electrocatalysts for oxygen evolution reaction (OER) and oxygen reduction reaction (ORR). The surface plasma treatment was conducted under different powers, times, gases, and pressures. The resulting samples were first characterized using X-ray diffractometer, scanning electron microscope, transmission electron microscope, energy dispersive spectrometer, X-ray photoelectron spectroscopy. Electrochemical performance was evaluated using electrochemical impedance spectroscopy, linear sweep voltammetry, cyclic voltammetry. The effect of surface treatment using plasma on the bifunctional OER/ORR performance is addressed.

New Horizons in Coatings and Thin Films
Room Pacific E - Session F1-FrM

Nanomaterial-based Coatings and Structures

Moderators: Ondrej Kylian, Charles University, Prague, Czechia, **Vladimir Popok**, Aalborg University, Denmark

8:20am **F1-FrM-2 Giant Actuated Van der Waals Metal/Muscovite Heteroepitaxy**, ***Jia-Wei Chen,*** National Yang Ming Chiao Tung University, Taiwan; *Y. Chu,* National Tsing Hua University, Taiwan

A large-response bimorph thermal actuator plays a vital role in the research field of actuation. Various architectures were designed using polymer-based materials with significant differences in thermal expansion. However, polymers' undesirable thermal and chemical instabilities severely hinder their applications. This work achieves a giant thermal actuation via van der Waals heteroepitaxy composed of room-temperature deposited metal and layered muscovite. A maximum bending curvature of 264 m^{-1} at 243 °C can be obtained in the Ag/muscovite heteroepitaxy through uniform heating. Moreover, the outstanding performance of the designed systems in both retention (>10^5 s) and cycling tests (>10^5 cycles) was observed through the electromechanical measurements, delivering the robustness and superior interface quality of the heterostructure. In addition, the robust interface and giant thermal actuation were supported by theoretical calculations and electron microscopy. The electrothermal and photothermal methods were conducted to demonstrate the generality of the control of actuators. This work presents the manufacturable actuator with a giant actuation based on metal/muscovite heteroepitaxy, invoking potential applications in robotic technology and intelligent systems.

8:40am **F1-FrM-3 Brain-Like Behaviour in Percolating Films of Nanoparticles**, ***Simon Brown,*** The MacDiarmid Institute for Advanced Materials and Nanotechnology, School of Physical and Chemical Sciences, University of Canterbury, New Zealand **INVITED**

Recent progress in artificial intelligence and machine learning means that humans are now far inferior to computers at playing games like chess and go. However the brain is still far more efficient than even the largest supercomputers at performing some types of tasks, such as pattern or image recognition.

This has motivated a worldwide effort to build brain-like, or "neuromorphic", computers using a number of different approaches. [Note that the focus of neuromorphic computing is on *hardware*, in contrast to the usual *software* approaches to AI.] I will review some of those approaches, which include the use of traditional silicon transistors to emulate neurons and synapses, and new solid-state devices which have synaptic and neuronal functionality.

I will then talk about how my group has attacked a key remaining challenge, which is to achieve truly brain-like networks using self-assembled nano-components. I will show that we have not only been able to build highly complex brain-like networks but that the dynamical signals within those networks are remarkably similar to those of the brain. Further, I will show that stochastic signals from these networks can be used to engineer high quality true random number generators, which have applications in secure information processing, and that the devices can be used to perform classification and time series prediction tasks within a reservoir computing framework.

