Topical Symposia
Room On Demand - Session TS3

In-Silicio Design of Novel Materials by Quantum Mechanics and Classical Methods (jointly sponsored by ICMCTF and AQS)

TS3-1 INVITED TALK: Computational Modeling of 3D Thin Film Growth Morphology: Influence of Angular and Energy Distribution of Particle Flux, ***Grégory Abadias (gregory.abadias@univ-poitiers.fr)***, *C. Mastail, C. Furgeaud, F. Nita, R. Mareus, A. Michel,* Institut Pprime - CNRS - ENSMA - Université de Poitiers, France **INVITED**

Considerable work has been done in recent years, both experimentally and theoretically, to characterize and predict

the properties of thin films from external conditions, including substrate temperature, deposition rate, angular distribution of atoms, and incident kinetic energy. The interplay between some deposition parameters often renders the task to obtain the desired film morphology challenging. On the other hand, the control of the desired morphology is essential for the applications searched for. Predictions from computational approaches are therefore very helpful in this sense.

We have developed a 3D kinetic Monte Carlo (kMC) atomistic code to help understand the role of the elementary atomistic diffusion mechanisms and impact of deposited energy on the resulting thin film growth morphology. The simulation model aims at mimicking the full sputter-deposition process, from ejection of atoms from the target, their transport in the gas phase, and film formation. First-principle calculations are also implemented to determine the potential energy landscape for preferable adsorption sites, or energy barrier for surface diffusion.

In the work presented here, the code has been applied to simulate the growth of TiN and Cu thin films. Examples will be provided for the growth at either normal or oblique angle incidence. The code is capable of reproducing the development of TiN columnar morphology, with column tilt angle in good agreement with experimental findings. For the case of Cu, the growth proceeds in a 3D mode, with nucleation of isolated islands, percolation and formation of continuous layer. The influence of kinetic energy on film morphology and defect incorporation will be also discussed.

TS3-3 Prediction of Composition, Crystalline Structure and Microstructure of Sputtered Multi-Component Coatings by a Virtual Machine, ***David Böhm (david.boehm@tuwien.ac.at)***, Vienna University of Technology, Austria*; T. Schrefl,* Danube University Krems, Austria*; A. Eder,* MIBA High Tech Coatings GmbH, Austria*; C. Eisenmenger-Sittner,* Vienna University of Technology, Austria

To be able to predict the composition and the structural properties of multi-component thin films deposited by magnetron sputtering a so-called Virtual Machine (VM) was designed. The VM is an interactive ray tracing software that simulates film growth by a line-of-sight model, also taking into account the decay of the flux density of the particles due to gas phase scattering.The VM is initiated with a 3D model of a real sputter system which includes the static arrangement of multiple targets and the substrate and eventual obstacles, as well as dynamics like e. g. rotating substrate holders. Then the composition, the microstructure and the crystallographic phases with their associated XRD patterns are calculated for the simulated film. On each sampling point a composition is calculated over several time steps associated with an adjustable temperature which can be different for each step enabling the correlation of the real temperature distribution during the coating experiment. Depending on the material and the applied simulation parameters e.g temperature or coating rate models of grain growth and island formation are applied.With this information and a library of binary phase diagrams the corresponding crystallographic phase can be calculated and displayed per time step. The XRD patterns are calculated from the crystallographic phases and summed over all time steps. This procedure allows to construct a diffractogram which can be compared to the diffractogram of an accordingly produced sample. Another way to display the data is to stack the appearing composition and phases over all time steps. Such a phase stack is equivalent to an EDX line scan performed on a metallurgical cross section from the substrate to the surface of the coating. Several phase stacks can be compared with an element mapping of the cross section. Since surfaces and volume diffusion are not yet considered, only immiscible multilayer systems can be investigated at present. On the basis of examples the above mentioned comparisons are presented.

TS3-4 Atomistic Modelling of Diffusion in Quasi-amorphous Nanocomposite Coatings, ***Ganesh Kumar Nayak (ganesh.nayak@unileoben.ac.at)***, *D. Holec,* Montanuniversität Leoben, Austria

TiN-based materials are widely established as protective coatings for cutting tools. Grain interiors (single crystal regions) could serve as reservoirs for functional species, e.g. Al or V, which provide effective lubrication and wear protection at high temperatures by diffusing to the coating surface where they form a protective oxide scale (Al) or a lubricious oxide to reduce friction (V). The microstructure of real coatings has a polycrystalline or nanocomposite nature. Here, the intergranular region consists of quasi-amorphous (amorphous materials interfaced with TiXN, X=Al, V) tissue which serves as a diffusion highway for transporting species from bulk to the coating surface.

While approaches exist for estimating diffusivity in crystalline materials, the situation is much less explored in the case of (quasi-)amorphous materials. In this contribution, we will report on our recent progress in addressing issues related to the atomistic modeling of mass transport. To do so we employ complementary computational investigations to determine elementary point-defect migration mechanisms in crystalline as well as amorphous materials and subsequently their relative rates. Molecular dynamics (MD), which traces the motion of each particle contained in the system by numerically solving Newton's equations, coupled to the accuracy of density functional theory (DFT) to describe interatomic forces, is the most reliable computational tool to calculate atomic jump rates as a function of temperature. We will present the DFT-based "5-frequency model" allowing us to calculate the diffusion coefficient in the crystalline fcc material. Furthermore, we also demonstrate that pressure has a notable impact on the diffusivity of V, Al, and Ti in TiN. Next, we show how to approach both crystalline and amorphous materials by employing the Green-Kubo relation together with a detailed analysis of diffusion pathways as provided by MD.

