## Functional Thin Films and Surfaces
## Room Pacific D - Session C2-2-ThM
### Thin Films for Electronic Devices II

**Moderators: Julien Keraudy**, Oerlikon Balzers, Oerlikon Surface Solution AG, Liechtenstein, **Jörg Patscheider**, Evatec AG, Switzerland

9:00am **C2-2-ThM-4 Thermal, Plasma-enhanced and Spatial Atomic Layer Deposition as an Enabling Nanotechnology for Electronic Devices*, Erwin Kessels (w.m.m.kessels@tue.nl),*** Eindhoven University of Technology, Netherlands **INVITED**

Atomic layer deposition (ALD) is a true enabling nanotechnology that allows for the preparation of high-quality thin films on challenging surface topologies with excellent step coverage and precisely controlled nanometer dimensions. The semiconductor industry has been the main driving force behind the industrial implementation of ALD in high-volume manufacturing in the last 2 decades as it has been key for the materials- and 3D-enabled scaling to continue Moore's law in computing and data storage. Yet currently processing at the nanoscale has also become critical for other electronic devices including power electronics, microsystems and photonics.

In this presentation, the method of ALD will be introduced including a description of its underlying mechanisms, key features and hallmarks. Subsequently major developments in the field of ALD for electronic devices will be discussed covering thermal, plasma-enhanced and spatial ALD. Aspects that will be addressed include: the use of (spatial) ALD in advanced patterning, area-selective deposition using inhibitor molecules in advanced ALD-cycles, conformal deposition and gap-filling in high-aspect ratio structures including the role of surface recombination of radicals for plasma ALD, the role of ions and their energy (with respect to damage and microstructure control) in plasma ALD, etc. Examples will be given for a variety of materials systems and device applications.

9:40am **C2-2-ThM-6 Effects of Annealing Conditions on Temperature Coefficient of Resistance of Pt/AlO$_X$ Thermistors*, Atasi Dan (atasi.dan@nist.gov)***, *E. Antunes, C. Yung, N. Tomlin, M. Stephens, J. Lehman,* Applied Physics Division, National Institute of Standards and Technology (NIST), Boulder, USA

The emergence of microfabricated, uncooled microbolometer arrays incorporating vertically-aligned carbon nanotube (VACNT) absorbers is opening opportunities for monitoring the Earth's radiative energy budget using electrical substitution techniques. In microbolometers, a thermistor having high sensitivity to temperature changes is an important component. In the present work, Pt/AlO$_x$ thermistors are fabricated on SiN$_x$/SiO$_2$/Si substrates using magnetron sputtering. In order to achieve enhanced adhesion of Pt film (175 nm), an AlO$_x$ layer with a thickness of 10 nm is deposited as an interlayer on the substrate via reactive high-power impulse magnetron sputtering (HiPIMS), while the Pt layer was deposited by direct current (DC) sputtering process. To maximize the negative temperature coefficient of resistance (TCR), Pt/AlO$_x$ is subjected to different annealing conditions by varying annealing temperature, time, and environment. With an increase in the annealing temperature and duration, Pt/AlO$_x$ exhibits a significant improvement in TCR. The microstructural and morphological investigations suggest that the improvement in TCR is related to the recrystallization process of Pt and the increase in grain size. The fabricated Pt/AlO$_x$ thermistor with a high negative TCR and provides a great potential for its use in microbolometer applications as well as ensures its capability while performing any post-processing step at high temperature.

10:00am **C2-2-ThM-7 Ultrathin Transition Metal Silicides Investigated In Situ Using Ion Scattering*, Philipp M. Wolf (philipp.wolf@physics.uu.se)***, *H. Bruce, W. Hallén, E. Pitthan, Z. Zhang,* Uppsala University, Sweden*; C. Lavoie,* IBM T. J. Watson Research Center, USA*; T. Tran, D. Primetzhofer,* Uppsala University, Sweden

Transition metal silicides are an essential building block of MOSFETs, where their low resistivity makes them the preferred choice for contact metallization.[1] As the silicide layer thickness continues to decrease with the reduction in the size of MOSFETs, methods with a high sensitivity to the outermost atomic layers are needed to investigate potential differences in phase transitions of ultrathin films as compared to thicker films. Here, we utilize a time-of-flight low-energy ion scattering (ToF-LEIS) approach capable of resolving structure and composition of ultrathin films with a sub nm resolution[2] to study phase transitions of ultrathin silicides. Our ToF-LEIS setup is connected to a preparation chamber equipped with an e$^-$-beam evaporator for thin film deposition, a heating filament, an ion sputter gun, an Auger electron spectrometer and a low-energy electron diffraction setup, enabling us to perform in situ characterization. Additional ex situ measurements, including time of flight medium-energy ion scattering, Rutherford backscattering spectrometry and transmission electron microscopy are performed to provide additional information on total areal densities, crystallographic structures and phases present in the films.

