

## Functional Thin Films and Surfaces

### Room Pacific C - Session C1-WeM

#### Optical Materials and Thin Films

Moderator: **Nikolas Podraza**, University of Toledo, USA

8:00am **C1-WeM-1 Engineering Ultra-thin Films for Extreme Optics and Photonics**, **Jeremy Munday** ([jnmunday@ucdavis.edu](mailto:jnmunday@ucdavis.edu)), University of California at Davis, USA

**INVITED**

Ultra-thin optical coatings have a variety of applications from antireflection coatings to optical sensors. The simplicity of using a single optical film makes it an excellent candidate for large scale applications; however, this simplicity also results in design space constraints and limitations. In this talk, I will discuss how we are able to circumvent a number of these issues using specially designed ultra-thin films in unique ways. I will discuss how ultra-thin metal films can convert a visible silicon detector into a near-infrared detector, how hydrogen can be optically detected in ultra-thin metal films, how materials with epsilon-near-zero (ENZ) optical properties can enhance these effects, and how high-melting-point materials can be used to create custom thermal emitters and their application to thermophotovoltaics. I will conclude with an outlook on these technologies and future applications.

8:40am **C1-WeM-3 Study of Cs<sub>x</sub>(CH<sub>3</sub>NH<sub>3</sub>)<sub>1-x</sub>PbBr<sub>3</sub> Perovskite with XPS Imaging and Small Area Spectra**, **Tatyana Bendikova** ([tatyana.bendikova@weizmann.ac.il](mailto:tatyana.bendikova@weizmann.ac.il)), Weizmann Institute of Science, Israel; **Y. Rakita**, Columbia University, USA; **H. Kaslasi**, **G. Hodes**, **D. Cahen**, Weizmann Institute of Science, Israel

Interest in halide perovskite (HaPs) is motivated by the combination of superior optoelectronic properties and ease in synthesizing these materials with a surprisingly low density of electrically active defects. HaPs possess high chemical sensitivity, especially those having an organic cation at their A position (AMX<sub>3</sub>). Although a direct role of the A cation in this sensitivity is unclear, and the structural and optoelectronic backbone lie within the M-X bond, the type of the A cation was shown to impact the chemical stability and, usually indirectly, affect optoelectronic properties of HaPs.

X-ray Photoelectron Spectroscopy (XPS), is a surface sensitive technique with a sensitivity that goes down to a single atomic layer, and can provide unique information that relates the elemental composition with the chemical and electronic states of the different elements in the material. Our study focuses on the XPS imaging in combination with selected small area XPS spectra and uses solution-grown, single crystals of mixed A-cation Cs<sub>x</sub>MA<sub>1-x</sub>PbBr<sub>3</sub>(MA = CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>) HaPs as a candidate for investigating heterogeneity within the crystals. With XPS we followed the variations in chemical composition of these crystals. By observing the surface, we found significant changes in the N/Cs ratio, which increases towards the interior of the crystal. Similar variations in N/Cs, but also in Pb/(N+Cs) ratios were found when we studied cross-sections of cleaved crystals. This compositional heterogeneity within the HaPs crystal was not previously reported and was discovered and monitored due to exclusive capabilities of the XPS technique.

9:00am **C1-WeM-4 Tuning the Optical Properties of PVD Deposited SiC Coatings by a Design of Experiments Approach**, **Vincent Tabouret** ([vincent.tabouret@grenoble-inp.fr](mailto:vincent.tabouret@grenoble-inp.fr)), **A. Crisci**, **M. Morais**, **G. Berthomé**, **E. Garel**, **G. Renou**, **D. CHaussende**, CNRS, France

Silicon carbide (SiC) is a wide bandgap semiconductor that is currently driving a profound evolution in power electronics, thanks to a unique combination of outstanding physical properties. In addition, SiC also exhibits very promising optical properties, making it very suited for applications in photonics, such as waveguides and frequency combs. For this purpose, amorphous SiC (a-SiC) thin films are deposited at very low temperature with the main challenges being the control of bulk properties and the formation of perfect interfaces. Today, the relationships between the deposition conditions and the optical properties of the films is still not clear. This paper aims to provide a comprehensive picture of these relationships and finally to give some hints for further optimization.

Coatings of a-SiC were deposited by Physical Vapor Deposition (PVD) on different types of substrates, such as sapphire and silica on silicon wafers, and using a polycrystalline SiC target as source material. A design of experiments (DOE) methodology was implemented to identify and weight the main deposition parameters with respect to the optimization of the refractive index and attenuation coefficient of the films, measured by

spectroscopic ellipsometry. In parallel, a systematic investigation of the chemical and structural properties of the films was carried out, using a combination of XRD, FTIR, XPS and TEM.

9:20am **C1-WeM-5 Submicron Structures Obtained by Laser Dewetting of Metallic Thin Film Stacks**, **Bruno Felipe Leitao Almeida** ([bruno.almeida2@saint-gobain.com](mailto:bruno.almeida2@saint-gobain.com)), **L. Gallais**, Institut Fresnel, France; **J. Fonné**, **D. Guimard**, Saint-Gobain Research Paris, France

Patterned thin films can have interesting applications in functional glazing provided by their optical and electrical properties. Some examples are: Plasmonic effects of the dewetted structures, anisotropic electrical properties (polarizers) and high resistivity and good transparency, that could be used as transparent electrodes. In this context, dewetting is an interesting way of patterning thin films, including metallic ones.

Although most of the literature work on the laser induced dewetting is on uncapped metallic films (substrate / metallic film) using pulsed laser, the laser induced dewetting can also take place in metallic thin films encapsulated by dielectrics using a continuous wave laser. An example is the stack of Glass / Si<sub>3</sub>N<sub>4</sub> / Ag / Si<sub>3</sub>N<sub>4</sub> deposited on soda-lime glass by magnetron sputtering, depicting morphologies of lines and islands after laser annealing. According to the temperatures achieved during laser treatment, different mechanisms can take place in continuous wave laser dewetting (solid-state or liquid-state dewetting).

In this stack configuration, our work was interested in studying the different structures that could be obtained. The structuration substantially changed the optical properties of the films. A set of *ex-situ* characterizations has been done on the stack before and after structuration. The techniques used were: ellipsometry, spectrophotometry, Fourier-transform infrared spectroscopy, SEM, AFM and XRD.

