Functional Thin Films and Surfaces
Room Palm 5-6 - Session MB2-3-TuM

Thin Films for Electronic Devices III

Moderators: Dr. Jiri Houska, University of West Bohemia, Czechia, **Dr. Ufuk Kilic**, University of Nebraska - Lincoln, USA

8:00am **MB2-3-TuM-1 Morphological Effects and Impurity Levels on the High-Temperature Electrical Insulation of reactively sputtered AlN*, Norma Salvadores Farran [norma.salvadores@tuwien.ac.at],*** Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; Tomasz Wojcik,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, Austria*; Carmen Jerg,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; Astrid Gies,* Oerlikon Balzers, Oerlikon Surface Solutions, Liechtenstein*; Jürgen Ramm,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; Szilard Kolozsvári, Peter Polcik,* Plansee Composite Materials GmbH, Germany*; Jürgen Fleig, Tobias Huber,* Institute of Chemical Technologies and Analytics, TU Wien, Austria*; Eleni Ntemou, Daniel Primetzhofer,* Department of Physics and Astronomy, Uppsala University, Sweden*; Helmut Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

Aluminum nitride-based ceramics are renowned for their insulating properties and high thermal conductivity. Consequently, these materials have been employed for various applications across a range of temperature conditions, with a particular focus on insulating purposes. Nevertheless, as the electrical conductivity is a thermally activated process, the mobility of charge carriers at elevated temperatures presents a significant challenge for insulating thin film materials.

The aim of this study is to explore the effect of morphological features (i.e. grain size or porosities) and impurities on hexagonal structured AlN thin films using different physical vapor deposition techniques. Given the difficulties associated with maintaining process stability during the deposition of insulating coatings, various reactive PVD techniques have been explored, including magnetron sputtering (DCMS), high-power pulsed magnetron sputtering (HIPIMS), and pulsed magnetron sputtering (PMS). All films were grown in an in-house developed magnetron sputter system using 3’’ Al targets in a mixed Ar/N2 atmospheres. Phase formation has been examined using X-ray diffractometry (XRD), while the morphology was investigated in detail through scanning and transmission electron microscopy (SEM and TEM). The insulating behaviour of all films grown on metallic substrates was analysed using in-situ impedance spectroscopy across a temperature range from 400°C to 750°C – utilizing differently sized Ti/Pt lithography pads. The concentration of impurities, especially oxygen, was determined through the use of electron-induced X-ray emission spectroscopy (ERDA).

The results of the impedance measurements demonstrated a correlation between the electrical properties of the films and their morphological characteristics. The films grown via HIPIMS exhibited the highest morphological density and the greatest resistance over temperature. The samples deposited via PMS also demonstrated high electrical resistivity, although the values decreased at a certain level. It was not possible to determine the insulating properties of the films grown via DCMS, due to the presence of pinholes in the samples which also signifies a less dense morphology. Moreover, the influence of impurities as O2 has a significant effect on reducing the electrical resistivity of the films.

8:20am **MB2-3-TuM-2 Pulsed Laser Deposition of Epitaxial Ti3AlC2 Mxene Thin Films on Al2O3(0001) Substrate*, Pramod Kumar [pramod.kumar@surrey.ac.uk],*** Indian Institute of Technology Roorkee, India, University of Surrey, UK*; Ananya Bansal,* Indian Institute of Technology Roorkee, India*; Satheesh Krishnamurthy,* University of Surrey, UK*; Ramesh Chandra,* Indian Institute of Technology Roorkee, India

The newly explored two-dimensional transition metal carbides/nitrides, popularly known as MXene, are a new family of 2D materials with diverse applications. The coexistence of both ceramic and metallic nature, giving rise to exceptional mechanical, thermal, electrical, chemical properties and wide range of applications. Although several solution process techniques are there to deposit the MXene on substrate, but there is a need of high-quality epitaxial thin films for the above stated applications. In this work, $Ti_3C_2T_x$ MXene powder was synthesized using acid etching method. Epitaxial thin films were deposited on sapphire substrate (Al_2O_3, 0001) for the first time using pulse laser deposition (PLD) with $Ti_3C_2T_x$ pellet as the source. The X-ray diffractometer and morphology studies showed the epitaxial nature of the film with columnar growth. The electrical conductivity of the film was found to be ~9421 S/cm. Resistance-temperature graph showed semiconductor-like behaviour for all the thickness tested.The thin film was also highly corrosive resistant in nature when tested with standard acidic, alkaline and saline solutions, which makes it ideal for anticorrosive coatings. Moreover, the p-n and n^+-n devices on silicon substrate also resulted in a high switching ratio compared to other 2D materials. Our results demonstrate the potential of PLD as a novel method for the growth of epitaxial MXene thin films.