We present detailed studies of two relevant silicide systems, ultrathin Ni and Ti silicide films, grown on Si(100). For Ni silicide films with an initial Ni thickness of 3.6 nm, using the above-described approach, we found an unprecedented direct transition from orthorhombic δ-Ni$_2$Si, displaying long-range order covering the whole film thickness, to epitaxial NiSi$_{2-x}$ at 290°C skipping the intermediate NiSi phase observed for thicker films.[3] Considering previous studies we suggest that the ordered δ-Ni$_2$Si phase occurs regardless of the initial Ni film thickness but is limited in thickness by competing orientations of the δ-Ni$_2$Si crystal. Whether or not the NiSi phase is found absent, depends on whether the formed δ-Ni$_2$Si can consume all deposited Ni or not. For Ti silicide, formed from a Ti thickness of 6 nm annealed in steps up to 680°C, we do not observe an epitaxial phase but instead agglomeration of the silicide film. Further, an even thinner Ti silicide film, with an initial Ti thickness of 3 nm, is annealed in situ and characterized. Together these results show the analytical power of the presented approach and the increasing need for methods with a sub nm resolution in the field of thin film electronics.

[1] S.-L. Zhang and Z. Zhang, Met. Films for Electron., Opt. and Magn. Appl., Elsevier, 244–301, 2014
[2] M. Draxler et al., Phys. Rev. A, 68, 022901, 2003
[3] P. M. Wolf et al., Small, 2106093, 2022

10:20am **C2-2-ThM-8 Synthesis of a New Ternary Nitride Semiconductor - Zn$_2$VN$_3$: A Combinatorial Exploration of the Zn-V-N Phase Space***, S. Zhuk,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; A. Kistanov,* University of Oulu, Finland*; S. Boehme,* ETH Zürich, Switzerland*; N. Ott, M. Stiefel,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; M. Kovalenko,* ETH Zürich, Switzerland*; **Sebastian Siol (sebastian.siol@empa.ch)**,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Nitrides are promising functional materials for a variety of applications. Despite their technological importance, many promising theoretically predicted metal nitrides are yet to be discovered. This is partly rooted in their challenging synthesis as compared to oxides. Non-equilibrium PVD in UHV conditions, such as reactive RF-magnetron sputtering, provides ideal prerequisites for the formation of novel metastable nitride thin films.

In this work, a computationally guided combinatorial PVD screening of the entire Zn-V-N phase space is performed, resulting in the synthesis of the previously unreported ternary nitride Zn$_2$VN$_3$.[1] Reactive RF co-sputtering of Zn and V targets is performed in Ar/N$_2$ atmosphere with N$_2$ is supplied directly to the sputter plasma to increase the N$_2$ dissociation rate and consequently increase the N chemical potential. The combinatorial libraries are grown with composition and deposition temperature gradients to quickly cover large areas of the synthesis phase space. A comprehensive automated mapping characterization of the sample is performed to investigate the structure, composition, chemical-state as well as optoelectronic properties. XRD mapping analysis reveals the presence of a wurtzite Zn$_{1-x}$V$_x$N phase over a large compositional range from Zn$_2$VN$_3$ to ZnVN$_2$, with a narrow process window for single-phase Zn$_2$VN$_3$.

Following the combinatorial screening we isolate the phase and synthesize single-phase polycrystalline Zn$_2$VN$_3$ thin films with wurtzite structure on conventional borosilicate glass substrates. In addition, we demonstrate that cation-disordered, but phase-pure (002)-textured wurtzite Zn$_2$VN$_3$ thin films can be grown using epitaxial stabilization on α-Al$_2$O$_3$ (0001) substrates at remarkably low growth temperatures well below 200 °C as evidenced by (S)TEM analysis. The composition as well as chemical state of the constituent elements are studied using RBS/ERDA as well as XPS/HAXPES methods. These analyses reveal a stoichiometric material with no oxygen contamination, besides a thin surface oxide.

We find that Zn$_2$VN$_3$ is a weakly-doped p-type semiconductor demonstrating broadband room-temperature PL spanning the range between 2 eV and 3 eV, consistent with the bandgap of similar magnitude predicted by density functional theory-based calculations. In addition, the electronic properties can be tuned over a wide range via isostructural alloying on the cation site, making this a promising material for optoelectronic applications.

