Advanced Characterization, Modelling and Data Science for Coatings and Thin Films
Room Golden State Ballroom - Session CM-ThP

Advanced Characterization, Modelling and Data Science for Coatings and Thin Films (Symposium CM) Poster Session

CM-ThP-1 Localized Surface Plasmon Resonance of Silver Nanoparticle Thin Films on Moissanite: Simulation, Fabrication, and Characterization*,* ***Tsung-Jen Wu (d09224004@ntu.edu.tw)****, S. Song, W. Chen,* National Taiwan University, Taiwan*; W. Lin,* National Taiwan University of Science and Technology, Taiwan*; M. Phan,* National Taiwan University, Taiwan*; S. Tseng,* National Synchrotron Radiation Research Center, Taiwan

The fabrication and characterization of silver nanoparticle (Ag NPs) thin films on a moissanite (silicon carbide) substrate and their inherent localized surface plasmon resonance (LSPR) properties were investigated in this study. The preliminary phase of this investigation employed Finite-Difference Time-Domain (FDTD) simulations to anticipate the LSPR effects and the resultant hue of the films. The size of the silver nanoparticles was maintained within a range of 10-25 nm, producing a greenish yellow hue attributed to the LSPR effect.

Two methods were harnessed to produce these size-specific Ag NP films. The first approach involved a dual-target co-sputtering technique utilizing silver and silicon dioxide. It prompted the spontaneous formation of Ag NPs, leading to a visible coloration due to the LSPR effect. The other method involved a single-target sputtering of silver, followed by an annealing process to foster the emergence of Ag NPs, yielding a characteristic color induced by the LSPR effect.

CM-ThP-2 Greybox-Models to Describe the Wear Behavior of Coated Cutting Tools*,* *K. Bobzin, C. Kalscheuer,* ***Nina Stachowski (stachowski@iot.rwth-aachen.de)****,* Surface Engineering Institute (IOT) - RWTH Aachen University, Germany

The real application behavior of coated carbide tools can neither be satisfactorily measured, nor described within existing models with the current state of research. The wear development, beginning tool failure as well as the remaining tool life cannot be accurately identified or predicted. This inhibits the knowledge-based qualification of coated tools for more efficient cutting processes. In the current state of research, the tribological system of machining must be evaluated and repeatedly analyzed for every small change in the cutting condition. This is despite the fact that both involved disciplines of production and material engineering have already detailed whitebox models. However, not all available data from both disciplines can be integrated into these models.The main objective is therefore to combine the existing whitebox models with new data driven blackbox models in greybox models. These new greybox models are used to determine the temporal changes of the tools in use, which cannot be described in purely deterministic terms, right up to the end of their service life. Further developments in machining, material and coating technology enable the evolution of new methods for analyzing and simulating the wear behavior of coated cutting tools. This includes the investigation of time- and temperature-dependent coating properties such as indentation modulus, indentation hardness, thermal diffusivity and surface roughness with increasing cutting time. Such changes have not been considered in simulation models up to now. However, by taking such data into account, the description of the wear behavior can be probably significantly more accurate. Another key factor within the SPP 2402 is the data storage as well as the comparison of measurement methods. This enables a better estimation of quality within all participating consocial projects. The final greybox models allow the description of the time-dependent changes in the material properties and the stress collective during machining.

CM-ThP-3 Flow Curve Determination of TiAlSiN Coatings Using Nanoindentation and Iterative FEM Simulations*,* *K. Bobzin,* ***Christian Kalscheuer (kalscheuer@iot.rwth-aachen.de)****, X. Liu,* Surface Engineering Institute - RWTH Aachen University, Germany

