Hard Coatings and Vapor Deposition Technologies
Room Town & Country B - Session B6-MoA

Computationally-aided Materials Design

Moderators: Dr. Davide G. Sangiovanni, Linköping University, Sweden, **Prof. Wan-Yu Wu**, National United University, Taiwan

1:40pm **B6-MoA-1 Selection of Photosensitive Materials on Metal Oxide Surface by Using Machine Learning**, ***Yen-Hsun Su,*** National Cheng Kung University, Taiwan **INVITED**

Sustainable energy strategies, particularly solar-to-hydrogen production, are anticipated to overcome the global reliance on fossil fuels. Thereby, materials enabling the production of green hydrogen from water and sunlight are continuously designed, e.g., ZnO nanostructures coated by gold sea-urchin-like nanoparticles, which employ the light-to-plasmon resonance to realize photoelectrochemical water splitting. Due to the complex growth of Gold sea-urchin-like nanoparticles (GSNPs) and the need for a precise prediction of their surface plasmon wavelength, genetic-algorithm-based artificial neural networks (GANNs) are used to determine the relationship between synthesis parameters and the surface plasmon wavelength of GSNPs grown via seed-mediated growth assisted by machine learning. Herein, a low-data test is trained by varying the ratio and concentration of gold seeds, sodium citrate, hydroquinone, and $HAuCl_4$. Then, a big data confirmation is conducted through massive parameter collection from over 684 samples. The well-trained GANN can guide parameter selection for seed-mediated growth to obtain the desired surface plasmon wavelength. In additions, such light-to-plasmon resonance is strongly impacted by the size, the species, and the concentration of the metal nanoparticles coating on the ZnO nanoflower surfaces. Therefore, a precise prediction of the surface plasmon resonance is crucial to achieving an optimized nanoparticle fabrication of the desired light-to-plasmon resonance. To this end, we synthesized a substantial amount of metal (gold) nanoparticles of different sizes and species, which are further coated on ZnO nanoflowers. Subsequently, we utilized a genetic algorithm neural network (GANN) to obtain the synergistically trained model by considering the light-to-plasmon conversion efficiencies and fabrication parameters, such as multiple metal species, precursor concentrations, surfactant concentrations, linker concentrations, and coating times. In addition, we integrated into the model's training the data of nanoparticles due to their inherent complexity, which manifests the light-to-plasmon conversion efficiency far from the coupling state. Therefore, the trained model can guide us to obtain a rapid and automatic selection of fabrication parameters of the nanoparticles with the anticipated light-to-plasmon resonance, which is more efficient than an empirical selection. The capability of the method achieved in this work furthermore demonstrates a successful projection of the light-to-plasmon conversion efficiency and contributes to an efficient selection of the fabrication parameters leading to the anticipated properties.

2:20pm **B6-MoA-3 On the Modeling of Particle Growth in Film Deposition**, ***Rahul Basu,*** JNTU, India

The understanding and simulation of the nucleation of particles in a thin substrate is of importance in many areas of deposition technology. The deposition or insitu growth of disperse particles requires tuning of parameters to avoid continuous growth and agglomeration. Thin film nucleation can be modeled with spherical or cylindrical particle morphology. Among the parameters involved are Heat transfer coefficients and the "under cooling" or thermal driving force dependent on the boundary and initial conditions. A stable moving interface can be expressed as a function of time and radius and hence, the radial growth can be expressed as a power of time, and other parameters. A simulation using WOLFRAM with the equations of heat and mass transfer is used. A quasi-steady state solution results where the growth is stabilized until a desired size and distribution is arrived at. The prediction of this state is important in formation of various structures like in-situ growth for thin film devices and protective coatings.

2:40pm **B6-MoA-4 First-Principles Investigations of the Physical Properties of Experimentally Feasible Novel Aluminum Nitride Polytypes**, ***Mowafaq Mohammad Al-Sardia,*** Jejun University, Republic of Korea