[1] S. Zhuk *et al.* 2021 arXiv:2109.00365

10:40am **C2-2-ThM-9 Theoretical and Experimental Approaches for the Determination of Functional Properties of a New Semiconductor: MgSsnN$_2$***, Agathe Virfeu (agathe.virfeu@univ-lorraine.fr)**, F. Alnjiman, S. Diliberto, J. Ghanbaja,* Institut Jean Lamour - Université de Lorraine, France*; E. Haye,* University of Namur, Belgium*; S. Migot, J. Pierson,* Institut Jean Lamour - Université de Lorraine, France

III-N materials are commonly used as active layers in LEDs, transistors, solar cells and mechanical devices. The main spinneret is based on the use of InGaN alloys. However, such layers contain indium and gallium. Significant volatility in their price and supply over the last years has led to considerable concern given their critical roles and their use in a wide range of large-scale electronic devices. It is important to study and develop new earth abundant materials with optimized properties for the realization of innovative optoelectronic devices that could be competitive cost for mass production. Over the past 10 years, the study of Zn based II-IV-N$_2$ family has shown that they are interesting semiconductors due to the tunability of their properties. However, oxygen contamination and high vapor pressure of zinc make it difficult to control the stoichiometry and the structure order. In this work, we aim at developing a new kind of inexpensive, indium/gallium-free, nitride material that could be the basis of new way for optoelectronic applications. The studies are focusing on MgSnN$_2$ thin films (bandgap energy ≈ 2 eV) that is a good candidate for green emitters in LEDs and an absorber material in tandem photovoltaics.

MgSnN$_2$ thin films have been deposited by magnetron co-sputtering at different substrate temperatures (up to 500 °C).The Mg/Sn atomic ratio has been controlled by the current applied to the Mg and Sn targets. The structure of the films has been studied by X-ray diffraction. Whatever the deposition temperature, the films crystallize in a wurtzite-like structure with a strong preferred orientation in the [002] direction. The columnar microstructure of MgSnN$_2$ thin films have been studied by transmission electron microscopy and the chemical environment of the Sn and Mg atoms has been investigated using Mössbauer spectrometry and X-ray photoemission spectroscopy.The optical band gap deduced from UV-visible spectroscopy is ranging in the 2.1 – 2.4 eV range. These experimental optical properties of MgSnN$_2$ films were compared to those obtained by *ab initio* calculations. Finally, the electrical resistivity, carrier concentration, type and carrier mobilityhave been measured by Hall effect.

11:00am **C2-2-ThM-10 Relative Effects of Pulsed Laser Deposition Parameters on the Stoichiometry of Multiferroic Thin Films***, **W. C. McGinnis (wayne.mcginnis@spawar.navy.mil)**, A. Hening, T. Emery-Adleman,* Naval Information Warfare Center Pacific, USA

Pulsed laser deposition has a reputation for maintaining the stoichiometry of the ablation target in the deposited film. Exceptions to this "rule" occur, however, for materials such as multiferroic $Bi_xDy_{(1-x)}FeO_3$ (BDFO), which contain elements with large differences in volatility, such as Bi and Fe. The relative effects of various pulsed laser deposition parameters on the resulting stoichiometry of BDFO films as a function of time (or number of laser pulses) has been examined using an interactive spreadsheet, as well as experimentally. The adjustable parameters include target composition, elemental ablation yield from the target, plume spreading effects, sputtering of the growing film by ablated atoms, and thermal evaporation of deposited atoms from the heated substrate. Examples of how the calculated film composition might evolve will be presented (as seen in the supplementary figure), along with experimental results showing how these deposition parameters individually affect BDFO film stoichiometry.

11:20am **C2-2-ThM-11 Effects of Carbon Addition on $Ge_2Sb_2Te_5$ Film Structure and Properties***, **David Adams (dpadams@sandia.gov)**, E. Lang, T. Clark, C. Sobczak, E. Scott, J. Custer,* Sandia National Laboratories, USA*; T. Beechem,* Purdue University, USA*; K. Hattar, M. Rodriguez,* Sandia National Laboratories, USA

Phase change thin film materials continue to attract interest for applications such as non-volatile electronic memory, sensors, and optical data storage, because the material can be rapidly switched between contrasted amorphous and crystalline states. In particular, the germanium antimony tellurium (GST) system remains a benchmark for many current studies wherein $Ge_2Sb_2Te_5$ has received much attention. Recent research has demonstrated how quaternary additions (C, N, Se, O) improve thermal stability. The addition of a few mol.% C, for example, increases crystallization temperature which positively impacts data retention. In this presentation, we examine additional consequences of carbon addition. We describe sputter-deposited $Ge_2Sb_2Te_5$ thin films fabricated with different amounts of carbon up to 12 mol.% and assess how this fourth species affects film phase, order, microstructure and key properties. Similar phase evolution is observed upon heating (amorphous –> face-centered cubic -> trigonal), and phase transformation temperatures are elevated when adding carbon. Grain size is also refined with increased carbon addition within the compositional range studied. The effects of carbon on thin film thermal properties are revealed by frequency domain thermoreflectance wherein a decreased thermal conductivity is observed even when adding small amounts (2 mol. % carbon). Finally, we investigate the response of C-doped GST films to heavy ion irradiation. Films have been irradiated to different doses with 2.8 MeV Au ions in order to explore the potential for ion-induced phase changes and modification of electrical resistivity and thermal conductivity.The response of films having different amounts of carbon (up to 6 mol.%) will be described wherein phase modifications are reported.

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