Physical vapor deposition (PVD) coatings are extensively employed to improve the service life of tools under high thermomechanical load in forming processes. The wear resistance of coatings is highly related to their mechanical properties, especially elastic and plastic properties that can be delineated by the flow curve. Consequently, the accurate determination of the flow curve holds paramount significance in the coating development process. While the elastic modulus can be easily measured using nanoindentation, other flow curve parameters are difficult to determine. The current analytical Juliano approach for determining the yield stress lacks precision and becomes challenging to use when the Juliano signal is not obvious, particularly evident in the investigated TiAlSiN coatings that exhibit minimal plastic behavior. Therefore, an easier and more precise flow curve determination method is required. In this study, flow curves of TiAlSiN coatings are determined combining nanoindentation and iterative finite element simulations (FEM). Initially, nanoindentation using a spherical indenter is performed accompanied by the measurement of time-load and time-displacement curves. Then the nanoindentation is simulated time-dissolved using FEM based on the load at each time step directly derived from the time-load curve. The flow curve parameters in FEM including the Young's Modulus E, yield stress Y, strain hardening coefficient B and strain hardening exponent n are iteratively adjusted by comparing the experimental and simulated time-displacement curves until a good match between two curves. Consequently, the flow curve can be obtained from the FEM model with the best match. The simulated time-displacement curves with physically reasonable flow curve parameters have a good agreement to the experimental time-displacement curves of various TiAlSiN coatings. The method uses FEM simulations to determine all flow curve parameters without measuring the Young's Modulus using nanoindentation and determining the yield stress using the Juliano approach.

CM-ThP-4 Material Property Distributions of Sputter-Deposited Thin Films on a Two-Dimensional Diagram with Incident Particle Energy and Substrate Temperature*,* ***Ichiro Ikeda (ichiro-ikeda@osakavacuum.co.jp)****, K. Kuroshima,* Osaka Vacuum, Ltd., Japan*; Y. Gotoh,* Department of Electronic Science and Engineering, Kyoto University, Japan*; M. Iguchi, S. Sugimoto,* Osaka Vacuum, Ltd., Japan

Recently, we have confirmed that Anders' structure zone model (SZD)[1] is applicable to the case of conventional magnetron sputtering[2-3]. TheSZD shows the difference of the film structure on a two dimensional diagram with the normalized incident particle energy and normalized substrate temperature. Based on the fact that the properties of the films depend upon the film structure, we assumed that the distribution of mechanical or electrical property is also well expressed on this two-dimensional diagram. We named the diagram the material property diagram (MPD)[4].

In this study,we attempted to make MPDs ofelectrical conductivity and optical reflectancedistribution of Ti films. Titanium thin films were deposited under various deposition conditions. The deposition conditions were translated to the particle energy incident on a film surface using the computer simulation[2-3] to identify the deposition condition on MPD. From the accumulated data, we drew contour lines for each film property. As a result, it was confirmed that contour lines for electrical conductivity were arranged in parallel to ZONE border on SZD. The electrical conductivity is well explained by the SZD, reflecting the fact that film structure. On the other hand, the contour lines for the optical reflectance were not arranged in parallel to the ZONE border of the SZD. The optical reflectance has relationship different from the film structure. The film property will be well expressed on the MPD, and the diagram differs depending on the material and property itself. About the film property distribution, we confirmed little difference between equipments.

We made the simulation program calculating the sputtering condition from the requested film property value (ex. the conductivity) using the MPD on the assumption that the MPD does not depend on the sputtering condition and the equipment. We may be able toleave out the experience, the intuition or the test sputtering by the use of this program.

References

[1] K. Kuroshima et al., Annual Meeting of the Japan Society of Vacuum and Surface Science 2023,

Nagoya, October 31-November 2, 2023.

[2] K. Kuroshima et al., International Conference on Metallurgical Coatings & Thin Films 2024,

San Diego, May 19-24, 2024 (to be presented).

[3] A. Anders, Thin Solid Films, **518**, 4087 (2010).

[4] I. Ikeda et al., Annual Meeting of the Japan Society of Vacuum and Surface Science 2023,

Nagoya, October 31-November 2, 2023.