In order to obtain more information on the mechanisms responsible for these structures in our systems, a set of *in-situ* techniques (fast microscopy and thermal measurements) has been developed and used to obtain the thermal and temporal dependency of the phenomena. *In-situ* thermal measurements were afterwards confronted to results obtained through numerical simulation. These results showed good accordance for temperatures below the structuration threshold regarding the temporal evolution and the spatial distribution of temperature. For temperatures above the structuration threshold, this is no longer the case. From this point on, the film presented changes in the morphology that affects the optical properties (emissivity and absorption).

We shall present in more details these unique structures and their characterizations, the strategies used to take these changes in account to obtain a better correlation measurement/simulation in elevated temperatures and our interpretation of the mechanisms responsible for its structuration.

11:00am **C1-WeM-10 Design of High-Performance VO<sub>2</sub>-Based Thermochromic Coatings, and Pathway for Their Industry-Friendly Preparation**, **Jiri Houska** ([jhouska@kfy.zcu.cz](mailto:jhouska@kfy.zcu.cz)), **D. Kolenaty**, **T. Barta**, **J. Rezek**, **J. Vlcek**, University of West Bohemia, Czechia

**INVITED**

The contribution reports our latest results [1-5] concerning energy-saving thermochromic multilayered VO<sub>2</sub>-based coatings for smart window applications prepared by reactive magnetron sputtering. First, we show that and how reactive high-power impulse magnetron sputtering with a pulsed O<sub>2</sub> flow control allows reproducible preparation of crystalline VO<sub>2</sub> of the correct stoichiometry under exceptionally industry-friendly deposition conditions: on soda-lime glass substrates without any substrate bias or post-deposition annealing at a low temperature of around 300 °C. Second, doping of VO<sub>2</sub> by W is employed in order to shift the thermochromic transition temperature (68 °C for bulk, 57 °C for our thin film VO<sub>2</sub>) toward the room temperature (40 °C for V<sub>0.988</sub>W<sub>0.012</sub>O<sub>2</sub>, 20 °C for V<sub>0.982</sub>W<sub>0.018</sub>O<sub>2</sub>), without concessions in terms of transmittance and its modulation. Third, we employ ZrO<sub>2</sub> antireflection layers both below and above the thermochromic V<sub>1-x</sub>W<sub>x</sub>O<sub>2</sub> layer, and explain an optimum design of the resulting ZrO<sub>2</sub>/V<sub>1-x</sub>W<sub>x</sub>O<sub>2</sub>/ZrO<sub>2</sub> coatings. While utilizing a first-order interference on ZrO<sub>2</sub> leads to a tradeoff between the luminous transmittance (T<sub>lum</sub>) and the modulation of the solar energy transmittance (ΔT<sub>sol</sub>), utilizing a second-order interference allows one to optimize both T<sub>lum</sub> and ΔT<sub>sol</sub> in parallel. Fourth, we discuss multilayered designs leading, without any further doping, to thermochromic coatings of optimized color (chromaticity as close to white as possible). The state-of-the-art T<sub>lum</sub> and ΔT<sub>sol</sub> values achieved under the aforementioned industry-friendly deposition conditions and at lowered transition temperature are in agreement with those predicted during the coating design.

# Wednesday Morning, May 25, 2022

- [1] J. Vlcek et al., J. Phys. D Appl. Phys. 50, 38LT01 (2017), 10.1088/1361-6463/aa8356
- [2] J. Houska et al., Sol. Energy Mater. Sol. Cells 191, 365 (2019), 10.1016/j.solmat.2018.12.004
- [3] D. Kolenaty et al., Sci. Rep. 10, 11107 (2020), doi.org/s41598 020 68002-5
- [4] J. Houska, Sol. Energy Mater. Sol. Cells 230, 111210 (2021). 10.1016/j.solmat.2021.111210
- [5] J. Houska et al., Design and reactive magnetron sputtering of thermochromic coatings (invited perspective paper), J. Appl. Phys., submitted (2022)

## Functional Thin Films and Surfaces

### Room Town & Country D - Session C2-1-WeA

#### Thin Films for Electronic Devices I

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

3:20pm **C2-1-WeA-5 Developing Electronic Materials With an Eye Towards Packaging**, **Marcel A. Wall** ([marcel.a.wall@intel.com](mailto:marcel.a.wall@intel.com)), Intel Corporation, USA

**INVITED**

Heterogeneous integration of multiple types of Integrated circuit chips on a single package is an emerging area in advanced packaging that has made significant impact to High Performance Computing (HPC) devices. In this presentation, we will discuss the evolution of heterogeneous System in Package (SiP) packaging technologies. We will provide an overview of key drivers and metrics for enabling advanced die to die and on package interconnect technologies. We will cover the areas of innovation needed in materials, equipment, process and design in advancing the next generation of heterogeneous SiP packaging technologies. Finally, we will cover some of the unique requirements needed of basic thin film materials used in electronics, as it applies to packaging.

4:00pm **C2-1-WeA-7 Crystallographic Study of Non-polar  $Al_{0.7}Sc_{0.3}N(11-20)$  Grown on r-plane  $Al_2O_3$  Using Magnetron Sputter Epitaxy**, **Akash Nair** ([akash.nair@iaf.fraunhofer.de](mailto:akash.nair@iaf.fraunhofer.de)), L. Kirste, Fraunhofer Institute for Applied Solid State Physics IAF, Germany; N. Manuel Feil, University of Freiburg, Germany; M. Prescher, A. Žukauskaitė, Fraunhofer Institute for Applied Solid State Physics IAF, Germany