We present the results of a first-principles study on the structural stability and electronic and optical properties of new aluminum nitride (AlN) polytypes. The study includes the experimentally or theoretically known phases of AlN wurtzite (WZ), zincblende (ZB), and rock salt (RS) structures, which complement the pressure-dependent phase diagram of this industrially important compound. In addition to the structures of AlN considered in previous studies, we evaluated the dynamic stability of various novel phases: viz., SiC(4H), ZnS(15R), BeO, 5-5, TiAs, NiAs, MoC, Li_2O_2 , and NiS. These were predicted recently in a high-pressure data-mining study of more than 140000 variations of the AlN structure, which claimed that they were either stable or nearly stable based on first-principles calculations. On the basis of the new AlN polytypes, the physical properties of all considered phases were compared, and the common trends and differences were determined. According to the phonon band structure calculations, nine phases of these new polytypes are free from imaginary frequencies. This indicates adequate dynamic stability and the experimental accessibility of the polytypes. Additionally, the calculated cohesive energies of the dynamically stable phases are comparable to those of WZ-AlN and those specified in the available literature. Furthermore, the observed electronic structures and optical properties indicate that the polytypism of AlN can be a practical tool for refining its physical and chemical properties. The new phases show significant potential for use in future AlN electronic and optoelectronic applications.

3:00pm **B6-MoA-5 Computational Supports to Identify Structural and Elastic Relationship of Metastable Crystalline And Amorphous Thin Films Alloys: $Mo_{1-x}Ni_x$ and $Mo_{1-x}Si_x$ Case Studies**, *C. Li,* 1State Key Laboratory of Superlattices and Microstructures, Institute of Semiconductors, China*; G. Abadias,* Institut Pprime - CNRS - ENSMA - Université de Poitiers, France*;* ***Philippe Djemia,*** LSPM UPR 3407, France **INVITED**

Metastable $Mo_{1-x}Si_x$[1]and $Mo_{1-x}Ni_x$[2] alloy films with $0 \le x \le 1$ were elaborated by magnetron co-sputtering. Amorphous or crystalline state were identified by x-ray diffraction while their mass density and atomic volume by x-ray reflectivity. Their elastic properties were investigated by combining the Brillouin light scattering (BLS) and the picoseconds ultrasonics (PU) techniques with additional conventional nanoindentation tests. A transition from bcc-crystalline to amorphous state is observed for a Si content, x_{Si} ~ 0.19 and Ni content, x_{Ni} ~ 0.26 while fcc-crystalline to amorphous state transition is observed for x_{Ni} ~ 0.73. These structural transitions are accompanied by modifications of physical and mechanical properties s, namely, longitudinal out-of-plane modulus C_{33}, and out-of-plane shear modulus C_{44}. In the crystalline regions, a pronounced softening of the shear elastic C_{44} constant from 110 GPa to 60 GPa for MoSi and from 65 GPa to 45 GPa for MoNi, is observed. The longitudinal modulus C_{33} has experienced a softening from 420 GPa to 300 GPa for MoSi and from 390 GPa to 280 GPa from both pure Mo and Ni. This behavior is an intrinsic consequence of the high Si and Ni supersaturation, leading to lattice instability. In the MoSi amorphous state, the evolution of the elastic properties exhibits two distinct behaviors depending on the electronic properties and metallic or covalent character of the amorphous alloys. For $0.19 \le x_{Si} \le 0.5$, the metallic character of the solid solutions is maintained and the elastic properties are remarkably stable. For $x_{Si} > 0.5$, a reduction in the atomic density is progressively observed and the amorphous alloys acquire a covalent character. We are again witnessing a progressive softening of the elastic stiffness constants while, surprisingly, both the longitudinal and transverse acoustic velocities increase continuously. In general, the analysis of the evolutions generally highlights the interdependence between the structural and elastic properties of the non-equilibrium phases formed between Mo and Si or Ni. Inter-relationships are discussed with help of ab initio molecular dynamics (AIMD) and density functional theory calculations (DFT).Glassy solid state of alloys made of 256 atoms, was obtained from cooling down the melt from 3500 K to 300 K using the NVT ensemble and the Nose thermostat, followed by a relaxation of the cell with NPT ensemble and Langevin thermostat for at least 15 ps by steps of 1.5 fs. Special quasi-random structures were built to mimic the random crystalline alloys.

[1]A Fillon *et al.*, Phys.Rev.B 88, 174104(1-16) (2013)

[2]G. Abadias *et al.*, Phys.Rev.B 65, pp. 212105(1-4) (2002)

3:40pm **B6-MoA-7 On the Quantification of Lattice Distortions and Their Correlation with Kinetics in High Entropy Sublattice Nitrides**, ***Ganesh Kumar Nayak,*** Montanuniversität Leoben, Austria*; A. Kretschmer,* TU Wien, Austria*; J. Sälker,* RWTH Aachen University, Germany*; P. Mayrhofer,* TU Wien, Austria*; M. Hans, J. Schneider,* RWTH Aachen University, Germany*; D. Holec,* Montanuniversität Leoben, Austria

Nitride-based ceramic materials serve high hardness and good thermal stability and have been attractive for high-temperature applications for

decades. To improve these properties of materials in ceramics, the concept of alloying was revolutionized in multi-component or high-entropy alloys (HEAs), where five or more elements are distributed randomly on a crystalline lattice in equiatomic or near-equiatomic composition. One crucial form of these ceramics is high-entropy sublattice nitride (HESN), which is built upon the concept of HEAs. Four core effects have been postulated for such materials to stem from the configuration entropy: high configurational entropy, severe lattice distortion, sluggish diffusion, and cocktail effects.

