Advanced Surface Engineering Division
Room C123 - Session SE1+TF-MoM
Advanced Multi-Functional Thin Film Materials
Moderator: Suneel Kumar Kodambaka, Virginia Tech

8:20am **SE1+TF-MoM-1 AVS John A. Thornton Memorial Award Talk: Low Temperature Thin Film Growth Using Metal-ion/Surface Interactions*, Lars Hultman*[1]**, *G. Greczynski,* Linköping University, Sweden*; I. Petrov,* University of Illinois, Urbana-Champaign **INVITED**

Ion irradiation is a key tool for controlling epitaxy-to-nanostructure, phase content, and properties of refractory ceramic thin films grown by magnetron sputtering, as described in extended Thornton's structure-zone diagrams. Until recently, film growth relied on enhancing adatom mobility by inert and/or reactive gas ion irradiation to obtain dense layers at low deposition temperatures. The development of high-power pulsed magnetron sputtering (HiPIMS), which provides metal-ion plasmas with tunable degree of ionization, enabled systematic studies of the effects of metal-ion irradiation on refractory ceramic thin films. Metal ions are film constituents, hence they provide the benefits of ion-mixing without causing the high compressive stresses associated with trapping of gas ions.

This presentation reviews our growth experiments of pseudobinary TM nitride model systems including TiAlN, TiSiN, VAlN, TiTaN, TiAlTaN, and TiAlWN [1] carried out in a hybrid configuration with one target powered by HiPIMS, and the other operated in direct current magnetron sputtering (DCMS) mode. [2] A substrate bias potential Vs is synchronized with the metal-ion-rich portion of the HiPIMS pulses to allow for a control of metal-ion energy. Essential input is provided by time-resolved mass spectrometry analyses performed at the substrate position, which reveals the temporal evolution of metal- and gas-ion fluxes. This enables us to suppress the role of gas ion irradiation and study the influence of intense $M_1(^{n+})$ and $M^{(n+)}_2$ metal-ion fluxes (*n* = 1, 2) on film growth kinetics over a wide range of M_1M_2N alloy compositions.

The effects of metal-ion irradiation depend on the mass of incident ion with respect to that of film constituents. Irradiation with lower-mass metal-ions (Al^+ or Si^+) results in near-surface trapping with the depth determined by Vs amplitude. This enables growth of NaCl-structure Me1Me2N solid solutions far above the Me1N concentration range achieved with DCMS.[3] At the other extreme, bombardment of the growing film surface with pulsed high-mass metal ion fluxes (W+ or Ta+) during hybrid HiPIMS/DCMS high-rate deposition of dilute $Ti_{1-x}Ta_xN$, $Ti_{1-x-y}Al_xTa_yN$, and $Ti_{1-x-y}Al_xW_yN$ alloys provides fully-dense/low-stress films without intentional substrate heating (temperature ≤130 oC). The high metal-ion mass irradiation leads to low-energy recoil generation that provide sufficient adatom mobility, necessary to obtain high-quality fully-dense films, in the absence of resistive heating. Such energy-efficient PVD contributes to a sustainable development.

For cubic-TiAlWN, we recently discovered that Guinier-Preston (GP) zone hardening- known from soft light-metal alloys - can operate also in refractory ceramics. [4] The present GP hardening at 1000 °C is by the formation of atomic-plane-thick W islands populating {111} planes.

[1] G. Greczynski, I. Petrov, J.E. Greene, L. Hultman, J. Vac. Sci. Technol. A 37 (2019) 060801

[2] G. Greczynski, J. Lu, M. Johansson, J. Jensen, I. Petrov, J.E. Greene, L. Hultman, Surf. Coat. Technol. 206 (2012) 4202

[3] G. Greczynski, S. Mráz, J.M. Schneider, L. Hultman, J. Appl. Phys. 127 (2020) 180901

[4] O.Pshyk, X.Li, I.Petrov, D.G.Sangiovanni, J.Palisaitis, L.Hultman, G.Greczynski (Submitted 2023)

9:00am **SE1+TF-MoM-3 Multi-Component Materials – Bonding, Disorder and Possibilities*, Erik Lewin,*** Uppsala University, Sweden **INVITED**

Multi-component, often referred to as high-entropy, materials have received a large amount of attention during the past two decades. There are several reasons for this, including applicable properties and the fundamental design aspects connected to the large compositional space available, as well as the so-called core effects. The first research in the field was concerned with bulk alloys, but the concept has been expanded to compounds of metals and p-elements, e.g. nitrides, carbides, oxides, borides. Today, much of the research is on coating materials. In the field of coating research, popular properties and potential applications include hard materials, diffusion barriers, as well as corrosion or radiation resistant coatings.

This presentation will focus on solid solution phases with simple crystal structures where at least five different metallic elements share a crystalline sub-lattice. Recent results on the chemical bonding in multi-component alloy, nitride, and carbide coatings based on the early transition metals Ti, V, Zr, Nb and Hf will be presented. These results are based on the combination of *ab-initio* DFT simulations and electron spectroscopy using, both in-house XPS and synchrotron-based methods, and show that there is a charge transfer between the different metal atoms in a multi-component alloy, and that this effects the size of the atoms. Similar effects are also observed in corresponding nitrides and carbides, despite that all metal atoms have a first coordination of nitrogen or carbon. The results illustrate that chemical bonding matters, and that to fully understand and exploit the possibilities of multi-component materials this need to be considered. The results also show that the variation in local chemical environment effect the local electronic structure, giving rise to a range of chemically different sites.