Aluminium scandium nitride (AlScN) has emerged as a promising material for fabrication of bulk acoustic wave (BAW) and surface acoustic wave (SAW) devices by virtue of its high piezoelectric properties and improved electromechanical coupling. Despite the high interest, AlScN remains relatively unexplored material in terms of the structural properties and device applications. We recently demonstrated that non-polar  $Al_{0.7}Sc_{0.23}N$  offers a pathway for further improvement in electromechanical coupling for SAW resonators by aligning the acoustic wave along the c-axis direction with the largest piezoelectric response[1]. The metastable nature of  $Al_{1-x}Sc_xN$  at higher scandium concentrations, that causes formation of abnormally oriented grains (AOG) protruding from surface of the films, has been a challenge for its adoption for SAW applications. We succeeded in achieving the growth of completely AOG-free non-polar in-plane oriented  $Al_{1-x}Sc_xN$  films with even higher Sc content of  $x=0.3$  by reactive magnetron sputter epitaxy. Various sputtering process conditions were investigated focusing on the  $Al_{0.7}Sc_{0.3}N(11-20)/Al_2O_3(1-102)$  film. Surface quality and films with RMS roughness less than 0.5 nm could be obtained. The atomic force microscopy (AFM) and x-ray diffraction (XRD) studies of films show a unique striated grain morphology along the c-axis of the film revealing in-plane anisotropy. While the XRD measurements confirm the in-plane orientation of  $Al_{0.7}Sc_{0.3}N(11-20)$ , the  $\varphi$  scans also reveal a distorted wurzitic structure and structural anisotropy. The structural anisotropy is studied by combining transmission electron microscopy, high resolution XRD and AFM. Furthermore, the optimized  $Al_{0.7}Sc_{0.3}N(11-20)$  films were used to fabricate SAW resonator test structures. Different in-plane SAW propagation directions were used to map the angular distribution of effective electromechanical coupling as well as piezoelectric properties of non-polar AlScN thin films and correlated to the results of structural anisotropy study.

[1] A.Ding, et al., APL 116(10), 101903 (2020).

4:20pm **C2-1-WeA-8 Tuning Barrier Properties of Metal Nitride Thin Films for GaN Transistor Applications**, **Clemens Nyffeler** ([clemens.nyffeler@evatecnet.com](mailto:clemens.nyffeler@evatecnet.com)), B. Attarimashalkoubeh, J. Patscheider, B. Heinz, Evatec AG, Switzerland

Due to their thermal stability and barrier properties, conductive metal nitrides are often used in the fabrication of electronic devices, such as contact layers on the surface of a field-effect transistor's (FET) gate region. Specifically, in the case where a metal nitride layer is in direct contact with a semiconductor's surface, for example in heterojunction FETs made from III-V materials such as Gallium Nitride, the barrier function requirements are twofold. The material must prevent both, migration of metal species (diffusion barrier), and also electrical conduction into the semiconductor (Schottky barrier), thus preventing shorts between gate and channel and ensuring efficient device operation.

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In this context, we investigate the mentioned barrier function, electrical conductivity, and other relevant properties of thin  $TiN_x$  and  $WN_x$  layers ( $t < 200nm$ ) deposited by reactive magnetron sputtering. Sputter deposition was performed on an Evatec Clusterline® 200II industrial production system for automated processing of 200mm substrates at high throughput.

Our experiments show that good barrier properties in tungsten nitride are achieved for a sub-stoichiometric, nitrogen-deficient composition of  $WN_x$  with a nitrogen content of only 20at% showing a predominant phase of (111)-oriented  $W_2N$ . For  $TiN_x$  on the other hand, we see evidence for diffusion through the barrier layer in annealing experiments for sub-stoichiometric films only. Conversely, the barrier remains effective for films deposited in a nitrogen-rich ambient, with a  $N_2:Ar$  gas-flow ratio of larger than 1:1, resulting in over-stoichiometric films.

The diffusion experiments are conducted on stacks of 25nm Ti / 100nm  $TiN_x$  / 75nm Al layers (top-to-bottom, on Si substrates). Four-point probe measurements before ex-situ annealing at temperatures up to 400°C and after annealing exhibit a significant change of the measured sheet resistance. These changes are correlated to failure of the Schottky barrier function.

4:40pm **C2-1-WeA-9 Advancements in Metallic Interconnects for the Semiconductor Industry**, **Thomas Ponnuswamy** ([Thomas.Ponnuswamy@lamresearch.com](mailto:Thomas.Ponnuswamy@lamresearch.com)), Lam Research Corp, USA

**INVITED**

The semiconductor industry is advancing from a SoC (system on chip) approach towards developing various integration schemes involving SiP (system in package) to meet the future requirements of performance and cost. This is commonly referred to as heterogeneous integration and is being utilized for 2.5D/3D chip stacking, high density fanout and chiplets. All these approaches rely on the use of metallic interconnects including TSVs (through-silicon vias), micropillars, fine line RDL, and hybrid bonding.

In the case of 3D stacking with TSVs for memory, we see an increase in the number of stacking layers and reduction of critical dimensions to accommodate higher I/O counts. The interconnects in high density fanout comprise of fine line RDL and megapillars. To meet the performance requirements line dimensions are shrinking from  $5x5\mu m$  to sub  $2x2\mu m$  L/S, along with incorporation of a multilayer approach. Megapillars typically range from 100 to 200 $\mu m$  CD with varying aspect ratios depending on the integration scheme and performance needs. Copper pillars with sub-40 $\mu m$  pitch are referred to as micropillars which will eventually need to be replaced by hybrid bonding as the dimensions shrink below 10 $\mu m$ .

Scaling requirements for each of these interconnects pose challenges that need to be addressed by making process, materials, and integration changes. In the case of TSVs, higher aspect ratios necessitate the need for alternate metallization schemes. For micropillars, increase in bump density results in challenges to assembly yield and reliability, while for fine line RDLs stress induced damage and topography control needs to be solved. Finally, in the case of hybrid bonding the key requirement of lower thermal budget for yield improvement needs to be addressed for die-to-wafer and wafer-to-wafer stacking.

This presentation will cover how select deposition processes and material changes provide solutions to the scaling challenges posed by interconnects utilized in various heterogeneous integration schemes.