9:20am **F1-FrM-5 RBS Study of Silver/Copper Diffusions in the Matrix of Amorphous Carbon Coatings Produced by Magnetron Sputtering**, *G. Sanzone,* Teer Coatings Ltd, UK; *M. Sharpe, P. Couture, J. England,* University of Surrey, UK; *S. Field, H. Sun,* ***Jinlong Yin,*** Teer Coatings Ltd, UK

In previous work, we have developed Ag-, Ag/Cu-, and Ag-cluster doped amorphous carbon coatings using magnetron sputtering techniques, for antimicrobial applications in space stations [1]. Inside a spacecraft, the temperature and humidity, suitable for the human crew onboard, also creates an ideal breeding environment for the proliferation of bacteria and fungi; this can present a hazard to human health, and create issues for the safe running of equipment. Utilising the antimicrobial properties of Ag and copper particles, we embedded these particles in a thin film of amorphous carbon and created an antimicrobial solution. These nanocomposite thin films have shown extremely high antimicrobial activities under both terrestrial gravity and micro-gravity conditions [1]. In addition, these thin films are scratch-resistant and wear-resistant with high hardness, providing a long lifetime which is critical for the applications in a space station. The slow diffusion of Ag towards surface from the carbon matrix body can replenish those Ag particles lost over time due to daily wear and tear.

However, the mechanism of Ag diffusion inside the carbon matrix has not been well understood. If the diffusion rate were too fast, the process of losing Ag would be too quick which would inevitably lead to a much shortened antimicrobial lifetime. On the contrary, too slow a diffusion rate would mean those lost Ag particles could not be replenished in time, which would severely impair the coatings' antimicrobial activity. Therefore, it becomes apparent and critical to identify the key factors that influence the Ag diffusion rate in a carbon matrix, and also to understand how they influence it.

In this presentation, we are going to report the latest results on RBS (Rutherford Backscattering Spectrometry) and TOF-ERD (time of flight elastic recoil detection) study of silver and copper diffusion in amorphous carbon coatings. The samples have been annealed at 100°C, 150°C and 200°C, to investigate the temperature influence on the metal species migration. Preliminary results have shown that higher temperature causes a higher diffusion rate, and the addition of copper has slowed down the diffusion rate of silver.

References

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9:40am **F1-FrM-6 C:H:N:O Plasma-polymer with Anchored LSPR Active Ag Nanoparticles for Detection of Borrelia Pathogen**, *S. Kumar,* University of South Bohemia, Czechia; *H. Maskova,* University of South Bohemia, Biology Centre ASCR, Institute of Parasitology Branisovska, Czechia; *A. Kuzminova,* Charles University, Czechia; *R. Rego,* University of South Bohemia, Biology Centre ASCR, Institute of Parasitology Branisovska, Czechia; *J. Sterba,* University of South Bohemia, Czechia; *O. Kylian,* Charles University, Czechia; ***Vitezslav Stranak,*** University of South Bohemia, Czechia

The contribution focuses on Ag/C:H:N:O nanocomposite acting as a transducer for Localized Surface Plasmon Resonance (LSPR) detection of borrelia pathogen with high selectivity and sensitivity. The nanocomposite composes of gas-phase synthesized Ag nanoparticles (of about 20 nm in diameter) anchored onto/into C:H:N:O plasma-polymer matrix deposited by magnetron sputtering of nylon 6.6 target. The stability of Ag nanoparticles is achieved by the thermal treatment during the deposition process. The produced nanocomposites with plasmonic Ag nanoparticles may detect changes in the distance of several tens of nanometres observed as an LSPR shift of the absorption spectra. Hence, surface changes, e.g. immobilization of pathogens onto the surface, can be easily monitored.

The immobilization of pathogens is achieved by the C:H:N:O surface functionalization done here in a sequence of (i) thin-film plasma polymer deposition for the introduction of -NH_2 groups that (ii) enable subsequent immobilization of specific antibodies for (iii) binding of the target agents. Borrelia proteins-specific polyclonal antibody, Borrelia lysate, and live Borrelia were employed as testing target agents. Detailed investigation indicates both a high selectivity for the target agents and high sensitivity with a practical detection limit in the range of 50 Borrelias per sample effective area 0.785 cm^2 causing LSPR red-shift Dl_{50}» 2.2 nm. The proposed concept could be used as a platform for the detection of a wide family of species depending on the suitable surface functionalization.