This leads to a forward looking discussion on the fundamental understanding of the multi-component materials, and the possibilities that may arise from understanding and designing the chemical bonding (charge transfer) in multi-component materials.This will include the both the array of different chemical sites, as well as the intriguing combination of order (the crystalline lattice) and disorder, in the form of unordered occupation of the lattice points by different metals, as well as displacive disorder where the atoms are not on the lattice points (commonly called lattice distortion).

9:40am **SE1+TF-MoM-5 High-k Gate Dielectrics for InAlN and ScAlN Barrier GaN HEMT Structures*, Neeraj Nepal,*** *B. Downey, M. Hardy, D. Meyer, V. Wheeler,* U.S. Naval Research Laboratory

InAlN and ScAlN-barrier GaN high electron mobility transistors (HEMTs) have shown the ability to generate larger two dimensional electron gas (2DEG) densities for a given barrier thickness, leading to improved frequency and power performance in these devices [1-2]. However, HEMT devices utilizing these thin barriers often suffer from higher leakage current [2,3] and premature electric field breakdown, requiring the integration of gate dielectrics in order to realize the full potential of novel InAlN and ScAlN-barrier HEMTs by reducing leakage current, maintaining high electric field breakdown, and mitigating dc-RF dispersion.

In this talk, we report growth optimization and electrical properties of atomic layer deposition (ALD) grown TiO_2 gate dielectric on InAlN and ScAlN HEMTs structures. ALD process windows were initially monitored and optimized on Si substrates using *in-situ* ellipsometry. Films were deposited using tetrakis(dimethylamino)titanium (TDMAT) at 75 ^{o}C and an Ar/O_2 plasma at 300 W. Optimization of TiO2 films was done by varying the typical growth parameters, such as TDMAT pulse duration and growth temperature, as well as the plasma gas chemistry.Optimum films were then deposited and characterized on HEMT structures to determine electrical performance for device applications.

Atomic force microscopy on HEMT structures measured before and after ALD deposition showed minimal change in roughness as a result of the conformal TiO_2 deposition.Contactless resistivity measurements performed before and after ALD showed negligible change, indicating that no plasma induced damage was occurring during ALD gate deposition. Vertical current-voltage and capacitance-voltage measurements were made on a Schottky-contacted HEMT structure and compared to devices with TiO_2 gate dielectrics deposited at different temperatures to discern the full electrical impact of the ALD process. As an example, an extracted dielectric constant of TiO_2 layer deposited on ScAlN surface at 200°C with O_2 flow of 20 sccm was 50 with no significant change in 2DEG density ($2.6-2.7x10^{13}$ cm^{-2}). Using only a 7 nm gate TiO_2 film, the off-state gate leakage in InAlN/GaN HEMTs was reduced by ~10^4 compared to a Schottky gate. Additional electrical HEMT characterization and the band alignment of an optimum ALD TiO_2 on ScAlN structure will be discussed to show the full potential of these films in novel structures.

References:

1. Li et al., *IEEE Electron Device Lett.* 41, 689 (2020).
2. Hardy et al., *Appl. Phys. Lett.***110**, 162104 (2017).
3. Green *et al*., *IEEE Electron Device Lett.***40**, 1056 (2019).

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[1] **John A. Thornton Memorial Award Winner**

10:00am **SE1+TF-MoM-6 Molecular Layer Deposition for Alumina Gas Separation Membranes***, **Lucie Badouric**, C. Charmette, J. Cartier, M. Drobek, A. Julbe, M. Bechelany,* University of Montpellier, France

Making hydrogen a reliable energy vector in future decades requires the implementation of complex technologies related namely to its production, storage or transport. Intensive research is also underway to optimize its use by increasing its purity and to ensure the safety of hydrogen facilities.

Techniques such as cryogenic distillation, pressure swing adsorption (PSA) or membrane processes can be used to purify hydrogen. Both cryogenic distillation and PSA are used at commercial scale although these techniques are energy intensive. In comparison, membrane processes appear as a promising technology to separate H_2 from gas mixtures, by consuming less energy and operating in a continuous way. They can be either dense or porous, and made of polymers, metals, carbon, ceramics, hybrids or composite materials. Different gas transport and separation mechanisms are involved depending on the type of membrane. In microporous membranes (pore sizes < 2 nm) the separation of gas molecules might occur by molecular sieving, difference in diffusivity and/or competitive adsorption. Molecular sieving is an efficient thermally activated separation mechanism, particularly attractive for gas mixtures with different kinetic diameters. A good compromise between selectivity and permeability values can be reached with pore sizes smaller than the kinetic diameters of the molecules to be retained.

This work is dedicated to the development of a new type of alumina microporous membrane using the Molecular Layer Deposition (MLD) technique. As Atomic Layer Deposition (ALD), MLD allows to synthesize hybrid organic-inorganic materials by conformal coatings on various substrates using both organic and inorganic precursors. We developed a MLD process able to coat uniformly the pores (size~ 5-8 nm) of an alumina tubular support with alucone (aluminum alkoxide). Then, the film was calcined to transform the organic layer into a microporous alumina frame. Maximum pore sizes around 0.3 nm are targeted to obtain a molecular sieve membrane able to extract H_2 from mixtures with larger gas.

The MLD parameters have been optimized to obtain homogenous layers. Then, we investigated the influence of post-synthesis parameters to improve the membrane selectivity and permeability, as well as its stability. Single gas permeance measurements with He (H_2 simulant) and N_2 were used to validate the membrane quality and molecular sieving performance before testing them with gas mixtures under various working conditions (e.g., temperature, transmembrane pressure).

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