## 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/AIO<sub>x</sub> 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/AIO<sub>x</sub> thermistors are fabricated on SiN<sub>x</sub>/SiO<sub>2</sub>/Si substrates using magnetron sputtering. In order to achieve enhanced adhesion of Pt film (175 nm), an AIO<sub>x</sub> 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/AIO<sub>x</sub> is subjected to different annealing conditions by varying annealing temperature, time, and environment. With an increase in the annealing temperature and duration, Pt/AIO<sub>x</sub> 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/AIO<sub>x</sub> 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.<sup>1</sup> 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<sup>2</sup> to study phase transitions of ultrathin silicides. Our ToF-LEIS setup is connected to a preparation chamber equipped with an e<sup>-</sup>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<sub>2</sub>Si, displaying long-range order covering the whole film thickness, to epitaxial NiSi<sub>2-x</sub> at 290°C skipping the intermediate NiSi phase observed for thicker films.<sup>3</sup> Considering previous studies we suggest that the ordered δ-Ni<sub>2</sub>Si phase occurs regardless of the initial Ni film thickness but is limited in thickness by competing orientations of the δ-Ni<sub>2</sub>Si crystal. Whether or not the NiSi phase is found absent, depends on whether the formed δ-Ni<sub>2</sub>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.

<sup>1</sup>S.-L. Zhang and Z. Zhang, *Met. Films for Electron., Opt. and Magn. Appl.*, Elsevier, 244–301, 2014

<sup>2</sup>M. Draxler et al., *Phys. Rev. A*, 68, 022901, 2003

<sup>3</sup>P. M. Wolf et al., *Small*, 2106093, 2022

10:20am **C2-2-ThM-8 Synthesis of a New Ternary Nitride Semiconductor - Zn<sub>2</sub>VN<sub>3</sub>: 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 Sjol (sebastian.sjol@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<sub>2</sub>VN<sub>3</sub>. [1] Reactive RF co-sputtering of Zn and V targets is performed in Ar/N<sub>2</sub> atmosphere with N<sub>2</sub> is supplied directly to the sputter plasma to increase the N<sub>2</sub> 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<sub>2-x</sub>V<sub>x</sub>N phase over a large compositional range from Zn<sub>2</sub>VN<sub>3</sub> to ZnVN<sub>2</sub>, with a narrow process window for single-phase Zn<sub>2</sub>VN<sub>3</sub>.

Following the combinatorial screening we isolate the phase and synthesize single-phase polycrystalline Zn<sub>2</sub>VN<sub>3</sub> thin films with wurtzite structure on conventional borosilicate glass substrates. In addition, we demonstrate that cation-disordered, but phase-pure (002)-textured wurtzite Zn<sub>2</sub>VN<sub>3</sub> thin films can be grown using epitaxial stabilization on α-Al<sub>2</sub>O<sub>3</sub> (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<sub>2</sub>VN<sub>3</sub> 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: MgSnN<sub>2</sub>**, *Agathe Virfeu (agathe.virfeu@univ-lorraine.fr)*, *F. Alnjjman, S. Diliberto, J. Ghanbaja*, Institut Jean Lamour - Université de Lorraine, France; *E. Hays*, 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<sub>2</sub> 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<sub>2</sub> thin films (bandgap energy ≈ 2 eV) that is a good candidate for green emitters in LEDs and an absorber material in tandem photovoltaics.

MgSnN<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> films were compared to those obtained by *ab initio* calculations. Finally, the electrical resistivity, carrier concentration, and carrier mobility have 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.mcginis@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<sub>x</sub>Dy<sub>(1-x)</sub>FeO<sub>3</sub> (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<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> 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<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> 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<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> 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.

This work was supported by the Laboratory Directed Research and Development program at Sandia National Laboratories, a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science. The views expressed in the article do not necessarily represent the views of the U.S. DOE or the United States Government.

## Functional Thin Films and Surfaces Room Pacific D - Session C3-1-ThM

### Thin Films for Energy Storage and Conversion I

**Moderators:** *Clio Azina*, RWTH Aachen University, Germany, *Tushar Shimpi*, Colorado State University, USA

8:00am **C3-1-ThM-1 Designing Optimal Environments for Surface Catalytic Reactions in Perovskite Oxide Electrodes**, *L. Martin, Abel Fernandez (abel\_fernandez@berkeley.edu)*, University of California, Berkeley, USA  
**INVITED**

Solid-gas interactions at electrode surfaces determine the efficiency of solid-oxide fuel cells and electrolyzers. Of particular relevance are the local chemistry and electronic structure at the exposed electrode surface. Using epitaxial thin films as model systems, we studied the evolution of surface chemistry and electronic structure in perovskite electrodes with different surface orientations and epitaxial strain states. First, synthesizing La<sub>0.8</sub>Sr<sub>0.2</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3</sub> films on SrTiO<sub>3</sub> (001)-, (110)-, and (111)-oriented substrates wherein the surface orientation of the film is set by the substrates. Electrochemical impedance spectroscopy and electrical conductivity relaxation measurements reveal a strong surface-orientation dependency of the gas-exchange kinetics, wherein (111)-oriented surfaces exhibit an activity >3-times higher as compared to (001)-oriented surfaces. First-principles calculations suggest that the formation energy of vacancies and adsorption at the various surfaces is different and influenced by the surface polarity. Finally, synchrotron-based, ambient-pressure X-ray spectroscopies reveal distinct electronic changes and surface chemistry among the different surface orientations. Taken together, thin-film epitaxy provides an efficient approach to control and understand the electrode reactivity ultimately demonstrating that the (111)-surface exhibits a high density of active surface sites which leads to higher activity.<sup>1</sup> Outside of surface chemistry, manipulation of the surface electronic structure via epitaxial strain presents another route toward enhancing surface reaction rates. Combining high-temperature electrical-conductivity-relaxation studies and synchrotron-based X-ray absorption spectroscopy studies of La<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3</sub> and La<sub>0.8</sub>Sr<sub>0.2</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3</sub> thin films under varying degrees of epitaxial strain reveals a strong correlation between orbital structure and catalysis rates. In both systems, films under biaxial tensile strain exhibit the fastest reaction kinetics, in agreement with previous reports. Films under tensile biaxial strain also possess the lowest electron occupation in the d<sub>z<sup>2</sup></sub> orbitals, suggesting the orbital occupation plays an important role in determining the electrocatalytic properties of perovskite cathodes.<sup>2</sup>

