Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B6

Coating Design and Architectures

Moderators: Nina Schalk, Montanuniversität Leoben, Shou-Yi Chang, National Tsing Hua University

1:30pm B6-1 Radial Symmetry of the Compound Layer Growth in Plasma Nitriding of Pure Iron, F Castillo, **Joaquin Oseguera**, E Hernánez, J Otero, D Melo-Maximo, A Jimenez, Instituto Tecnologico y de Estudios Superiores de Monterey, Mexico

Radial symmetry plays a fundamental role in tribological systems, where spinning on axes takes place. This is the case for crankshafts, camshafts and driveshafts among others.Thermochemical treatments, which involve diffusion of one element such as nitrogen, oxygen or boron, produce a concomitant layer growth. Usually, layer growth kinetics has been studied by modeling from a Cartesian coordinate perspective, using plane fronts. The use of thermochemical treatments on radial symmetry surfaces makes relevant to employ different approaches in order to improve the obtained results so far.

The present work proposes a mathematical model which describes the compact layer growth kinetics during plasma nitriding of a pure iron solid cylinder. The erosion effect at the plasma-solid interface due to sputtering is taken into account. The model constitutes a moving boundary value problems, for which radial symmetry solutions are found. The numerical simulation of the model is performed using both finite differences and the Heat Balance Integral Method (HBIM).

1:50pm B6-2 Self-assembled Nano-lamellar $Ti_{1-x}Al_xN$ LP-CVD Coatings: Development and Analysis, **Jakub Zalesak**, J Todt, Montanuniversität Leoben, Austria; I Matko, Institute of Physics, Slovak Academy of Sciences, Slovakia; M Petrenec, Tescan Brno s.r.o, Brno, Czech Republic; B Sartory, Materials Center Leoben Forschung GmbH (MCL), Austria; R Pitonak, Böhlerit GmbH & Co KG, Austria; R Daniel, J Keckes, Montanuniversität Leoben, Austria

Recent progress in low-pressure chemical vapour deposition introduced self-organized nano-lamellar $Ti_{1-x}Al_xN$ coating system with outstanding mechanical and thermal properties [1]. This system exhibits a complex three-dimensional ordering of nano-lamellar microstructure, whose composition and period depend on the overall composition. A combinatorial search for optimal process gas flow ratios, to reach dedicated phase composition, microstructure and mechanical properties, was performed using a „graded coating" concept [2]. The analyses of the phasecomposition, microstructure and mechanical properties were performed by using X-ray nanodiffraction, TEM imaging and micromechanical testing of microcantilever beam specimens. Based on the iterative multi-parameter-analysis, refinedprocess gas flow ratios were identified. The optimized cubic self-organized nano-lamellar coating with overall composition of $Al_{0.8}Ti_{0.2}N$ was subsequently heteroepitaxially grown onto a single crystalline 0001 sapphire substrate and subjected to further detailed analyses with the aim to understand the self-organisation mechanisms. For semi-quantitative compositional characterization, EFTEM, EELS and EDX methods were employed. The combination of elemental composition analyses and imaging revealed multi-dimensional periodical compositional oscillations of Ti, Al and N. This singularity, in combination with oriented nano-lamellar microstructure, pointed out that the self-organization effect has its origin in oscillating reactions.

[1] Todt et al. / Surface & Coatings Technology 291 (2016) 89-93

[2] J. Zalesak et al. / Acta Materialia 102 (2016) 212-219

2:10pm B6-3 Fundamental Properties of TM Nitrides: Materials Design Strategies for Extreme Properties, **Joe Greene,** University of Illinois at Urbana-Champaign, USA   **INVITED**

Transition-metal (TM) nitrides exhibit an enormous range of properties; they offer a smorgasbord of opportunities for materials scientists. Cubic TM nitrides have wide single-phase compound fields which can be exploited. We show results for vacancy hardening (not associated with film strain) in 3d Group-IV $TiN_x(001)$ and Group-V $VN_x(001)$; the hardness H of epitaxial layers increases dramatically, while the elastic modulus E and the relaxed lattice constant decrease linearly, as x is decreased from 1.0 to 0.67 and 0.80, respectively. Over the same x range, the resistivity $\rho(x)$ increases linearly due to electron scattering from N vacancies. In contrast, H(x), E(x), and $\rho(x)$ for 5d Group-V $TaN_x(001)$ remain constant due primarily to the presence of isoelectronic antisites.