CM-ThP-5 AI-Enabled Construction and Prediction of Atomic Models for Thin-Film Heterostructures via Materials Genome Approach, ***Po-Liang Liu* (*pliu@dragon.nchu.edu.tw*)**, *J. Dai,* National Chung Hsing University, Taiwan

Successful heteroepitaxial film growth enables the integration of heterogeneous films despite lattice mismatches. Exceptional heteroepitaxial films alleviate lattice mismatch stress and diminish material defect density, resulting in smoother surfaces and reduced deposition time for subsequent thin-film epitaxial growth. This study introduces a materials genome approach to predict heterostructures. Employing this novel method, we explore new thin-film heterostructures on flexible muscovite mica substrates. As flexible electronic devices rapidly advance, traditional epitaxial substrates are being supplanted by flexible alternatives, yielding substantial economic benefits. While polymers are commonly used for such devices, they suffer from poor thermal stability, low solvent resistance, and a low thermal expansion coefficient. Layered muscovite mica materials have emerged as a promising solution. Muscovite mica, with its two-dimensional layered structure, can be easily divided into flakes, offering mechanical flexibility, optical transparency, and high thermal stability. We have successfully developed a novel artificial intelligence-generated heterostructure for studying the GaN(001)/Muscovite(001) heterostructure. Our findings reveal that the GaN thin film, characterized by the gene T1, epitaxially grows on muscovite substrate models characterized by gene arrangements S1 and S3. The heterojunction demonstrates the potential to form 12 Ga-O bonds, with a calculated lowest interface energy of −1.21 eV/Å².

CM-ThP-8 In-Situ Characterization of the Crystallization Kinetics of Sputtered TiO_2 Thin Films, ***Daniel Félix Fernandes* (*daniel.f.fernandes@angstrom.uu.se*)**, Department of Electrical Engineering, Division of Solid-State Electronics, The Ångström Laboratory, Uppsala University, SE-751 03 Uppsala, Sweden; *J. Hérnandez,* Madrid Institute for Advanced Studies in Nanoscience (IMDEA Nanoscience), Ciudad Universitaria de Cantoblanco, C/ Faraday 9, 28049 Madrid, Spain; *J. Martínez,* ALBA Synchrotron, Carrer de la Llum 2-26, 08290 Cerdanyola del Vallés, Barcelona, Spain; *T. Kubart,* Department of Electrical Engineering, Division of Solid-State Electronics, The Ångström Laboratory, Uppsala University, SE-751 03 Uppsala, Sweden, Spain

Crystalline TiO_2 thin films are attractive owing to their photocatalytic, electronic, and optical properties.Anatase is the lower-temperature metastable phase of this material system and is the desired phase in many applications.While the phase formation can be controlled by both the deposition and post-depositionannealing temperatures, it is often desireable to reduce the overall thermal budget. Forthe large majority of cases, the employed temperaturesfor the crystallization of suchfilms areconsiderablyhigh, making it incompatiblewith heat-sensitive substrates.

In this study, the crystallization kinetics of TiO_2thin films during post-deposition annealing is investigated.These were grown by reactive magnetron sputtering at different temperatures and the kinetics assessedby in-situ Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS), with synchrotron radiation. The films were heated for 2 hours and, using an adapted Avrami model for phase change kinetics, the crystallization times were compared for three annealing temperatures: 225, 250 and 300°C. The growth conditions achieved in pulsed-DC (pdcMS) and High Power Impulse Magnetron Sputtering (HiPIMS) were investigated. For both techniques, the influence of the mode of reactive operation, the ionization of the sputtered flux and the deposition temperatures were studied.

All studied films were X-ray amorphous in their as-deposited state. However, the depositionconditions have a significant impact on the transformation kinetics. The results show that the deposition temperature is the single most influential parameter. While the reactive mode of operation also affected the transformation dynamics, HiPIMS was found to facilitate sthe crystallization compared to pdcMS films, and generally promoteda faster formation of the anatase phase. Additionally, from the GIWAXS experiments, a set of optimal growth conditions are identified for ex-situpost-deposition annealing. The optimized conditions were investigated for a 2 hour periodat 250°C. In all cases, anatase was achieved. Depending on the growth conditions, specific anatase planes were favored, as seen in GIXRD measurements.