TS3-5 Identifying Fingerprints of Point Defects in X-ray Photoelectron Spectroscopy Measurements of TiN and TiON with *ab initio* Calculations, ***Pavel Ondračka (ondracka@mch.rwth-aachen.de)***, RWTH Aachen University, Germany*; D. Holec,* Montanuniversität Leoben, Austria*; M. Hans, J. Schneider,* RWTH Aachen University, Germany

Point defects have great influence on mechanical, electrical, optical and other properties of (not only) nitrides and oxynitrides. Significant point defect concentrations are produced by highly energetic deposition processes such as high power pulsed magnetron sputtering (HPPMS), or, in the case of oxynitrides, are a direct consequence of the O incorporation. As the direct observation of point defects is complicated, the characterization of point defects is usually based on indirect information, such as the lattice parameter and composition measurements. In this work we explore a new combined theoretical and experimental approach for obtaining information about point defects from the X-ray photoelectron spectroscopy (XPS) measurements and *ab initi*o calculations of cubic TiN and TiON.

Density functional theory calculations using the all electron Wien2k code with the core-hole approach were used to calculate the N 1s and Ti 2p core electron binding energy shifts in TiN_x and TiO_xN_y. Considered point defects include N and Ti vacancies, different N and Ti interstitials and Frenkel pairs. It was shown that the majority of point defects have a significant influence on the binding energy of its first neighbours. For example, a single Ti vacancy decreases the binding energy of its nearest nitrogen neighbours by 0.6 eV. The aim of the *ab initio* calculations was to create a fingerprint database which could be used when analyzing experimental data.

The *ab initio* calculations were later utilized when analyzing XPS data from TiN and TiON thin films deposited by reactive DC and HPPMS magnetron sputtering. Thereby we were able to identify point defect-introduced features in the XPS spectra and, combined with lattice parameter and composition data, propose a quantification method. This work represents an important step on the road towards a more precise point defect identification and quantification in these materials.

TS3-6 Structural Ordering of Molybdenum Disulfide studied via Reactive Molecular Dynamics Simulations*, Paolo Nicolini (nicolpao@fel.cvut.cz),* Czech Technical University in Prague, Czech Republic*; R. Capozza,* Italian Institute of Technology, UK*; T. Polcar,* Czech Technical University in Prague, Czech Republic

Molybdenum disulfide, the most studied member of the transition metal dichalcogenides family, has been used as solid lubricant for several decades, showing extremely low friction coefficients[1] and stability to high temperature. Its lubricating properties are ascribed to the weak van der Waals interactions between sulfur atoms in the crystalline layered structure. Moreover MoS_2, even when prepared in the amorphous state or made of randomly oriented domains, can undergo shear induced structural transitions to the more ordered layered state affecting its tribological properties[2].

Exploiting a reactive classical force field[3] able to treat explicitly formation and breaking of bonds, we investigated by means of molecular dynamics simulations, the shear-induced structural changes and the possible layer formation in amorphous molybdenum disulfide. The ordering process is studied in details, with particular regard to the estimation of the thermodynamic properties that govern the process itself. A connection with crystallization theories is finally found, conferring a predictive power to the achieved results.

Overall, this study aims at gaining an atomic level understanding of the dynamics of layer formation process in MoS_2, thus controlling and possibly improving its tribological properties.

References:

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TS3-7 Strength, Transformation Toughening and Fracture Dynamics of Rocksalt-structure $Ti_{1-x}Al_xN$ ($0 \le x \le 0.75$) Alloys*, Davide Sangiovanni (davide.sangiovanni@liu.se),* F. Tasnadi, M. Oden, I. Abrikosov, Linköping University, Sweden

We employ density-functional molecular dynamics simulations to determine the elastic response, ideal strength and toughness, and ability to plastically deform up to fracture of defect-free rocksalt-structure (B1) TiN and B1 $Ti_{1-x}Al_xN$ (x = 0.25, 0.5, 0.75) solid solutions subject to [001], [110], and [111] tensile deformation at room temperature. Overall, TiN exhibits greater ideal moduli of resilience and tensile strengths than TiAlN alloys. Nevertheless, the binary compound systematically fractures by brittle cleavage at its yield point. The simulations also indicate that 25% Al substitutions in $Ti_{1-x}Al_xN$ have negative effects on mechanical performances; the alloy remains brittle, while both strength and resilience slightly decrease. In sharp contrast, $Ti_{0.5}Al_{0.5}N$ and $Ti_{0.25}Al_{0.75}N$ solid solutions exhibit inherently high resistance to fracture and greater toughness than TiN due to the activation of local B1 → wurtzite-like structural transformations beyond the elastic-response regime. The results of this work illustrate the inadequateness of elasticity-based criteria for the prediction of strength, brittleness, ductility, and toughness in materials able to undergo phase transitions at extreme loading. Furthermore, we discuss rationales for design of hard ceramic solid solutions that are thermodynamically inclined to dissipate extreme mechanical stresses via transformation toughening mechanisms.

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