1. R. Gao *et al.* *Adv. Mater.* 33, 2100977 (2021).

2. A. Fernandez *et al.* *Adv. Energy Mater.* 2102175 (2021).

# Thursday Morning, May 26, 2022

8:40am C3-1-ThM-3 Halide Perovskites: Advanced Photovoltaic Materials Empowered by a Unique Bonding Mechanism, **Matthias Wuttig** ([wuttig@physik.rwth-aachen.de](mailto:wuttig@physik.rwth-aachen.de)), Sommerfeldstrasse, Germany; *C. Schön*, *M. Schumacher*, RWTH Aachen University, Germany; *J. Robertson*, University of Cambridge, UK; *P. Golub*, Heyrovsky Institute of Physical Chemistry, Czechia; *E. Bousquet*, Liege University, Belgium; *C. Gatti*, CNR-SCITEC, Italy; *J. Raty*, University Liege, Belgium

Outstanding photovoltaic (PV) materials combine a set of advantageous properties including large optical absorption and high charge carrier mobility, facilitated by small effective masses. Halide perovskites ( $ABX_3$ , where  $X = I, Br \text{ or } Cl$ ) are among the most promising PV materials. Their opto-electronic properties are governed by the B-X bond, which is responsible for the pronounced optical absorption and the small effective masses of the charge carriers. These properties are frequently attributed to the  $ns^2$  configuration of the B atom, i.e.  $Pb 6s^2$  or  $Sn 5s^2$  ('lone-pair') states. Our analysis of the PV properties in conjunction with a quantum-chemical bond analysis reveals a different scenario. The B-X bond differs significantly from ionic, metallic or conventional 2c-2e covalent bonds. Instead it is better regarded as metavalent, since it shares about one p-electron between adjacent atoms. The resulting s-bond, formally a 2c-1e bond, is half-filled, causing pronounced optical absorption. Electron transfer between B and X atoms as well as lattice distortions open a moderate band gap resulting in charge carriers with small effective masses. Hence metavalent bonding explains favorable PV properties of halide perovskites, as summarized in a map for different bond types, which provides a blueprint to design PV materials.

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*Halide perovskites: third generation photovoltaic materials empowered by an unconventional bonding mechanism*

**Advanced Functional Materials, 202110166 (2021)**

## Functional Thin Films and Surfaces

### Room Town & Country C - Session C3-2-ThA

#### Thin Films for Energy Storage and Conversion II

**Moderators:** Clio Azina, RWTH Aachen University, Germany, Tushar Shimpi, Colorado State University, USA

3:00pm **C3-2-ThA-6 Atomic/Molecular Layer Deposition of Layer-Engineered Inorganic-Organic Thin Films for Emerging Energy Technologies**, Maarit Karppinen (maarit.karppinen@aalto.fi), Aalto University, Finland

INVITED

The ALD/MLD (atomic/molecular layer deposition) technique allows the combination of inorganic and organic layers into any arbitrary frequency pattern. We have exploited ALD/MLD for (i) textile-integrated thermoelectrics, (ii) photo-switchable high-coercivity magnets, (iii) artificial SEI layers for Li-ion batteries, and (iv) active components for Li-organic microbattery. For thermoelectrics, we pioneered ZnO:organic superlattice structures, in which monomolecular organic layers alternate with nm-scale thermoelectric ZnO layers, to drastically suppress the thermal conductivity without comprising the electrical conductivity; when deposited on textiles, these films coat the textile fibers conformally so that the entire textile becomes an active part of the thermoelectric device.<sup>1,2</sup> To realize flexible and photo-switchable magnets, we have combined nanoscale layers of the rarest trivalent iron oxide polymorph  $\epsilon$ -Fe<sub>2</sub>O<sub>3</sub> exhibiting giant coercive field values with azobenzene layers undergoing reversible trans-cis-trans isomerization reactions upon successive UV and visible light irradiations.<sup>3,4</sup> To mimic the composition of the naturally forming SEI layers in Li-ion batteries, we developed a three-precursor ALD/MLD process, Li-HMDS+ethylene glycol+CO<sub>2</sub>, for the targeted lithium ethyl carbonate films.<sup>5</sup> Finally, for the Li-organic microbattery application, our new active-material arsenal comprises various intriguing intercalated-type layered Li-organic materials that experience minimal changes in crystal structure upon the electrochemical Li<sup>+</sup>-ion intercalation.<sup>6</sup>

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2. G. Marin, R. Funahashi & M. Karppinen, *Adv. Eng. Mater.* **22**, 2000535 (2020).
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6. J. Multia, J. Heiska, A. Khayyami & M. Karppinen, *ACS Appl. Mater. Interfaces* **12**, 41557 (2020).

3:40pm **C3-2-ThA-8 Transparent Niobium-Doped Titanium Dioxide Thin Films With High Seebeck Coefficient for Thermoelectric Applications**, Joana Ribeiro (joanaribeiro93@hotmail.com), F. Correia, F. Rodrigues, University of Minho, Portugal; S. Reparaz, A. Goni, Institut de Ciència de Materials de Barcelona-CSIC, Spain; C. Tavares, University of Minho, Portugal

The design of a transparent thermoelectric material is a promising technology for touch-screen displays and solar cell applications, rendering a more sustainable powering of the device. In order to enhance the thermoelectric performance, the material must have a high Seebeck coefficient, high electrical conductivity but low thermal conductivity [1]. Modifying the atomic structures of TiO<sub>2</sub> by deliberately introducing defects can enhance its properties to a great extent, while a cationic doping of TiO<sub>2</sub> has been documented to improve its electrical conductivity [2]. This work reports the production and characterization of optically transparent Nb-doped TiO<sub>2</sub> thin films with enhanced thermoelectric properties deposited on glass and Si by reactive d.c. magnetron sputtering in high vacuum. The purpose of these films is to harvest thermal energy from the environment and convert it to electrical energy. Several process parameters, such as reactive and working gas flow rate, deposition temperature, target current density and post-annealing conditions, directly affect the morphology and crystalline structure of the thin films. The optimization of these parameters results in thin films with thickness of 120-300 nm, maximum average optical transmittance in the visible range of 73 %, n-type electrical

resistivity of 0.05 W·cm, thermal conductivity below 1.7 W·m<sup>-1</sup>·K<sup>-1</sup> and a maximum absolute Seebeck coefficient of 223 mV·K<sup>-1</sup>. The resulting maximum thermoelectric power factor is 60 mW·K<sup>-2</sup>·m<sup>-1</sup> and the maximum thermoelectric figure of merit is 0.014. Hence, modifying the optical, electric, thermal and thermoelectric properties of the thin films enables their suitability for applications as transparent electrodes in photovoltaic systems and touch displays, amongst other devices.

