Hard Coatings and Vapor Deposition Technologies
Room On Demand - Session B6

Interplay Between Computational and Experimental Design of Coatings and Processes I

B6-1 Data-driven Assessment of Chemical Vapor Deposition of MoS2: a Meta-Study Based on Published Growth Experiments, *A. Costine,* University of Virginia, USA*; P. Delsa,* Lousiana School for Math, Science, and the Arts, USA*; T. Li,* ***Petra Reinke (pr6e@virginia.edu)****, P. Balachandran,* University of Virginia, USA

Transition metal dichalcogenides (TMD) are highly coveted materials with unique properties. The growth of high quality two-dimensional TMD monolayers is critical for enabling key technological solutions. Proof-of-concept devices can be assembled using micromechanical exfoliation from multilayer material, but this is a prohibitively slow process. Another challenge remains the control and minimize defects including point defects and grain boundaries, which have an outsized impact on electronic properties. It is therefore necessary to understand the complex parameter space of TMD monolayer growth, and then adapt, and extrapolate to conditions suitable for materials integration. For this purpose we asked a deceptively simple question: how much can we learn from the published data on MoS_2 growth with chemical vapor deposition from solid precursors (MoO_3 and S)? Can machine learning predict the processing conditions resulting in single layer MoS_2? [1] This work consists of two parts, which are equally important, and combine experimental and computational expertise: firstly, the data mining of the literature, assessment of the experimental descriptions, and isolation of suitable and reliable parameters which can be entered into ML algorithms, and secondly, testing and identification of suitable ML approaches. This is a non-trivial problem because the processing space is vast and lack of *a priori* guidelines impedes rapid progress. Starting from the literature data on MoS_2 thin films a database is manually constructed from 82 publications. Unsupervised and supervised machine learning methods are used to learn from the compiled data by extracting trends that underlie the formation of MoS_2 monolayers. Design rules are uncovered that establish the phase boundaries classifying monolayers from other possible outcomes such as incomplete layers, and multilayer, which offers future guidance of CVD experiments. Ideally the design rules can be connected to fundamental processes of growth, but the data sparsity and missing critical information did not allow us to take this path. The presentation will focus on the challenges of constructing a suitable database, the statistical challenges incurred due to its relatively limited size, and offers a view into the wealth of information which can be accessible from a combination of experiment and ML in advancing complex growth processes. An important conclusions remains a call to experimentalists to report failed experiments, which are an important aspect in building an informative map of the multidimensional growth parameter space. [1] A. Costine, P. Delsa, T. Li, P. Reinke, P.V. Balachandran, J. Appl. Phys. **128** 235303 (2020)

B6-2 Kinetic Monte Carlo Simulations of Residual Stress Evolution, ***Eric Chason (eric_chason@brown.edu)****, A. Bower,* Brown University, USA

Kinetic Monte Carlo (KMC) simulations have been a useful way to model the evolution of surface morphology during thin film growth. However, it has been difficult to include stress in KMC simulations because of the long range nature of stress fields. In this work, we have used an approximation that focuses on the stress development at the grain boundaries that allows us to overcome this problem. The results enable us to investigate how residual stress depends on the growth conditions (growth rate, temperature, particle energy) and microstructure (grain size) during thin film growth. . In particular, the KMC shows how the flux of deposited atoms on the surface leads to a supersaturation that creates compressive stress in the film.

B6-3 Maximum N Content in a-CN_x and other Amorphous Nitrides, ***Jiri Houska (jhouska@kfy.zcu.cz)****,* University of West Bohemia, Czech Republic