Acknowledgments: This work was supported by the Czech Science Foundation (Grant Number GACR 19-20168S).

10:00am **F1-FrM-7 Aln Nanostructures for Piezoelectric Nanogenerators**, ***Manohar Chirumamilla***, *M. Sandager, V. Popok, K. Pedersen,* Aalborg University, Denmark

With recent advancements in bioelectronic devices, self-powered sensors and smart wearables, efficient nanogenerators are required to harvest biomechanical energy. In this respect, aluminium nitride (AlN) is an excellent material choice for nanogenerators due to its piezoelectric nature, high chemical and thermal stability, high thermal conductivity and resistivity, and mechanical strength [1, 2]. Thin films and nanostructures of AlN can be grown using a direct current (DC) reactive magnetron sputtering process.

In this work, c-axis oriented wurtzite AlN nanostructures consisting of a number of laminas grown by sputter deposition on Si substrates are investigated. Ag nanoislands were preliminarily formed acting as a catalyst to initiate the nucleation of individual and separated nitride nanostructures. The quality of the deposited AlN is optimized by utilising ellipsometry, AFM, SEM and XRD, where the nanostructures grown at different conditions, like Ar to N_2 gas ratio, applied bias power, working pressure, substrate temperature, etc., are investigated. By optimizing the AlN growth parameters, well-defined AlN nanostructures with lengths up to 600 nm can be obtained. The piezoelectric behaviour of the structures was investigated using piezoresponse force microscopy (PFM). It was found that piezoelectric coefficients of the grown nanostructures can exceed the values typical for continuous AlN films, thus, forming a good basis for applications towards AlN-based nanogenerators. In this presentation, the AlN structures and their piezoelectric response for various nanofabrication conditions will be discussed.

Acknowledgements

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10:20am **F1-FrM-8 Super-Amphiphobic Nano-Wall Structured Teflon Films Deposited by Microwave Plasma***, **Ta-Chin Wei**,* Chung Yuan Christian University, Taiwan

Super-hydrophobic and oleophobic surfaces have attracted much interest for both fundamental research and practical applications. In this study, Teflon-like fluorocarbon films with nano-wall structure were deposited on various substrates by microwave-generated C4F8/CF4 plasma. The reactor was a long tubular quartz tube with diameter of 5 cm. The substrates were placed in 22 different locations along the flow direction in upstream region, plasma discharge, and afterglow region. It was found that the surface morphology of the deposited film is very location-dependent. As seen in Figure 1, the results are relatively symmetrical to the center of plasma discharge, which reveals the diffusive behavior of the plasma process. The fluorocarbon film is rough with low F/C atomic ratio when substrate is located in the center discharge region (No. 11~15). Fluorocarbon films with nano-wall structure can be deposited on substrates located in the end of upstream region (No. 8) and in the beginning of the afterglow region (No. 18). The F/C ratio of the nano-wall film is 2.0, namely the Teflon structure. It was also found that water contact angle on the Teflon-like nanowall film was above 160° and the CH2I2 contact angle was above 140°. Actinometric OES showed that Teflon-like nanowall film deposited on locations with high CF2 relative intensity. Combining the location dependency and OES result, it is suggested that Teflon-like nanowall film is deposited by soft ion bombardment and abundant CF2 radicals. Finally, by using the same operating parameters, we successfully deposited transparent super-amphiphobic fluorocarbon nanowall film onto various substrates such as glass, copper, polycarbonate, and etc. Moreover, we found that Teflon-like films with nano-wall structure could also be deposited from other fluorocarbon plasmas. We will discuss more details at the conference.