CM-ThP-9 On the Utility of SiMTra Analysis for Forecasting Atomistics of Confocal Deposition of Bimetal Alloys, ***Kyle Dorman* (*krdorma@sandia.gov*)**, *R. Kothari, N. Bianco, M. Kalaswad, C. Sobzcak, R. Dingreville, D. Adams,* Sandia National Laboratories, USA

Nanocrystalline thin films feature the potential for enhanced or altered material properties compared to their bulk single crystal counterparts. Assessing thermally stable binary metal systems that feature solute enrichment of grain boundaries (J.R. Trelewicz et al., PRB, 2009) for specific material properties, it is a complex task to survey the full compositional range. High-throughput methods of combinatorial sputtering (McGinn, ACS Comb. Sci., 2019) and complementary high-throughput automated data collection systems potentially permit swift accumulation of a large quantity of data on a broad selection of alloy compositions, if provided.

In this poster, we describe the application of the binary collision Monte Carlo program SiMTra (D. Depla et al., Thin Solid Films, 2012) to the challenge of efficient guidance of depositions to access a large range of compositions in a minimal set of depositions. A series of compositionally varied Cu-Ag and Ni-Pt bimetal alloy thin films were prepared by pulsed DC magnetron sputter deposition with varied sputter power and gun-tilt angle. SiMTra simulations provided estimates of film composition for the employed sputter chamber geometry and parameters involved with the simultaneous confocal sputter deposition of each pair of elements. The result is demonstrated with the near-full range of composition achieved, in only three depositions for Cu-Ag, onto 112 samples of 1 cm2 per 150 mm-diameter silicon wafer. The simulation results are presented in comparison to verifying Wavelength Dispersive Spectroscopy (WDS), to demonstrate the degree of accuracy with which SiMTra can specify the binary composition. Successful modeling of film compositions relied on the use of accurate global angular distributions of each elemental target which accounts for target erosion geometry, redeposition, material specific ejecta distributions, and sputter yield amplification with incidence angle following the method of Boydens et al. (Thin Solid Films, 2013). Additionally, we investigate the potential role of off-normal- vs. normal-oriented local ejecta distributions on final film composition by varying these orientations within separate simulations for comparison with WDS. Finally, we present other SiMTra outputs including the energy and incidence angle distributions of species arriving at the film growth surface, which are being used to optimize key film properties such as film hardness and resistivity.

SAND2023-14869A. Sandia National Laboratories is managed and operated by NTESS under DOE NNSA contract DE-NA0003525.

CM-ThP-10 Investigation of Lithium-Ion Battery Cathodes as a Function of Drying, ***Tatyana Kravchuk* (*tkravchu@ford.com*)**, *S. Peczonczyk, T. Misovski, M. Trought, B. Emley, A. Straccia,* Ford Motor Company, USA

Studying the elemental distribution and morphology in Li-ion battery electrodes prepared under various drying conditions is crucial for comprehending the connection between processing conditions and battery performance. Efficiency in time, cost, and energy usage are common goals in large-scale battery manufacturing, and a deeper understanding of these connections can aid in the development of precise drying protocols for ensuring consistent and high-performance Li-ion batteries at a large scale.

This study describes an analysis performed using Time-of-Flight Secondary Ion Mass Spectroscopy on electrode coatings prepared under various drying conditions, including different temperatures of system components and airflow. The significance of sample preparation is underscored, with a discussion of various methods such as ion milling and microtoming. Subsequently, differences in element distribution and surface morphology between electrodes processed under different conditions are investigated. Experimental findings obtained via TOF-SIMS are compared to those obtained through other surface-sensitive techniques and to those predicted by computational simulation methods. Lastly, the implications of the results for manufacturing are deliberated.