#### References

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4:00pm **C3-2-ThA-9 X-Ray Absorption Spectroscopy Study of Local Order in Transparent Thermoelectric Thin Films of Doped ZnO**, F. Correia, J. Ribeiro, F. Barbosa, M. Andriutschky, Centre of Physics of the Universities of Minho and Porto (CF-UM-UP), University of Minho, Portugal; A. Kuzmin, I. Pudza, Institute of Solid State Physics, University of Latvia; A. Kalinko, Deutsches Elektronen-Synchrotron – A Research Centre of the Helmholtz Association, Gibraltar; E. Welter, Deutsches Elektronen-Synchrotron – A Research Centre of the Helmholtz Association, Germany; A. Mendes, LEPABE, Faculty of Engineering of the University of Porto, Portugal; A. LaGrow, International Iberian Nanotechnology Laboratory (INL), Portugal; O. Bondarchukat, International Iberian Nanotechnology Laboratory (INL), Portugal; N. Sadrine, R. Correia, T. Monteiro, i3N, Departamento de Física, Universidade de Aveiro, Portugal; Carlos J. Tavares (ctavares@fisica.uminho.pt), Centre of Physics of the Universities of Minho and Porto (CF-UM-UP), University of Minho, Portugal

Ga, Bi- and Sb-doped ZnO thin films with thermoelectric properties were produced by magnetron sputtering. All undoped and doped films crystallise in a ZnO phase with the hexagonal wurtzite crystal structure. The local structure of the thin films was investigated by temperature-dependent X-ray absorption spectroscopy at the Zn, Ga, Sb K-edges, as well as at the Bi L<sub>3</sub>-edge. The experiments were done in transmission and fluorescence modes at the P65 Applied XAFS beamline of the PETRA III storage ring. It was found that doping with Ga<sup>3+</sup> and Bi<sup>3+</sup> ions in the ZnO wurtzite structure produces a distinct effect on the thin film microstructure. The substitution of Zn<sup>2+</sup> ions by smaller Ga<sup>3+</sup> ions introduces a static disorder to the thin film structure, which is evidenced by an increase in the mean-square relative displacements (MSRD)  $\sigma^2(\text{Zn-O})$  and  $\sigma^2(\text{Zn-Zn})$ . At the same time, large Bi<sup>3+</sup> ions do not substitute zinc ions, but are likely located in the disordered environment at the ZnO grain boundaries. This conclusion was directly supported by energy-dispersive X-ray spectroscopy combined with TEM and STEM observations as well as by resonant and non-resonant m-Raman experiments at room temperature, where the ZnO and ZnO:Bi spectra are similar, suggesting a lack of structural disorder in the wurtzite cell. Similar experiments were performed for ZnO:Sb<sub>x</sub> (x=2-14 at%) thin films to determine the coordination environment of Sb impurities and their influence on the local structure and lattice dynamics of the ZnO matrix. XANES and EXAFS suggest that doping of ZnO by Sb impacts the crystallinity of the films leading to amorphization at high Sb concentrations. As a result, a significant increase of MSRD due to static disorder for higher Sb concentration has been found in the first and second coordination shells of zinc, when compared to crystalline w-ZnO.

## Functional Thin Films and Surfaces Room Golden State Ballroom - Session CP

### Functional Thin Films and Surfaces (Symposium C) Poster Session

**CP-1 Cross-Linking Processes in Antimicrobial UV-Sol-Gel and Thermal-Sol-Gel Systems Initiated by Atmospheric Pressure Plasma Characterized by FTIR**, *Simon Chwatal (Simon.Chwatal@joanneum.at)*, *J. Lackner, W. Waldhauser*, Joanneum Research Forschungsgesellschaft GmbH, Austria; *M. Stummer*, INOCON Technologie GmbH, Austria; *H. Steiner*, Aerospace & Advanced Composites GmbH, Austria; *A. Coclite*, Graz University of Technology, Austria

The versatile adjustability of the sol-gel chemistry is a great technological advantage over other coating systems, especially due to the usability of organic and inorganic precursors as well as the variation of the reaction control and drying, curing, compaction. Alongside the many promising possibilities for producing functional coatings using the sol-gel process, challenges remain by (1) the temporal stability of sol-gel systems, (2) sensitivity of sol-gel systems to slight fluctuations in the ambient conditions during production but also processing, (3) crack formation caused by shrinkage during drying and curing, and (4) widely required curing temperatures of up to 180 °C for several minutes to hours. The last two challenges can be solved by very quick plasma curing instead of using UV or heat-based, long-lasting processes separately. Plasma combines both high and short UV and temperature impacts on the sol-gel system. INOCON Technologie GmbH has developed and patented a hot gas atmospheric pressure plasma source for exactly this purpose. In the current work, special attention is given to the atomic bonding and cross-linking processes initiated by the hot plasma and the occurring interactions. In order to better show the influence of both main plasma characteristics, a thermal and a rather new UV curing sol-gel system developed by Aerospace & Advanced Composites GmbH are used once. FTIR analyses are a base for evaluating and providing information about the intensity and position of the peaks. They also show the progress of the curing process. The hardness of the layer is an indicator of the degree of cross-linking. The harder the system, the better the atomic structures are linked together.

In addition to these studies, the antimicrobial effect of the sol-gel systems is also tested. The biocidal effect should be further enhanced by applying zinc or copper particles on the cured sol-gel layer within a subsequent process step. Alongside the experiment and optical spectroscopy, gas flow simulations, with the software ANSYS, are used to include information on the processes within the plasma, initiated by gases, flow rates, plasma jet power, and admixed precursors. Therefore, INOCON Technologie GmbH carried out a CFD-simulation model. The temperature plays an important role here, must be estimated beforehand, since critical temperatures lead to discoloration or even decomposition in the layer, and thus renders the result unusable. For this purpose, a transient thermal simulation is conducted to take the influence of the curing speed into account.