Structures of amorphous CN_x materials are predicted by extensive ab-initio molecular-dynamics simulations (more than 800 trajectories) in a wide range of compositions and densities [1]. The predicted lowest-energy densities are in agreement with the experiment. The main attention is paid to the formation of N_2 molecules, with the aim to predict and explain the maximum N content in stable CN_x networks. The results show that the maximum N content is of »42 at.%. From the kinetics point of view, higher N contents lead to steeply increasing rate of N_2 formation during materials formation. The preferred structures may contain some unbonded N_2 molecules at N contents above »34%, and that they contain many unbonded N_2 molecules at N contents above »42%. From the thermodynamics point of view, networks with more than »42% of N bonded in them may be temporarily stabilized by N_2 molecules sitting in voids around the network, but a subsequent N_2 diffusion into the atmosphere makes them unstable. Next, the methodology is applied to other amorphous nitrides such as Si-C-N [2]. Increasing Si/C ratio from 0 to 100% leads to increasing maximum achievable content of bonded N: from 34% to 57% in the case of no N_2 formation and from 42% to 57% when the amorphous network forms in parallel to N_2 formation. The evolution of experimentally achieved N contens in Si-C-N films prepared by reactive magnetron sputtering is in an excellent agreement with the prediction. Further analysis shows that while the N_2 formation at a given total N content and in a wide range of Si/C ratios is given only by the packing factor, the lowest-energy packing factor increases with Si/C. The results are important for the design of amorphous nitrides for various technological applications, prediction of their stability, design of pathways for their preparation, and identification of what may or may not be achieved in this field.

[1] J. Houska, Acta Mater. 174, 189-194 (2019)

[2] J. Houska, ACS Appl. Mater. Inter. 12, 41666-41673 (2020)

B6-4 Transition Metal Carbonitride based Thin Films: A Critical Review on Thermal and Elastic Properties of Group IV to VI $TMC_{1-x}N_x$, *T. Glechner,* TU Wien, CDL-SEC, Austria*; P. Mayrhofer,* TU Wien, Austria*; S. Kodambaka,* University of California Los Angeles, USA*; R. Hahn,* TU Wien, CDL-SEC, Austria*; D. Holec,* Montanuniversität Leoben, Austria*; T. Wojcik,* TU Wien, Institute of Materials Science and Technology, Austria*; M. Arndt,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S. Kolozsvári,* Plansee Composite Materials GmbH, Germany*;* ***Helmut Riedl (helmut.riedl@tuwien.ac.at)****,* TU Wien, CDL-SEC, Austria

Cubic transition metal (TM) carbides and nitrides are well established in various industrial applications especially as thin films due to their refractory character including highest thermal stability, chemical inertness, as well as high hardness. Based on their bonding characteristics – dominated by mixtures of strong ionic, covalent, and metallic bonds between their metal and carbon/nitrogen atoms – these compounds are strongly limited with respect to ductility compared to metals and metallic alloys. Therefore, to overcome these limitations as well as further weak points, e.g. oxidation resistance or electrical properties, the formation of carbonitrides by substitutional alloying of non-metal sites is an interesting approach. Recent studies in the field of TM carbonitrides highlighted promising candidates as well as selection criteria [1,2]. Here the valence electron concentration (VEC) as well as structural defects such as point or Schottky defects play a prominent role.

Within this study, we therefore compared the thermal and elastic properties of selected carbonitride based coating materials of the group IV to VI (e.g. Hf-C-N or Ta-C-N) transition metals utilizing theoretical and experimental methods. Various coating materials, also including the binary base systems, have been deposited by reactive and non-reactive magnetron sputtering techniques and subsequently characterized with respect to structure, morphology, chemical composition, and mechanical characteristics – also including micro mechanical testing. These results have been correlated with ab initio calculations utilizing the Vienna Ab Initio Simulation Package. The obtained results clearly indicated that the synthesis of single phase structured fcc $TMC_{1-x}N_x$ structures gets more challenging from group IV to VI. Nevertheless, the enhancement of the fracture toughness through non-metallic alloying is an appropriate approach – e.g. an increase for K_{IC} from 1.8 to 2.9 $MPam^{1/2}$ for $TaC_{0.81}$ compared to $Ta_{0.47}C_{0.34}N_{0.19}$ [2]. In addition, thermal treatments suggest an enhancement of the hot hardness and oxidation resistance with deductions on the still high phase stability. In summary, $TMC_{1-x}N_x$ coatings depict an interesting alternative to other thin film materials but still require a more detailed scientific exploration.