Despite the significant progress in recent years, proper quantification of the lattice distortions in HESNs and their effect on kinetics by altered local chemistry is still missing. The HESN systems considered for this ab initio study are structurally stable. Their models consist of metals distributed on the metal sublattice by the special quasi-random structure (SQS) method. Taking advantage of knowing the positions of all atoms in our structural models, we present a novel statistical approach for measuring the lattice distortions and discuss their correlation with the activation energies for vacancy-driven migration mechanisms in HESNs. Our analyses focus on comparing low and high entropy systems (as measured by the number of elements) for systems exhibiting small and large local distortions and similar and different nominal bond lengths of the forming binary nitrides. With the help of quantum-mechanical calculation, we evaluate the impact of the local composition and increasing high-entropy environment, which can significantly alter the activation energies consisting of vacancy formation energy and migration barrier contributions.

Our results undoubtedly demonstrate that the claimed sluggishness of the diffusion in HESNs is more composition and/or environment-specific than a general feature of all high entropy systems. Explicitly we will also present this statistical approach that can be used to support the argument of spinodal decomposition. Finally, we will show that the diffusion also significantly correlates to the electronic structure, namely the *d*-states, of the diffusing transition metal impurity.

4:00pm **B6-MoA-8 Machine-Learning Guided Ab-Initio Exploration of Thermal/Mechanical Properties in Transition Metal Nitrides***, **Andreas Kretschmer,*** TU Wien, Institute of Materials Science and Technology, Austria*; M. Fedrigo,* Oerlikon Digital Hub, Germany*; L. Lezuo,* TU Wien, Institute of Materials Science and Technology, Austria*; K. Yalamanchili, H. Rudigier,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

Ab-initio calculations have proven an efficient tool for exploration of fundamental material properties. However, in the context of solid solutions, the required cell dimensions for accurate predictions still require significant computational expense, barring the progress in high-throughput exploration. We have remedied this weakness with machine-learning (ML) models that are trained on the results of density-functional theory calculations, thus guiding the computationally expensive ab-initio exploration by computationally cheap data science. We investigated the phase space of all equimolar fcc solid solution nitrides of the group IVb-VIb nitrides + Al, with 1 to 5 metals in the compounds.

Using the DFT calculated energies of the multinary nitrides (published in [1]), we obtained the driving force for decomposition of the equiatomic multinary solid solutions into more stable phases for more than 16000 individual reactions. We trained different ML modelson this data and we developed some feature encoding strategies for the models to work on. The outcome is that a simple linear regression on a particular feature encoding is able to predict the driving force for decomposition quantitatively with an R^2 score of about 90%. This model is also capable of applying the concepts of entropy or strain stabilization [1] to predict stable phases beyond the current dataset.

The elastic constants of 230 nitrides have been iteratively calculated, starting from a base of ~30 compositions. ML regression models were trained and optimized to extrapolate the properties of these compositions and suggest points of interest for further ab-initio calculations, including Elastic Net, Random Forest, Gradient Boosting and Support Vector Regression. In the end, an aggregated model built on top of these four showed the best performance as measured by the R^2 score. This ML model was then fed more data in every iteration, increasing the prediction efficacy. After calculation of 230 alloys, the performance of the different models was cross-checked in a blind-test using the existing data. The best performing models reached correlation scores R^2 between 0.79-0.92 for different elastic properties such as bulk, shear, and Young's modulus, and Cauchy pressure. Thus, the ab-initio trained ML model is able to make confident predictions on the mechanical properties within this chosen phase space of nitrides (~630 alloys), these properties were also validated on 12 magnetron sputtered nitride coatings.