**CP-2 Crystallization and Vitrification Kinetics by Design: The Role of Chemical Bonding**, *Matthias Wuttig (wuttig@physik.rwth-aachen.de)*, RWTH Aachen University, Germany

Controlling a state of material between its crystalline and glassy phase has fostered many real-world applications. Nevertheless, design rules for crystallization and vitrification kinetics still lack predictive power. Here, we identify stoichiometry trends for these processes in phase change materials, i.e. along the GeTe-GeSe, GeTe-SnTe, and GeTe-Sb<sub>2</sub>Te<sub>3</sub> pseudo-binary lines employing a pump-probe laser setup and calorimetry. We discover a clear stoichiometry dependence of crystallization speed along a line connecting regions characterized by two fundamental bonding types, metallic and covalent bonding. Increasing covalency slows down crystallization by six orders of magnitude and promotes vitrification. The stoichiometry dependence is correlated with material properties, such as the optical properties of the crystalline phase and a bond indicator, the number of electrons shared between adjacent atoms. A quantum-chemical map explains these trends and provides a blueprint to design crystallization kinetics.

C. Persch, M. Müller, A. Yadav, N. Honne, J. Pries, S. Wei, P. Fantini, E. Varesi, F. Pelizzer, M. Wuttig, *The Role of Chemical Bonding to Design Crystallization and Vitrification Kinetics*

**CP-3 Theoretical and Experimental Study to Simplify AgZn Alloy IR Refractive Index Calculation**, *Daniel Lin (ding@labforinvention.com)*, *T. Ding, G. Ding*, Labforinvention, USA

#### Abstract

The optical refractive index and electrical resistivities of Silver Zinc alloy were studied experimentally by a co-sputtering method. The theories on alloys refractive index currently are too complex, dependent on too many factors, so it can still only be a semi-practical prediction. In this study, a new method was developed to simplify the calculation of silver alloy IR refractive index by comparing silver refractive index at the same deposition condition, specifically: (1) theoretically, the refractive index ratio  $n_{\text{alloy}}/n_{\text{Ag}}$  between silver and its alloy at IR region is assumed to cancel out most factors so that it only depends on free electron density  $n_e$  and the film resistivity  $\rho$ ; further, only dependent on alloy concentration and resistivity  $\rho$ ; (2) Experimentally, this assumption was approximately met by: the deposition conditions between sputtering Ag and its alloy were identical except the alloy with an additional tiny Zinc co-sputtering power; (3) The experimental results agreed well with this simplified calculation. Further discussions are compared with the literature on how the zinc electrons contribute to the optical and electrical properties in low Zn concentration AgZn alloy (<10%) found in this study.

**CP-6 Sputter Deposited Advanced Anode Functional Layers for Solid Oxide Fuel Cells**, *K. Steier, Justyna Kulczyk-Malecka (j.kulczyk-malecka@mmu.ac.uk)*, *P. Kelly*, Manchester Metropolitan University, UK

Solid oxide fuel cells (SOFCs) convert the chemical energy stored in fuels, such as hydrogen and gaseous hydrocarbons, directly into electrical power and thermal energy through electrochemical reactions. State-of-the-art SOFC anodes consist of a cermet of nickel and yttria-stabilised zirconia (YSZ) to increase the reactive sites at the anode/electrolyte interface.

Nanostructured Ni-YSZ functional layers has been produced using reactive pulsed DC magnetron co-sputtering of metallic targets of zirconium-yttrium and nickel. Whilst recent studies show the deposited Ni-YSZ films from a single Ni-YSZ compound target, we present the co-deposition from decoupled Ni and Zr-Y targets, which allows the deposition of Ni-YSZ with a graded composition of nickel within the structure.

The sputtering process was performed in an oblique angle deposition mode, to deliberately generate columnar nanostructures, in mixed argon/oxygen atmospheres. Deposition parameters, such as deposition angle and deposition pressure have been studied to determine their influence on the structural and morphological properties in the context of their application as SOFC anode functional layers. The obtained films were characterised by SEM, EDS and XRD. We found that sputter deposited YSZ films led to a higher porosity within the YSZ scaffolds with increasing deposition angle and pressure. During the co-sputtering of Ni and Zr-Y, Ni was oxidised to NiO and then subsequently transformed to catalytically active nickel during the reduction in hydrogen, facilitating the required porosity for the gas transport.

Furthermore, two designs of Ni-YSZ anodes were deposited onto a spark plasma sintered YSZ electrolyte-supported button cell coupled with a commercial LSM cathode. The first design used a constant Ni composition and the second comprised of a graded Ni content within the structure. Finally, both configurations have been tested in fuel cell mode under hydrogen and air flows for anode and cathode, respectively, to characterise the performance of the functional layers.

**CP-8 Unraveling the Bisignate and Broadband Chiroptical Response from All-Dielectric Distorted L-Shape Metamaterials**, *Ufuk Kilic (UFUKKILIC@UNL.EDU)*, *M. Hilfiker, S. Wimer, A. Ruder, E. Schubert, C. Aryropoulos, M. Schubert*, University of Nebraska-Lincoln, USA

With a broad variety of nanofabrication technologies available, structures with different morphologies and subwavelength scale dimensions were proposed as strong candidates to manipulate light from visible to infrared spectral regions. [1,2]. Of particular interest, all-dielectric three-dimensional nanostructures have been frequently reported as prominent contestants which can tackle both the lossy nature of metals and the insufficient broadband chiral response of their planar thin film configurations [1,3].

Here, we propose a simplistic chiral nano-platform: all-dielectric distorted L-shape metamaterials so-called *nanoboomerangs*. Thanks to glancing angle deposition, a recently emerging bottom-up fabrication technique with precise sample stage manipulation ability, we successfully assembled achiral silicon columnar structures and fabricated three-dimensional, highly



porous, superlattice-type, distorted L-shape metamaterial. Using Mueller matrix generalized spectroscopic ellipsometry technique, we performed the chiroptical characterization of the *nanoboomerangs* which exhibit extremely broadband, large, tunable, and bisignate chiroptical response. We believe that this new metamaterial platform can be a strong candidate for a myriad of next generation photonic integrated technological applications including but not limited to chiral sensors, drug-delivery systems, and chiral-topological insulators.