10:40am **F1-FrM-9 Diamond-Based Nanostructured Interfaces for Electrochemical Applications***, **Robert Bogdanowicz**,* Gdańsk University of Technology, Poland

The most common material for electrodes in electrochemical systems is gold or other noble metals, as these can be applied through physical vapor deposition. The recently interesting novel, candidate materials for electrochemical studies are i.e.: (i) boron-doped diamond (BDD) or (ii) diamondized carbon nanowalls (B:CNW), and (iii) composite nanodiamond interfaces. The tailored diamond-rich sensing surfaces are grown by microwave plasma-assisted CVD. The effect of boron incorporation not only enhances the electrical or electrochemical properties but also influences the structure of electrodes by changing it from the maze-like to a heterogeneous distribution of nearly straight walls. B:CNW or BDD could be nanostructured to achieve microelectrodes.

The modification of diamondized boron-doped carbon nanowalls (BCNWs) with an electropolymerized polydopamine/polyzwitterion (PDA|PZ) coating revealing tunable mechanical and electrochemical properties. Zwitterions are codeposited with PDA and noncovalently incorporated into a structure. This approach causes a specific separation of the diffusion fields generated by each nanowall during electrochemical reactions, thus increasing the contribution of the steady-state currents in the amperometric response.

Morevoer, we have manifested also the scalable fabrication of flexible laser-induced graphene (LIG)-boron doped diamondized carbon nanowalls (BCNW) hybrid nanostructures for microsupercapacitors. Direct laser writing on polyimide film is tuned by the presence of BCNW powder where an appreciable absorbance of the BCNWs at the CO2 laser wavelength enhances the local film temperature. The thermal shock due to laser irradiation produces graphitized and amorphous carbon at the diamond grain boundaries which increases the thermal and charge transfer capacity between the LIG–diamond interfaces.

Among numerous materials, functionalized nanodiamonds are specific versatile nanocarbon material attracted ample attention thanks to their exceptional chemical, optical and electronic properties beneficial in the decomposition of harmful organic chemicals. Moreover, the stability of the nanodiamonds in the cocktail media was studied, along with various nature-originated compounds influencing their surface termination, polarity, and charge states. Thanks to the stability and biocompatibility of the nanodiamond, it can be applied in monitoring the condition of i.e. foodstuffs, and in the detection of toxins and pathogens in them.

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11:00am **F1-FrM-10 Engineering Nanostructured Metallic Thin Films by Pulsed Laser Deposition with an Outstanding Combination of Mechanical Properties***, **Francesco Bignoli**, D. Faurie,* CNRS, France*; C. Gammer, A. Lassnig,* Austrian Academy of Sciences, Austria*; S. Lee, C. Aguiar Teixeira,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany*; A. Li Bassi,* Politecnico di Milano, Italy*; M. Ghidelli,* CNRS, France

In recent years, thin metallic films have become object of intense research due to the activation of mechanical size effects enabling a combination of large yield strength (~3 GPa) and ductility (>10%) [1]. However, the correlation between microstructure and mechanical behavior is still not fully grasped and the research on new nanostructures with improved mechanical properties is ongoing. In this context, among the physical vapor deposition techniques, Pulsed Laser Deposition (PLD) have shown a great potential to widely tune the film morphology by simply changing the deposition pressure affecting the growth mechanisms ranging from atom-by-atom to cluster-assembled growth [2]. Nevertheless, very few studies focus on PLD deposited metallic films [3].

Here, I will show the potential of PLD to synthetize two (2) classes of emerging metallic thin films, namely metallic glasses (MGTFs) and high entropy alloys thin films (HEATFs). Firstly, I will cover the results involving the synthesis and the mechanical behavior of $ZrCuAl_x$ MGTFs with different compositions (x = 0,5,8,13 %at.) and morphologies i.e. compact and nanogranular. HRTEM shows a unique self-assembled nanolayered structure with local chemical enrichments alternating ZrCu and Al-rich nanolayers. This leads to a large and tunable elastic modulus and hardness, respectively up to 145 and 9.3 GPa. Furthermore, *in situ* SEM micropillar compression show that compact films have outstanding combination of yield strength (3.2 GPa) and ductility (5.5%), among the highest values reported in literature, while nanogranular films show a fully homogenous deformation (up to 20%) with the suppression of the shear bands process.