All Group IV TM nitrides TiN, ZrN, and HfN are very good metallic conductors with room temperature resistivities of 12-14 μΩ-cm. 3d Group-III ScN(001) is a transparent semiconductor with an indirect Γ-X gap of 1.3 eV and a direct X-point gap of 2.4 eV. Reflectivity measurements from $Sc_{1-x}Ti_xN(001)$ layers show TiN is strongly reflecting up to the reflectance edge at $\hbar w_e = 2.3$ eV, while ScN is transparent and w_e μ $x^{0.5}$. ZrN is intermediate with $\hbar w_e = 3.04$ eV. Thus, hard decorative coating can be obtained with a wide palette of colors.

Superconducting transitions T_c for the Group-IV TM nitrides range from 10.4 K for ZrN to 9.18 K for HfN to 5.35 K for TiN. For comparison, superconductivity is not observed for the Group-IV rare-earth (RE) nitride CeN. These results are consistent with electron/phonon coupling parameters of 1.11 (ZrN), 0.82 (HfN), 0.73 (TiN), and 0.44 (CeN). The acoustic phonon modes soften monotonically with increasing cation mass; optical mode energies remain approximately constant for the TM nitrides, but are significantly lower for the RE nitride due a lower interatomic force constant.

The extreme range of materials properties available in TM nitrides and related systems can be enhanced through the formation of self-organized superhard nanostructures consisting of commensurate nanolamellae, nanocolumns, nanospheres, and nanopipes. Self-organization strategies include controlled phase separation, surface-induced spinodal decomposition, surface segregation-induced renucleation, strain-induced roughening, surface anisotropy, and dynamic resputter yield amplification.

An issue with superhard ceramic films, however, is that they are typically brittle leading to failure by crack propagation. We show several approaches to obtaining TM nitride layers that are both hard *and* ductile (i.e., tough). Groups IV-V alloys such as $V_{1-x}W_xN$, exhibit metal-atom ordering on adjacent 111 planes in the cation sublattice leading to, in addition to increased hardness, enhanced ductility. Vacancy-induced toughening is also observed in understoichiometric VN_x and $(V,Mo)N_x$ alloys. A final example represents an entirely different approach: designing TM nitride multilayers which are defined not by composition differences, but by bonding differences in alternating layers of essentially the same composition.

2:50pm B6-5 Stabilisation of Cubic MoN and TaN Systems: the Role Point Defects, **David Holec,** Montanuniversität Leoben, Austria; N Koutná, F Klimashin, P Mayrhofer, TU Wien, Austria

Point defects are unavoidably present in materials, either due to thermodynamic reasons (equilibrium) or due to the growth process (non-equilibrium). The latter is the case of physical vapour deposition (PVD), a technique often employed for synthesising nitride-based protective coatings. Both MoN and TaN have recently received attention due their unique mechanical, electrical and chemical properties. The stable variants of both of them are hexagonal structures. However, under specific deposition conditions, they may be prepared in a cubic rock-salt structure. In this contribution we will present our recent *ab initio* based insights into the role of point defects on the stabilisation of these cubic phases. In particular we will show that both materials prefer a presence of vacancies. While in the case of MoN, both Mo and N vacancies possess the same stabilisation effect, in the case of TaN a strong preference for Ta vacancies is demonstrated. Furthermore, we can show that the vacancies are preferably distributed in a disordered fashion in MoN, while both ordered and disordered configurations yield comparable changes of the energy of formation in TaN. Phase diagrams for various deposition conditions will be presented and a relevance to our recent experimental data on N-deficient MoN will be also discussed.

