Topical Symposia

Room Town & Country A - Session TS6-1-MoA

A Session to Acknowledge the Contributions of Joe Greene to the ASED, ICMCTF, AVS, and IUVSTA I

Moderators: Michael Stüber, Karlsruhe Institute of Technology, Germany, **Samir Aouadi**, University of North Texas, USA

1:40pm **TS6-1-MoA-1 Low-Temperature Growth of Epitaxial and Polycrystalline Thin Films Under High-Fluxes of Low-Energy Gas Ions*, Ivan G. Petrov (petrov@illinois.edu),*** Linköping University, Sweden, University of Illinois at Urbana-Champaign, National Taiwan University of Science and Technology, Taiwan*; J. Sundgren,* Swedish Association of Engineering Industries, Sweden*; L. Hultman,* Linköping University, Sweden*; J. Greene,* inköping University, Sweden, University of Illinois at Urbana-Champaign, National Taiwan University of Science and Technology, Taiwan **INVITED**

From its inception the benefits of sputter deposition have stemmed from the presence of plasma in the vicinity of the growing film. Bombardment with charged particles and energetic photons affect the substrate initial condition and all stages of film growth: nucleation, coalescence, competitive growth, and recrystallization. Measuring and controlling the fluxes and energy of the charged particles to the substrate is essential in achieving low-temperature growth of high-quality thin films. Under typical conditions during direct current magnetron sputtering (DCMS), the dominant ion species incident at the growth surface while sputtering with N_2/Ar gas mixtures optimized to obtain stoichiometric films is typically Ar^+, while the ratio of the gas-ion flux to deposited metal flux $J_i/J_{Me} \leq 1$. Densification is achieved by increasing the ion energy $E_i$commonly above 100 eV.[1] However, at higher ion energies, a steep price is extracted in the form of residual ion-induced compressive stress resulting from both recoil implantation of surface atoms and trapping of rare-gas ions in the lattice.An alternative approach is offered by strongly magnetically-unbalanced magnetron sputter deposition system, which allows ion-to-neutral flux ratios J_i/J_{Me} incident at the growing film to be varied over extremely wide ranges (up to > 20) at very low (below the lattice displacement threshold) ion energies (E_i ~ 10-20 eV).[2] Using high-flux low energy ion irradiation during deposition opens new kinetic pathways to independently control the texture (from completely 111 to completely 200) and microstructure (from underdense to fully dense) in transition metal (TM) nitride films grown on amorphous substrates as well as to achieve low-temperature epitaxy of refractory materials as well as of metastable alloys.

[1]Petrov, I., Barna, P.B., Hultman, L., Greene, J.E. “Microstructural evolution during film growth” J. Vac. Sci. Technol. A,**21** (2003) S117

[2]Greene, J.E., Sundgren, J.-E., Hultman, L., Petrov, I., Bergstrom, D.B., “Development of preferred orientation in polycrystalline TiN layers grown by ultrahigh vacuum reactive magnetron sputtering” Appl. Phys. Let. **67** (1995) 2928

2:20pm **TS6-1-MoA-3 Advanced Materials, A Key for the Green and Digital Transformations and for Industrial Competitiveness (Virtual Presentation)*, Jan-Eric Sundgren (jesundgren@gmail.com),*** Swedish Association of Engineering Industries, Sweden **INVITED**

Large resources are allocated world-wide to the green and digital transitions. It is also obvious that research and development in close cooperation between different sectors in society play a crucial role for this twin transition. Another important part to achieve the necessary change is access to advanced materials and new innovative processes for sustainable production of these materials.

In this talk we will describe a mapping study that have conducted of the Swedish broad field of advanced materials. The results show that the value added for Swedish Industries manufacturing advanced materials has continuously increased in the years studied (2011-2019). The field is also expected to globally grow with 5-10% annually. In addition to the industry sector Sweden has also a strong academic community, with several research groups at the international forefront to which Prof Joe Greene has contributed significantly. Based on the mapping conducted and other recent studies we will present recommendations aimed to further boost the field of advanced materials both in Sweden and elsewhere.For example, an increased coordination and cooperation between different sectors and disciplines as well as the use of computational and AI methods are necessary to reduced lead times for industrial impact and thus to industrial competitiveness in the field.

3:00pm **TS6-1-MoA-5 Industrial Magnetron Sputtering: Interfaces & More*, Wolf-Dieter Münz (W_DM@gmx.at),*** Consultant, Austria **INVITED**

Magnetron sputter deposition of wear resistant hard coatings has found broad acceptance in many industrial applications serving e.g. the automotive, micro mashining, aeronautical and biomedical but also decorative industry. Perfect adhesion is a dominant precondition to meet reproducible production conditions. The paper discusses three types of substrate pretreatment prior to the actual film deposition: intensive Ar etching, metal ion etching by cathodic arc and HIPIMS technology respectively. Particular attention is paid to ion implantation during metal ion etching and the related epitaxy of the growing film. The resulting enhanced adhesion guarantees successful deposition of very hard and highly stressed e.g. TiAlN based superlattice coatings. The industrial realization of these methods of pretreatment is outlined by verification in a double (twin) cathode, combined cathodic arc/unbalanced magnetron and combined HIPIMS/unbalanced magnetron approaches. Two industrialized applications will be discussed in detail: (1) performance of superhard C-DLC coatings utilizing a five cathode batch type coater and (2) a simultaneous HIPIMS/UBM process depositing multilayer TiAlN/CrN coatingsproduced in a large scale multi cathode equipment.