[1] Kretschmer, A., et al. (2022). Strain-stabilized Al-containing high-entropy sublattice nitrides. *Acta Materialia*, *224*, 117483. https://doi.org/10.1016/j.actamat.2021.117483

4:20pm **B6-MoA-9 Descriptors Development for Stability Prediction of N-Doped High Entropy Alloy Coatings: A DFT Study***, **Chih-Heng Lee,*** National Tsing Hua University, Taiwan*; J. Lee,* Ming Chi University of Technology, Taiwan*; H. Chen,* National Tsing Hua University, Taiwan

To achieve the desire hardness, strength, or ductility in high entropy alloy (HEA) coatings, doping element into the interstitial sites of HEA is a good method. Density functional theory (DFT) is often used to analyze, predict and design the physiochemical properties of alloys in the wide range of composition space. However, although DFT modeling has great potential to predict and design of HEA coating, it is very difficult to consider all the inequivalent doping sites present due to the low symmetry characteristic of HEA. In this study, we use 1st nearest neighbor (1NN) environment, local potential, and electrostatic potential via DFT calculation to be descriptors to predict the N doping energy in $VNbMoTaWTiAl_{0.5}$ coating systems to construct more stable N-doped models. Our results show that the Pearson correlation coefficient between 1NN environment and the N doping energy reached ~ 0.80, implying that the (1NN) environment could be a good descriptor to predict the doping energy of N in each interstitial site. The Pearson correlation coefficient between local potential / electrostatic potential and N doping energy reached ~ -0.7 without outlier, revealing that the interstitial site with higher potential energy of electron behave lower doping energy. To explain this result, we proposed that the electrons at high-potential interstitial site are more energetically preferred to combine with the orbital of doped N atom due to the high electronegativity of N. To test the universality of these descriptors, we plan to use high-throughput screening method to find the capability of these descriptors in the wide range of different alloys. We hope our approaches could efficiently predict stable N-dopped HEA coating models (in interstitial sites) and further apply to broaden systems.

4:40pm **B6-MoA-10 Structural Configuration of Simple Functional Groups on (100) Si Surfaces***, **Benjamin Whitfield,*** *R. Fleming,* Arkansas State University, USA

Silicon is a widely utilized semiconductor material with applications ranging from computer chips to solar panels. A realistic description of the surface of Si can improve the understanding of Si surface chemistry, especially in the presence of functional groups. In this study, the structural configuration of the Si (100) surface is studied for several terminating groups, including methyl, hydroxyl, fluoromethyl, and double-bonded oxygen. Relaxed surface geometries are calculated using density functional theory (DFT) structural optimization, along with bond dissociation energies and bond lengths at 0 K. This study provides a deeper understanding of the structure of functionalized silicon surfaces, leading to pathways to produce new advanced silicon-based materials.

5:00pm **B6-MoA-11 Bayesian Optimization-Assisted Sputter Deposition of Molybdenum Thin Films with Desired Stress and Resistivity***, **Ankit Shrivastava,*** *M. Kalaswad, D. Adams, H. Najm,* Sandia National Laboratories, USA

We introduce a Bayesian optimization (BayesOpt) based approach to guide the sputter deposition of molybdenum (Mo) thin films with desired residual stress and electrical resistivity. Thin films are of key importance in various technologies, including, e.g., semiconductor and optical devices. In thin film sputter deposition, process parameters, such as deposition power, vacuum chamber pressure, and working distance, can affect film physical properties, such as residual stress and resistivity. Excessive film residual stress as well as high resistivity can negatively affect the performance of devices; hence, choosing the optimum combination of process parameters that produce thin films with residual stress and resistivity within a desired range is essential. However, considering that the experiment is the available black-box "function" to evaluate these physical properties from process parameters, it is clear that the associated expense of full exploration of the design space for process optimization purposes is prohibitively expensive. BayesOpt is ideal for optimizing black-box functions without reliance on gradient information, and can find optimal process parameters with minimal evaluations.

In this work, we seek a combination of two primary process parameters (deposition power and pressure) such that 1) residual stress and resistivity

of Mo thin films are within a specified range, and 2) the variations in the stress are least susceptible to stochastic fluctuations in the deposition process parameters. To achieve this, we use BayesOpt to optimize an objective function, custom-built using observed stress and resistivity data, targeting both criteria. This involves incorporation of knowledge of stress dependence on pressure obtained from existing experimental observations into a stress-pressure surrogate, whose gradients are employed in the objective function. This surrogate, and thus the objective function, are updated based after each new measurement, ahead of the next BayesOpt step. We illustrate the performance of BayesOpt in the exploration of the Mo thin film deposition design space (power and pressure), arriving at optimal conditions that meet desired constraints on stress and resistivity.

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