References:

[1] N. Koutná, D. Holec, O. Svoboda, F.F. Klimashin, and P.H. Mayrhofer, J. Phys. D Appl. Phys. **49**, 375303 (2016).

[2] F. F. Klimashin, N. Koutná, H. Euchner, D. Holec, and P.H. Mayrhofer, submitted.

3:10pm B6-6 Vacancy Induced Mechanical Stabilization of Cubic Tungsten Nitride, **Karthik Balasubramanian**, Rensselaer Polytechnic Institute, USA

First principle calculations are employed to determine the mechanical stability and the formation energies E_f of point defects in rock-salt phase group III B – VI B transition metal nitrides and carbonitrides. Interstitials and antisite defects have relatively high E_f values, in average 3.9 and 9.7 eV higher than those for anion and cation vacancies, such that the latter are the energetically preferred point defects to account for deviations from stoichiometry. The vacancy formation energy decreases when moving towards the right in the periodic table, from $E_f = 5.1$ to -7.1 eV for anion

vacancies in ScN and WN, respectively, and from E_f = 3.2 to -12.0 eV for the corresponding cation vacancies. This decrease is accompanied by a decrease in the single crystal shear modulus, from c_{44} = 161 for ScN to 164, 126, and -120 GPa, for TiN, VN, and CrN, indicating a transition to mechanical instability of rock-salt nitrides and carbonitrides with increasing valence electron concentration above 5.3. The negative E_f values for both cation and anion vacancies in group VI B nitrides indicate that the rocksalt structure is thermodynamically unstable, despite experimental observations of cubic rock-salt type WN and MoN. We investigate this discrepancy by comparing the energetic and mechanical properties of WN in the experimentally reported rocksalt and theoretically predicted NbO phases. The rocksalt WN is both mechanically and thermodynamically unstable with a formation enthalpy H_f= 0.637 eV per formula unit and a negative c_{44} = -86 GPa while the NbO phase is stable with H_f= –0.825 eV and c_{44}= 175 GPa. Charge distribution and electronic density of states analyses reveal that the mechanical instability of rocksalt WN is due an increased overlap of t_{2g} orbitals upon the application of shear strain along [100], resulting in electron migration from the expanded [110] to the shortened [1-10] direction and a negative shear modulus. The mechanical transition from the unstable NaCl to the stable NbO phase is further explored using supercell calculations of the NaCl structure containing C_v= 0 to 25 % of both cation and anion vacancies. The structure is mechanically unstable for C_v <5 %. At this critical vacancy concentration, the isotropic elastic modulus is zero but increases steeply to 445 GPa for C_v= 10 % and to 561 GPa for the NbO structure with C_v= 25 % which is in good agreement with experimentally measured elastic moduli ranging from 110 – 360 GPa. These results show that the experimental reports of a cubic WN phase can be explained by the mechanical stabilization of the rocksalt phase by a minimum of 5% anion and cation vacancies.

3:30pm B6-7 Nitrides and the Impact of Entropy on their Phase Stability, *Paul H. Mayrhofer*, TU Wien, Austria; *D Holec,* Montanuniversität Leoben, Austria; *F Klimashin, N Koutná,* TU Wien, Austria

Transition metal based nitrides are fascinating materials, owing to their excellent performance against mechanical attack. Since Jien-Wei Yeh's work in 2004 on "Nanostructured High-Entropy Alloys with Multiple Principal Elements: Novel Alloy Design Concepts and Outcomes", research activities on the impact of configuration entropy on the stability of solid solution phases increased. Corresponding to amorphous metals, also high entropy alloys have the potential for increased strength with a combined high fracture, corrosion, and oxidation resistance. Here we discuss in more detail the impact of configurational entropy on the phase stability, mechanical properties and thermal stability of hard ceramic coatings (like Ti-Al-N, Cr-Al-N, Mo-Al-N, Ta-Al-N and combinations thereof). Additionally, we will also treat vacancies (present especially in Mo, W, and Ta containing nitrides) as an important partner for the configurational entropy and discuss their impact on mechanical properties and phase stabilities.