3:40pm **TS6-1-MoA-7 Applying Thin Film Synthesis and Characterization Methods to Improving Photovoltaics*, Angus Rockett (arockett@mines.edu),*** Colorado School of Mines, USA **INVITED**

Prof. Joe Greene has been an amazing mentor and teacher to me. Without his help and patience, I would never have succeeded as I have. My career is entirely thanks to Joe both during my graduate study and more importantly afterward. This talk briefly reviews how the synthesis and characterization of thin films, particularly by sputter deposition, as I learned from or with the support of Joe, has been applied to the full spectrum of materials applied to photovoltaics. Film materials studied include silicon, binary, and ternary materials and alloys. Novel dielectrics and contact materials have been developed including a metastable alloy of 30% Cu in bcc Mo. Characterization methods include microstructural, microchemical, and optoelectronic approaches. The results have been simulated with continuum elasticity, finite element, Monte Carlo, and density functional methods. The result is a detailed picture of how defects in semiconductors affect the performance of photovoltaics and how they are related to process conditions.

4:20pm **TS6-1-MoA-9 May the Interatomic Forces be with You; Self-Organized Nanostructure Design in Functional Nitride Alloy Films (Virtual Presentation)*, Lars Hultman (lars.hultman@liu.se),*** *G. Greczynski,* Linköping University, Sweden*; I. Petrov, J. Greene,* Linköping University, Sweden; University of Illinois at Urbana-Champaign, USA; National Taiwan University of Science and Technology, Taiwan **INVITED**

During ~40 years our group has developed strategies for thin film formation during physical vapor deposition, spanning epitaxial growth and crystallographic texture control to self-organization of nanostructures. Both primary and secondary phase transformations from the vapor phase and in the as-deposited state, respectively, are explored. Self-organization from surface and bulk diffusion is used to enhance mechanical and electronic properties of functional ceramics by structural design, here exemplified by transition metal and group-III nitride metastable alloy model systems: TiAlN, ZrAlN, HfAlN, TiSiN, MoVN, VWN, and InAlN. Material characterization is performed by XRD, analytical STEM, FIB, and isotopic-substitution APT. Molecular dynamics simulations, *Ab initio* calculations, and phase-field modelling are employed to assess phase stability, diffusion, and decomposition behavior from lattice mismatch and electronic band structure effects. Our concept of age hardening is reviewed, where spinodal decomposition is established for TiAlN by the formation of cubic-phase nm-size domains in a {100}-checker-board pattern of TiN and AlN at temperatures corresponding to cutting tool operation. 2-D-nanolabyrinthine structuring in ZrAlN is obtained from intergrowth of non-isostructural phases *c*-ZrN/*w*-AlN: {110}║{11-20} interfaces. Superhardening in TiN/Si_3N_4 nanocomposites takes place due to Si segregation forming a few-monolayer-thick SiN_x tissue layer, which is shown to be vacancy-stabilized cubic-phase SiN_x. A hardness maximum at 34 GPa – short of ultrahard – is observed in TiN/SiN_x(001) superlattices at the epitaxial-to-amorphous thickness-limit for the SiN_x layers. For $In_xAl_{1-x}N$, we report inherently-curved-lattice epitaxial growth of nanospirals with controllable chirality as well as core-shell nanorod formation. The emerging inherently nanolaminate family of so-called MAX phases is briefly reviewed with examples from Ti_2AlN including for non-van-der Waals intercalation of noble metals. More recently, we discovered transmorphic heteroepitaxy

between CVD-grown AlN epilayer and SiC(0001) wafer substrates. The atomic configuration transits over two atomic layers from SiC ® $(Al_{1/3}Si_{2/3})_{2/3}N$ with ordered vacancies on 1/3 of the Al and Si positions ® $(Al_{2/3}Si_{1/3})N$ ® AlN. The resulting special epitaxial AlN layer has state-of-the-art low lattice defect density, enabling growth of high-quality thin GaN HEMT heterostructures for superior power electronics.

5:00pm **TS6-1-MoA-11 From Thin Films to Solid Oxide Fuel Cells***, Scott* ***Barnett (s-barnett@northwestern.edu),*** Northwestern University, USA **INVITED**

This talk will start with a brief history of how my background in thin films in Joe Greene's group helped lead to a new approach to making practical solid oxide fuel cells (SOFCs). Although thin film vapor deposition techniques have not supplanted conventional ceramic processing of SOFCs, this talk will highlight vapor deposition methods likely to play an increasing role going forward. Recent developments in SOFCs and solid oxide electrolysis cells (SOECs) will be discussed. SOFCs are being increasingly applied for clean efficiency electrical generation, and produce highly concentrated CO_2 exhaust that is nearly sequestration-ready. SOECs have potential for highest efficiency conversion of renewable electricity to hydrogen and other renewable fuels. The devices can also be operated in both SOFC and SOEC modes to allow large-scale electrical energy storage – a key technology needed for enabling increased utilization of renewable wind and solar energy resources. Current research areas will be highlighted including improving device performance via reduced electrolyte thickness and highly-active nano-scale electrodes, and determining the mechanisms that limit device long-term stability.

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