In the second case, I will present new results focusing on Al_xCoCrCuFeNi HEATFs deposited by PLD with different compositions (x = 0,9,16 %at.) and morphologies, i.e. compact and nanogranular. HRTEM reveal a unique nanolayered structure with nanoscale Al segregations resulting in a nanocomposite FCC/amorphous structure. This leads to enhanced mechanical properties with hardness up to 11 GPa and an exceptionally large (> 3.5%) onset of crack formation when deformed on polymer substrate.

Overall, the presented results show the potential of PLD to synthetize a novel class of metallic thin films with large and tunable mechanical properties and potential interest as structural coatings.

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11:20am **F1-FrM-11 Preparation and Properties of Fluoroalkyl End-Capped Oligomer/Cellulose Nanofiber Composites***, **Hideo Sawada**, Y. Endo, Y. Oikawa,* Hirosaki University, Japan

Cellulose reveals the great sensitivity to water and moisture, quite different from the traditional synthetic organic polymers.[1)] Therefore, the transformation of such hydrophilic materials into hydrophobic, especially superhydrophobic derivatives has been hitherto strongly desirable in order to open a new route to the development of novel cellulose-based materials.[2)] Here we report that sol-gel reaction of fluoroalkyl end-capped vinyltrimethoxysilane oligomer[3)] in the presence of cellulose nanofiber (CNF) under non-catalytic conditions can provide the corresponding fluorinated oligomeric silica/CNF composites. The fluorinated composites thus obtained were applied to the surface modification of poly(ethylene terephthalate) [PET] fabric swatch, affording a superoleophilic/superhydrophobic characteristic on the modified fabric surface. Modified PET fabric swatch was applicable to not only the separation membrane to separate the mixture of oil/water but also the perfect adsorption of oil droplets spread on water interface. In addition, we have prepared the fluorinated oligomeric CNF composites films by casting homogeneous aqueous methanol solutions containing the corresponding composites. Pristine CNF film afforded the superoleophilic property on the surface; however, it was demonstrated that the obtained transparent colorless CNF composite films can supply highly oleophobic characteristic on the surface. The mechanical properties such as Young's modulus, tensile strength and elongation at break of the CNF composite films were superior to those of the pristine CNF film.

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11:40am **F1-FrM-12 Synthesis and Electrical Properties of Single Crystalline Cu_3Ge Nanowires***, **Chang Ting- Hsiang**, L. Bo-Yan, W. Chiu-Yen,* National Taiwan University of Science and Technology, Taiwan

This study reports the synthesis of copper-germanide metal nanowires (NWs). First, the molten Cu_3Ge bulk was homogenized at 450 °C for 12 hours and cooled in the single-zone furnace tube to obtain a smooth and uniform bulk. In order to easily control the composition of Cu_3Ge nanowires, anodic aluminum oxide (AAO) template-assisted hydraulic press die-casting approach is used to obtain a large number of Cu_3Ge nanowires with uniform composition and straight. Second, we used the $H_2Cr_2O_7$ solution to etch and remove the AAO template substrate to obtain Cu_3Ge nanowires. According to the SEM images and EDS analysis, we can further realize the interface and the content information. It can be observed the existence of high-density nanowires, which have a length of more than 10~15 µm and a diameter of about 80~100 nm. In addition, the atomic ratio of copper to germanium is about 3/1. Furthermore, Cu_3Ge nanowires are fabricated into single-nanowire devices with Ti/Pt contacts through electron beam lithography (EBL), electron beam evaporation, and lift-off processes. Lastly, the I-V measurement shows Ohmic behavior. Cu_3Ge nanowires had a resistivity of 106.1 µΩ • cm and a relatively large current density of $6.35x10^7$ A/cm^2 which can be attributed to the massive free electron transport.

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