3:50pm B6-8 Molecular Dynamics Simulations of TiN/TiN(001) Growth, *D Edström, D Sangiovanni, L Hultman,* Linköping University, IFM, Sweden; *I Petrov, J Greene,* University of Illinois at Urbana-Champaign, USA; *Valeriu Chirita,* Linköping University, IFM, Sweden

The Modified Embedded Atom Method (MEAM) interatomic potential is used within the classical Molecular Dynamics (MD) framework to perform simulations of important model materials such as TiN, in order to understand the processes which control TiN growth modes on a fundamental level. We report the results of large-scale simulations of TiN/TiN(001) deposition using a TiN MEAM parameterization which reproduces experimentally-observed surface diffusion trends, correctly accounts for Ehrlich barriers at island step edges [1], [2], and has been shown to give results in good qualitative and quantitative agreement with Ab Initio MD based on Density Functional Theory [3], [4]. We deposit 85% of a monolayer of TiN on 100x100 atom TiN(001) substrates maintained at 1200 K, at a rate of 1 Ti atom per 50 ps, for total simulation times of 212.5 ns. We use N/Ti flux ratios of 1, 2, and 4, and incident N energies of 2 and 10 eV, to probe the effects of N_2 partial pressure and substrate bias on TiN(001) growth modes. We observe nucleation of Ti_xN_y molecules; N_2 desorption; formation, growth and coalescence of mixed <100>, <110>, and <111> faceted islands; as well as intra- and interlayer mass transport mechanisms. For N/Ti flux ratios of 1 at 2 eV incidence energy, films exhibit Ti-rich surface regions which serve as traps to nucleate higher layers, leading to multilayer growth. Increasing the N/Ti flux ratio shifts the growth mode to layer-by-layer and modifies the overall film composition from under- to over-stoichiometric. As the N content of films is increased, N-terminated <110>-oriented island edges become increasingly dominant and the substrate vacancy concentration changes from being N- to Ti-

dominated. We discuss the implications of these results on thin film growth and process tailoring.

[1] D. G. Sangiovanni, D. Edström, L. Hultman, V. Chirita, I. Petrov, and J. E. Greene, "Dynamics of Ti, N, and TiN_x (x=1–3) admolecule transport on TiN(001) surfaces," *Phys. Rev. B*, vol. 86, no. 15, p. 155443, 2012.

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[3] D. G. Sangiovanni, D. Edström, L. Hultman, I. Petrov, J. E. Greene, and V. Chirita, "Ab initio and classical molecular dynamics simulations of N_2 desorption from TiN(001) surfaces," *Surf. Sci.*, vol. 624, pp. 25–31, 2014.

[4] D. G. Sangiovanni, D. Edström, L. Hultman, I. Petrov, J. E. Greene, and V. Chirita, "Ti adatom diffusion on TiN(001): Ab initio and classical molecular dynamics simulations," *Surf. Sci.,* vol. 627, pp. 34-41, 2014.

4:10pm B6-9 Development of Reliable Interaction Potential for and Results of Molecular Dynamics Simulations of ZrO_2 Film Growth, *Jiří Houška,* University of West Bohemia, Czech Republic

Thin films of ZrO_2 are of high interest due to a wide range of useful technological properties. In this contribution the growth of ZrO_2 is studied by atom-by-atom molecular dynamics simulations, focused on intrinsic process parameters such as the energy (E) and energy distribution function (EDF) of arriving atoms or the surface temperature (T).