Keywords: MXene; pulsed laser deposition, epitaxial growth, corrosion resistance, switching diode

8:40am **MB2-3-TuM-3 Sputter Epitaxy of Predicted Dirac Semimetal $MgTa_2N_3$*, Julien Baptiste [baptiste.julien@nrel.gov],*** *Sage Bauers,* National Renewable Energy Laboratory, USA

Ternary nitrides exhibit a wide range of functional properties, including superconductivity, magnetism, thermoelectricity, as well as topological properties. Among these, $MgTa_2N_3$ (MTN) has been predicted to be a Dirac semimetal with an interesting potential for topological phases tunability. These unique electronic properties tied to its layered crystal structure. In this works, we synthesized epitaxial MTN thin films using reactive RF sputtering on *c*-cut sapphire substrates. The as-deposited films exhibit a (111)-oriented disordered rocksalt structure (rs-MTN), with a high-quality epitaxy, confirmed by X-ray diffraction (XRD) and rocking curve analysis. To transform the disordered rocksalt phase into the targeted layered phase ($P6_3/mcm$), we annealed the precursor films in NH_3. This method showed significant promise, successfully inducing the phase transformation at lower temperatures while maintaining film integrity, decent epitaxy and mitigating secondary phase formation. Structural analysis revealed that annealing the epi-film precursor under NH_3 yields to a phase transformation from the (111)-oriented rs-MTN into a c-axis textured layered MTN. Whereas the precursor rocksalt shows weak thermally activated conduction, preliminary electro and magneto-transport measurements on the layered MTN films reveal promising properties for a Dirac semimetal.

9:00am **MB2-3-TuM-4 Stabilization of Cubic or Orthorhombic Structure in Sputtered Tin Sulfide Thin Films for Thermoelectric Applications***, Rémy Juliac, David Pilloud, Sylvie Migot, Axel Tahir, Jaafar Ghanbaja, Brigitte Vigolo, Nicolas Stein,* ***Jean-François PIERSON [jean-francois.pierson@univ-lorraine.fr],*** IJL / CNRS / Univ. Lorraine, France

Tin sulfide (SnS) is a p-type semiconducting material with a band gap of approx. 1.3 eV. This compound is a promising material for thermoelectric applications, as an alternative to SnSe with the same crystallographic phase Pbnm but with no critical chemical elements [1]. Indeed SnS may crystallize in various structures, the orthorhombic phase (Hertzenbergite, α-SnS,) being the most stable one. Other structures are also reported in the literature, such as the π-SnS one that crystallizes in a cubic structure ($P2_13$) [2].

In the present work, SnS thin films have been deposited using pulsed-DC magnetron sputtering of a tin sulfide target. The effect of the experimental deposition conditions (total pressure and substrate temperature) to the structure, the microstructure, the composition and the functional properties has been studied.

The deposition total pressure strongly influences the structure of SnS thin films. The use of low pressure (0.5 Pa) favors the growth of the metastable cubic phase. A columnar microstructure with stacking faults has been evidenced by high resolution transmission electron microscopy for the films deposited at low pressure. Deposition at high pressure (1.5 Pa) induces the synthesis of the orthorhombic phase, the most stable phase. At intermediate pressure, the films are biphased: cubic + orthorhombic. The electrical properties of the films are strongly influenced by their structure. On one hand, the orthorhombic phase exhibits a high electrical resistivity that strongly decreases the transport properties. On the other hand, the cubic phase shows a low electrical resistivity that improves the film properties.

The cubic structure being a metastable one, this phase is not obtained anymore when the films are deposited on a heated substrate. For temperature lower than 100 °C, the orthorhombic phase is the only one detected by X-ray diffraction and Raman spectroscopy. The film microstructure becomes porous when the SnS films are deposited at a temperature higher than the ambient one. Such a porous microstructure has a negative impact on the electrical properties and therefore the thermoelectric properties.