CM-ThP-11 Actually Measuring Thin Film Elastic Constants by Combined X-ray Microdiffraction and Micromechanical Testing, ***Rebecca Janknecht (rebecca.janknecht@tuwien.ac.at)***, Institute of Materials Science and Technology, TU Wien, Austria; *R. Hahn,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria; *N. Koutná,* Institute of Materials Science and Technology, TU Wien, Austria; *J. Todt, M. Meindlhumer,* Department Materials Science, Montanuniversität Leoben, Austria; *A. Davydok,* Helmholtz-Zentrum Hereon, Institut für Werkstoffphysik, Germany; *P. Polcike, S. Kolozsvári,* Plansee Composite Materials GmbH, Germany; *J. Keckes,* Department Materials Science, Montanuniversität Leoben, Austria; *H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria; *P. Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria

Direction-dependent X-ray Elastic Constants (XECs) measurements are far from routine and pose significant technical challenges. While nanoindentation offers insights into reduced Young's modulus, accessing direction-dependent XECs necessitates innovative methodologies due to inherent challenges compared to bulk materials (e.g., tensile testing). Although ab initio Density Functional Theory (DFT) calculations offer theoretical input, discrepancies persist between model systems and real-world properties, primarily due to a lack of available experimental data for newly emerging—and often chemically and structurally complex—material systems.

Our study addresses this gap by proposing a novel experimental approach to measure XECs, combining synchrotron microdiffraction and micropillar compression testing to investigate the in-situ stress-strain relation within TiN-based physical vapor deposited (PVD) thin films. Our investigation focuses on two individual ceramic TiBN coatings with boron contents up to 10 at.%, where linear elastic failure prevails. By employing in-situ uniaxial testing at P03 beamline of PETRA III synchrotron at DESY in Hamburg, Germany, we create a controlled environment for the determination of the stress in loading direction and strain in three directions to calculate orientation-dependent Poisson's ratios and Young's modulo, facilitating the calculation of XECs for crystal orientations 111, 200, and 220. By correlating our experimental results with ab initio calculations, our study provides a robust and new method for validating theoretical predictions and advancing thin film material testing and design.

CM-ThP-12 The Influence of Cantilever Geometry on the Measured Fracture Toughness of Hard Coatings, ***Rainer Hahn (rainer.hahn@tuwien.ac.at)***, Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria; *S. Kolozsvari, P. Polcik,* Plansee Composite Materials GmbH, Germany; *C. Jerg,* Oerlikon Surface Solution AG, Liechtenstein; *H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

Fracture toughness, K_{IC}, is an essential material property representing the resistance to crack propagation in the most prevalent opening mode. The fracture toughness should be correspondingly high to prevent premature failure of a material or a thin film with subsequent environmental exposure of the substrate. As a result, toughness is an important safety factor when designing protective coating materials exposed to mechanical loads. The fracture toughness of coatings is typically determined using micromechanical methods due to the small dimensions. The microcantilever bending test should be particularly mentioned here, as it determines the intrinsic K_{IC} without possible substrate influences.

This study investigated the influence of the cantilever geometry, particularly the distance between the point of force application and the position of the predefined crack. For this purpose, cathodic arc evaporated TiN was selected as a reference material, and a series of cantilevers were fabricated via focused ion beam (FIB) milling, and subsequently tested with an in-situ indentation stage within the SEM. The calculated fracture toughness was found to be dependent on the distance: as the distance increased, the values decrease to a subsequently constant K_{IC}. In summary, this study discusses failure sources for any over- and under-estimations due to geometrical aspects and provides guidelines for properly conducting and interpreting microcantilever bending tests estimating K_{IC}.