The first part deals with the development of an interaction potential for a realistic description of atom-by-atom ZrO_2 growth. Owing to the fact that for many metal oxides including ZrO_2 only full-charge (Zr^{+4} and O^{-2}) interaction potentials are available in the literature, special attention is paid to the effect of the Zr and O elemental charges. Parameters of the short-range part of the Buckingham interaction potential leading to experimental lattice parameters and formation energies have been identified in a wide range of elemental charges. Simulations reveal that the structures grown using the presently available full-charge interaction potentials are in contradiction with the experiment (the atoms have too low coordination numbers). Correct partial charges and potential parameters leading to experimentally relevant structures (with correct coordination numbers) have been identified [1].

The second part shows how do the film densification, crystal nucleation and uninterrupted crystal growth depend not only on E delivered into the growing films (i) per fast atom (ion) or (ii) per any atom, but especially (iii) on the EDF (namely the fraction of fast atoms in the particle flux) and (iv) on the mass of fast atoms (Zr or O). On the one hand, the nucleation of c–ZrO_2 (the most desired phase) is T-dependent and requires (in order to take place on a short time scale) high E. On the other hand, the growth of previously nucleated (or epitaxial growth of) c-ZrO_2 is much easier, T-independent, and highly dependent on the EDF. Optimum EDFs which allow uninterrupted crystal growth at as low E delivered into the growing films as possible are characterized by (i) narrow EDF and (ii) high momentum delivered into the growing films (i.e. the combination of fast Zr and slow O leads to a better densification and crystallinity than the opposite) [2].

The results (in addition to the methodological importance of the interaction potential development) facilitate defining new synthesis pathways for ZrO_2, and constitute phenomena which may be relevant for other coating materials (isostructural HfO_2 at the first place) as well.

References

[1] J. Houska, Comp. Mater. Sci. 111, 209 (2016)

[2] J. Houska, Surf. Coat. Technol. 304, 23 (2016)

4:30pm B6-10 Experimental Validation of Metal-on-insulator Thin Film Growth Theory, *B Lü, L Souqui, V Elofsson, Kostas Sarakinos*, Linköping University, Sweden

The current understanding of thin film growth dynamics relies to a large extent on the widely accepted theory of morphology evolution in metal-on-metal homoepitaxial systems which exhibit a strong thermodynamic tendency towards 2D growth. This understanding is, however, challenged when considering the deposition of metal vapor on insulating surfaces; which is governed by a complex interplay between formation, growth, and coalescence of 3D atomic islands. This interplay is described quantitatively by the less established theory for metal-on-insulator (MOI) growth, which

originates from the literature of water vapor condensation and the formation of breath figures, most notably reviewed by Family and Meakin. In contrast to water clusters, 3D atomic islands formed upon vapor condensation, exhibit a size-dependent coalescence rate leading to a so-called elongation transition, which occurs upon sufficient deposition such that coalescing islands become kinetically frozen into elongated shapes. This transition is a key component in the MOI growth theory as it entails information about film growth dynamics encoded in scaling relations between the nominal film thickness (i.e., coverage θ) at elongation, θ_{Elong}, and the rates of vapor deposition, adatom diffusion and 3D island coalescence. While this scaling behavior has been confirmed quantitatively by computer simulations, the lack of a suitable method to measure θ_{Elong} has left experimental proof of the theory ambiguous. In this study, we combine experiments and kinetic Monte-Carlo simulations to develop and implement a method for measuring θ_{Elong} for Ag grown on amorphous SiO_2. Our data confirm the theoretically predicted θ_{Elong} power laws which are then used to calculate the adatom diffusion and coalescence rates for Ag/SiO_2 in good agreement with the literature. The data presented herein constitute a first step towards an experimental validation of the prevailing MOI growth theory and thereby lay the foundation for establishing a universal understanding of thin film growth dynamics. In practical terms, knowledge of the adatom diffusivity and coalescence rates, could facilitate more informed decisions regarding growth manipulation by, e.g., doping, surfactant action or tuning of the deposition rate and growth temperature. This may be of importance for a number of applications where MOI is relevant, such as architectural glazing, microelectronics, catalysis, and the metallization of graphene.

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