[1] Tan *et al.*, Thermoelectrics with earth abundant elements: low thermal conductivity and high thermopower in doped SnS, J. Mater. Chem. A 2 (2012) 17302

[2] Guc *et al.*, Structural and vibrational properties of α- and π-SnS polymorphs for photovoltaic applications, Acta Mater. 183 (2020) 1

9:20am **MB2-3-TuM-5 Governing Metal-Insulator Transition in Ultra-Thin VO_2 Films by Surface Engineering**, ***Andres Hofer [juhofer@ucsd.edu]***, UC San Diego, USA; *Ali Basaran,* ali.basaran@ga.com, USA; *Alexandre Pofelski,* Brookhaven National Laboratory, USA; *Damir Wang, Victor Palin,* UC San Diego, USA; *Yimei Zhu,* Brookhaven National Laboratory, USA; *Ivan Schuller,* UC San Diego, USA

The metal-insulator transition (MIT) in vanadium dioxide (VO_2) thin films is strongly affected by grain size, thickness, and interfacial properties. Typically, the MIT is substantially suppressed for thickness below 50 nm when substrates like sapphire and silicon are used. While some studies have shown that films below 20 nm thickness can be achieved without compromising the integrity of the MIT, complex pre or post-growth processing is required. We show that engineering the substrate surface before the deposition facilitates the direct deposition of ultra-thin 15 nm thick films, exhibiting over four orders of resistance change across the MIT, which is comparable to its bulk counterpart. Our findings indicate that the interface between the thin film and the substrate is crucial to the structural evolution during the initial growth layer. With the appropriate surface preparation, the desired VO_2 MIT transition can be obtained independently of the substrate's crystalline orientation. Furthermore, we propose a novel approach to obtain high-quality MIT in ultra-thin VO_2 films by magnetron sputtering. Unlike traditional film depositions, we incorporate a pre-deposited 1.5 nm thick vanadium oxide buffer layer, thereby eliminating the need of different materials besides vanadium oxide or complex pre- and post-growth processing. We also demonstrate that our unique growth methodology improves the MIT of 25 nm VO_2 thin films on standard silicon substrates. This study reveals a compelling approach for the direct growth of ultrathin VO_2 films exhibiting a high-quality MIT, which is commonly accepted as unattainable on technologically essential substrates such as sapphire and silicon.

9:40am **MB2-3-TuM-6 Probing the Metal-Insulator Transition at YTiO3/LaTiO3 Interfaces via Soft Chemical Synthesis**, ***Alexandre Simoes [zirpoli.simoes@unesp.br]***, Rua Souza Oliveira, Brazil

In this study, we present optimized growth conditions for the fabrication of YTO/LTO heterostructured thin films using the polymeric precursor method combined with spin coating. The films were deposited on (100) Pt/TiO2/SiO2/Si substrates at 850 °C, resulting in films with a mean grain size of approximately 20.0 nm and a surface roughness of 5.50 nm. X-ray diffraction (XRD) analysis reveals that the YTO/LTO heterostructured films, synthesized via the polymeric precursor method, are free of secondary phases and exhibit a highly homogeneous morphology with no evidence of interaction between the sublayers. The piezoelectric and magnetic properties of the YTO/LTO heterostructures are attributed to modifications in the Ti-O-Ti bond lengths and tilting of the oxygen octahedra, which in turn affect the electrons in the eg orbitals of the Ti atoms in both layers. This hypothesis is further supported by Rietveld refinement and X-ray photoelectron spectroscopy (XPS) results, which suggest that the magnetic behavior of the films is not only due to the non-integer 3d occupancy of Ti ions at the surface but also the structural distortion of the YTO/LTO interface, influenced by the underlying silicon-coated platinum substrates. The films exhibit a high intrinsic dielectric constant ($\varepsilon r \approx 70$) and a loss tangent (tan δ) of approximately 0.41 at 1 kHz, indicating structural distortions along the TiO_6 octahedra in the basal plane of the film. A metal-to-insulator transition observed in the heterostructured films supports the idea of a competing mechanism, where strong electron orbital dynamics and multi-orbital electronic correlations govern the switching behavior between SET and RESET states. Additionally, the electrode area and switching cycles influence the film's properties, making it suitable for use as a correlated random access memory (CeRAM). In conclusion, we demonstrate that this simple, low-cost chemical process yields high-quality heterostructured films with promising potential for applications in non-volatile resistive memories.

10:00am **MB2-3-TuM-7 the Influence of Substrate Bias on Properties and Microstructure of High-Density Nanotwinned Ag Thin Films for High Power Device**, ***Pinng-Chun Kuo [icanfire93@gmail.com]***, *Fan-Yi Ouyang,* Department of Engineering and System Science, National Tsing Hua University, Hsinchu, Taiwan

In response to the increasing demands for advanced technologies, including autonomous vehicles, self-driving systems, and artificial intelligence computing (AIPC), the concept of 3D-IC has emerged. Advanced packaging techniques that exhibit high reliability, superior properties, and the capacity to endure elevated operating temperatures are necessary to address these demands. The predominant technique employed is Cu-to-Cu direct bonding; however, this method necessitates high-temperature processing (>350°C), during which Cu tends to oxidation, thus requiring a high vacuum environment for execution. In contrast, Ag has demonstrated superior electrical and thermal conductivity, and great oxidation resistance, making it a promising candidate for metal-to-metal direct bonding techniques in atmospheric conditions.