CM-ThP-13 e-Poster Presentation: Finite-Temperature Shear Deformation and Phase Transformations of Transition Metal Diborides MB_2 (M=Ti, Ta, W, Re) via Machine-Learning-Potential Molecular Dynamics, ***Shuyao Lin (shuyao.lin@tuwien.ac.at)***, TU Wien, Institute of Materials Science and Technology, Austria; *D. Holec,* Montanuniversität Leoben, Austria; *D. Sangiovanni, L. Hultman,* Linköping Univ., IFM, Thin Film Physics Div., Sweden; *P. Mayrhofer, N. Koutná,* TU Wien, Institute of Materials Science and Technology, Austria

Transition metal diborides (MB_2s) adopt three types of layered hexagonal structures (α, γ, ω) which are different stackings of the metallic sublattice, thus, may be inter-changeable by a displacive transformation. To test this hypothesis, we develop machine learning interatomic potentials (MLIPs) targeted to molecular dynamics simulations of finite-temperature tensile and shear deformation. The chosen material systems, MB_2, M=(Ti, Ta, W, Re), exemplify different energetic preference for the α, γ, ω phase polymorphs. Following the MLIP fitting procedure, a detail validation for atomic-to-nanoscale simulations is presented using a relevant ab initio dataset (including snapshots of ab initio molecular dynamics simulations on shear-induced phase transformation) as well as through the concept of the extrapolation grade. Consequently, the here-developed MLIPs are employed for room-temperature simulations of {0001}[$\overline{1}2\overline{1}$0] and {0001}[10$\overline{1}0]$ shear deformation with nanoscale-sized supercells. Our results reveal a significant impact of the phase prototypes on the shear strength, which is the highest for the energetically most favourable stackings. Shear-induced phase transformations are predicted for TiB_2 and TaB_2. The transformations can be aided by applying additional tensile or compressive strain along the hexagonal [0001] axis. For WB_2 and ReB_2, a nucleations of other defects (e.g. local amorphization or lattice rotation) is typically favoured over changes in the stacking sequence. Our comprehensive study provides insights into the phase-dependent mechanical properties of MB_2 and underscores the strength of machine-learning-potential molecular dynamics for understanding mechanical response of ceramic materials under application-relevant conditions.

CM-ThP-14 Angle-Resolved XPS Characterisation of Thin Films Using Hard X-Rays, ***Tom Swift (tswift@kratos.com)***, *J. Counsell,* Kratos Analytical Limited, UK; *C. Tupei, Y. Li,* Nanyang Technological University, Singapore

High-energy X-ray photoelectron spectroscopy (XPS) was employed to analyze the structure and chemical composition of HfOx thin films deposited on Alumina substrates. The ongoing trend of shrinking device dimensions has led to an increased use of atomic layer deposition (ALD) to enhance uniformity and control of layer thickness. ALD's capability to deposit high dielectric constant (high-k) films has facilitated its widespread application in optical, optoelectronic, and electronic devices.

Using standard Al Kα excited XPS enabled the determination of film thicknesses up to 7nm. However, accurate quantification of the Si 2p peak from the substrate became challenging beyond this thickness. Employing Ag Lα excitation resulted in electrons with higher kinetic energy for the same photoemission peak, effectively increasing the overlayer's attenuation length. In practical terms, this led to a roughly twofold increase in the sampling depth.

In this study, high-energy Ag XPS (Ag Lα radiation - 2984eV) was utilized in a conventional angle-resolved XPS (ARXPS) experiment. The ARXPS data was analyzed using algorithms connected with physical data parameters based on thermodynamic models, maximizing entropy to achieve the best-fit solution [1]. This process generated a reconstructed depth profile over a greater sampling depth provided by the higher energy excitation source. This approach allowed the non-destructive elucidation of the structure of ALD thin films of hafnia, alumina, and a combination of the two. Importantly, the use of the higher photon energy excitation source eliminated the need for destructive depth profiling using Ar-ion beams, reducing the risk of ion beam-induced chemical changes.

The focus of this investigation encompassed film thickness, chemistry at the interfaces, and the efficacy of Ag Lα-excited XPS for such applications.

[1] K. Macak, SIA 43(13) 2011

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