References

[1] K. Balasubramanian, et al., Valence electron concentration as an indicator for mechanical properties in rocksalt structure nitrides, carbides and carbonitrides, Acta Mater. 152 (2018) 175–185.

[2] T. Glechner, et al., Assessment of ductile character in superhard Ta-C-N thin films, Acta Mater. 179 (2019) 17–25.

B6-5 INVITED TALK: Weakest Links in Superlattices: Insights from Ab Initio Modelling, ***David Holec (david.holec@unileoben.ac.at)***, Montanuniversität Leoben, Austria*; N. Koutná,* TU Wien, Austria*; L. Löfler, L. Hantzenbichler,* Montanuniversität Leoben, Austria*; P. Řehák,* Central European Institute of Technology (CEITEC), Brno University of Technology, Czech Republic*; M. Bartosik,* TU Wien, Austria*; M. Friák,* Institute of Physics, Academy of Sciences of the Czech Republic, Czech Republic*; M. Černý,* Central European Institute of Technology (CEITEC), Brno University of Technology, Czech Republic*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria **INVITED**

Superlattice design has been shown effective to improve Young's modulus, hardness and toughness of many nitride systems beyond the performance of individual building blocks, especially when the bi-layer period is very small, in nm range. Such developments are crucial in order to reach the ever-increasing demands on the coatings (often based on nitrides, carbides or oxides) protecting various working tools. While a structural heterogeneity---as interfaces---serves as an obstacle for dislocation motion, it could also act as a sink for impurities or other point defects with a possibly detrimental effect on interface strength. And even if one thinks about an ideal interface, chemical inhomogeneity certainly influences local electronic structure and hence bonding, which could lead to weakened bonding.

This contribution deals with a principal question whether interfaces are the weakest link in the superlattices. We will present examples of calculated tensile strength of various cubic nitride systems (TiN/CrN, TiN/AlN, AlN/VN, MoN/TaN...) and discuss the local strength together with details of the local atomic structure. A large set of systems (with different lattice mismatch, stability, magnetic state, etc.) we have treated in the past will serve as a basis for drawing general conclusions (e.g., can strength be locally enhanced by modifying interatomic distances?). In addition, we will compare these trends with those predicted for a purely metallic Ti/Ta superlattices as well as cubic/wurtzite TiN/AlN multilayers.

B6-7 Superlattice Design for Superior Thin Films, ***Nikola Koutná (nikola.koutna@tuwien.ac.at)***[1]*, R. Hahn, J. Buchinger,* TU Wien, Institute of Materials Science and Technology, Austria*; D. Sangiovanni,* Linköping University, Sweden*; M. Bartosik,* TU Wien, Institute of Materials Science and Technology, Austria*; D. Holec,* Montanuniversität Leoben, Austria*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

Superlattice architecture—comprising coherently grown nanolayers of two or more materials—provides a vast playground for tuning physical properties of thin films via altering different phases and their mutual orientation, the bilayer period, or the defect content and distribution close to interfaces. Changes in these parameters can induce remarkable effects, such as partial structural transformations, superhardening and/or supertoughening. Nevertheless, identifying the layer materials, optimising the film deposition setup and performing micromechanical testing requires delicate experimental work. This talk illustrates the necessary interplay between modelling and experimental techniques to understand and control bilayer-period-dependent trends coming hand in hand with microstructural changes in superlattices. The model superlattice systems are cubic-based MoN/TaN, TiN/WN, and TiN/TaN. In particular, we highlight the important role of vacancies triggering local changes in the electronic structure, stabilisation of (novel) metastable phases or compositional variations at different layer thicknesses, which directly influence mechanical properties. Furthermore, atomistic processes governing strength, plasticity, and fracture of superlattices subject to tensile and shear deformation are discussed in light of the experimental results as well as ab initio molecular dynamics simulations.

[1] **2020 Student Award Finalist**

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