This study successfully fabricated high-density nanotwinned Ag thin films on SiC substrates utilizing magnetron sputtering and investigated the impact of substrate bias on the microstructure and properties of the films. The results show that nanotwinned structures were found on all samples, characterized by a high density of nanotwins with an average twin spacing of 7 nm. The grain size remained relatively consistent as the substrate bias was increased from 0 V to -80 V; however, grain growth was observed when the substrate bias was further increased from -80 V to -120 V. In addition, the samples deposited without bias exhibit a resistivity of 2.17 μΩ·cm and a hardness of 1.9 GPa, significantly surpassing that of bulk Ag (0.58GPa). When the substrate bias increases to -60 V, the resistivity further decreases to 1.96 μΩ·cm and hardness reduce to 1.55 GPa. Moreover, a comparative analysis was also conducted on the microstructure and properties of nanotwinned Ag thin films deposited on Si and SiC substrates. The influence of the substrate bias on nanotwin formation of Ag thin films for both substrates is discussed and compared.

Key word：nanotwin, metal-to-metal direct bonding, advanced packaging techniques

10:20am **MB2-3-TuM-8 Electrodeposited Zirconium Titanate Thin Films: Structural, Magnetic, and Dielectric Properties for Spintronic Applications**, ***Ifra Saeed [ifrasaeed1998@gmail.com]***, University of Milano Bicocca, Milan, Italy, Pakistan

Zirconium titanate (ZrTiO4) thin films have emerged as a cornerstone material in the advancement of spintronic devices, owing to their exceptional structural, magnetic, and dielectric properties [1,2]. This study harnesses a precise electrodeposition technique to fabricate ZrTiO4 thin films, meticulously varying the molarity of electrolytes from 0.01M to 0.05M. X-ray diffraction (XRD) analysis reveals a transition from amorphous behavior at 0.01M to the formation of phase-pure, orthorhombic ZrTiO4 at higher molarities, with a notable increase in crystallite size, indicative of enhanced phase stability. Vibrating Sample Magnetometer (VSM) measurements demonstrate a pronounced soft ferromagnetic behavior, with an impressive saturation magnetization peaking at 29 emu/cm^3 at 0.05M. Dielectric studies reveal a significant dielectric constant of 180 at log f=2 and a minimal tangent loss of 0.02 at 0.05M, showcasing superior dielectric performance. Cole-Cole plots further elucidate the dielectric properties, indicating dominant grain boundary resistance. The comprehensive analysis underscores the potential of ZrTiO4 thin films as pivotal components in next-generation spintronic devices, offering unparalleled structural integrity, magnetic prowess, and dielectric efficiency [2].

These findings pave the way for the integration of ZrTiO4 thin films in high-performance, energy-efficient spintronic applications, marking a significant leap forward in material science and device engineering.

References:

Polliotto. V., Albanese. E., Livraghi. S., Agnoli. S., Pacchioni.G., & Giamello.E., (2020). Structural, electronic & photochemical properties of cerium doped zirconium titanate. Catalysis today, 340, 49-57.

Juma. A., Acik. I.O., Oluwabi. A.T., Mere. A., Mikli. V., Danilson. M., & Krunks. M., (2016). Zirconium doped TiO2 thin films by chemical spray pyrolysis. Applied surface science, 387, 539-54.

10:40am **MB2-3-TuM-9 Revolutionizing High-Entropy MEMS with Superior Thermal Stability and Scalability**, ***Li-Hui Tsao [nthu031239@gmail.com]***, National Tsing Hua University, Taiwan

Microelectromechanical Systems (MEMS) are essential in modern technology due to the increasing demand for multi-functional devices and Internet-of-Things (IoT) applications. In typical cases, the piezoelectric layers in MEMS serve as the main component for actuation, sensing, and transduction, which lead zirconate titanate (PZT) is widely used with high piezoelectricity. However, challenges, including poor thermal stability and degradation after long-term usage, have hindered its further development. Thus, it is crucial to introduce new material designs to solve these problems. In this work, a high-entropy material, $Pb(Mg_aNb_bTi_cHf_dZr_e)O_3$ (PMNTHZO), is developed with colossal piezo-response and superior thermal stability. The sluggish diffusion effect diminishes the critical phase transformation and contributes to the robust properties at 523 K. Meanwhile, the integration with an 8-inch silicon substrate further suggests the massive potential for practical usage. In conclusion, this work demonstrates a novel high-entropy material with several intriguing physical properties, paving the way for next-generation electronic devices.

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