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**CP-10 Microstructured Electrodeposition of Copper Templated by Photo-Induced Monolayer Patterning, David Sconyers (david.j.sconyers2.civ@army.mil), C. Longo, J. Maurer, US Army DEVCOM AC, Benet Laboratories, USA**

Materials presenting surfaces with antiviral or antibacterial properties represent a growing area of interest due to the threat of future global pandemics. Surface morphologies that are hostile to the adhesion and replication of microorganisms are a commonly employed defense system found in nature. Defined textures and patterns of this kind can be emulated artificially via directed electrodeposition of transition metals from aqueous solutions onto electrically conductive substrates relevant to human use. Here, we carry out the electrochemical generation of such surfaces, driven by the selective coating of self-assembled monolayers (SAMs) of alkylphosphonates and alkoxy silanes onto mild steel. Photo-induced monolayer patterning (PIMP) subsequently generates defect sites in these engineered coatings, characterized through Fourier-transform infrared spectroscopy (FTIR), matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF) and contact angle (CA) measurements. The exposed steel at these defect sites provide points of nucleation for the electrochemical reduction of copper, and have been shown to generate deposits that exhibit variable microstructure.

**CP-12 Ag Segregation in Co-sputtered ZrCuAlNi:Ag Thin Films, M. Steinhoff, D. Holzapfel, S. Karimi Aghda, D. Neuß, P. Pöllmann, M. Hans, RWTH Aachen University, Germany; D. Primetzhofer, Uppsala University, Sweden; J. Schneider, Clio Azina (clioazina@gmail.com), RWTH Aachen University, Germany**

The development of nanocomposites opens the door for new functional materials which combine the properties of two or more constituents. Herein, we report on the formation of Ag-reinforced thin film metallic glass nanocomposites by a hybrid direct-current magnetron sputtering and high-power pulsed magnetron sputtering process. The effects of Ag-content, substrate temperature and substrate bias potential on the phase formation and morphology of the nanocomposites were investigated.

While applying a substrate bias potential did not strongly affect the morphological evolution of the nanocomposites, the Ag content dictated the size and distribution of Ag surface segregations, while the bulk of the film remained featureless. However, at higher substrate temperatures, increased Ag contents led to the formation of lamellar-shaped Ag segregations in the bulk and that of a polycrystalline Ag layer at the surface, both of which were due to thermally enhanced surface diffusion.

The electrical resistivity of the produced nanocomposites was strongly affected by the segregations as a significant decrease was observed for the dual-phase systems, supporting the combination of properties of the metallic glass matrix and metallic reinforcement.

# Friday Morning, May 27, 2022

## Functional Thin Films and Surfaces

### Room Town & Country C - Session C4-FrM

#### Photo- and Electrochemically Active Surfaces

**Moderators:** Peter Kelly, Manchester Metropolitan University, UK, Carlos Tavares, University of Minho, Portugal

9:00am **C4-FrM-4 Shedding Light on Implant Biointerfaces: Designing Innovative Photocatalytic Coatings Towards Cell-Assisting and Bacteria-Killing Functions on Titanium**, Valentim Barão ([vbarao@unicamp.br](mailto:vbarao@unicamp.br)), B. Nagay, C. Dini, H. Pantaroto, University of Campinas (UNICAMP), Brazil

#### INVITED

A significant concern emerging from current Implant Dentistry is the increasing prevalence of peri-implant infections and the lack of consensus on the most effective therapeutic technique to treat such diseases. Therefore, new strategies for peri-implant biofilm control are urged to be developed to guarantee the long-term predictability of the implant treatment. Within the context of photochemical processes, the development of photocatalytic coatings and photofunctionalized surfaces can be alternatives for reducing the biofilm formed on and assisting cellular interactions with dental implants. Targeting these optimal biological functions, the outstanding concept of photofunctionalization and photocatalysis for environmental decontamination, using the well-known crystalline titanium dioxide (TiO<sub>2</sub>) coating as a photocatalyst, have shed light on scientists to the use of this strategy for biomedical implant application. Nevertheless, the use of photocatalysis for implant rehabilitation is still in its infancy. The main challenge of using TiO<sub>2</sub> as a photocatalyst for biomedical purposes is that, because of its wide band gap, TiO<sub>2</sub> can only produce bactericidal reactive oxygen species by ultraviolet (UV) light, which is harmful to human health due to its fast absorption by DNA. To overcome this limitation, photocatalytic coatings consisting of visible light-responsive photocatalysts have been developed for using with implants therapy. For this, to reduce the band gap to a level compatible with visible light ( $\lambda \geq 400$  nm), it is necessary to resort to alternative strategies, such as elemental doping with metals and anions. Therefore, this presentation aims to approach multifunctional coatings for biomedical implants using the concepts of photocatalysis under UV and visible lights and the antibacterial mechanisms of biocompatible metals. We will also discuss the UV photofunctionalization on pre-osteoblastic cell differentiation and mineralization potential. In addition, the modulation of key inflammatory markers by UV-modified surfaces will also be addressed. From a clinical perspective, the use of light might be an effective strategy to reduce biofilm-related diseases and accelerate the wound healing of dental implants.

9:40am **C4-FrM-6 Hematite and Titania Thin Films: Energy and Environmental Applications (Virtual Presentation)**, Josef Krysa ([Josef.Krysa@vscht.cz](mailto:Josef.Krysa@vscht.cz)), University of Chemistry and Technology, Czechia

#### INVITED

Titania (TiO<sub>2</sub>) and hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) have potential applications as semiconducting photoanodes for either hydrogen production *via* photoassisted water electrolysis or photoelectrochemical (PEC) oxidation of water pollutants. The advantages of TiO<sub>2</sub> are high stability, nontoxicity, and low price. However, it absorbs only a very small part of sunlight (3% of the total power). On the other hand, iron oxide ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) has a favourable band gap (2.0 – 2.2 eV), which enables absorption of a substantial fraction of solar light, resulting in the theoretical maximum power conversion efficiency of 27 %. This has created much interest in the past, which has been rekindled by the advent of new thin film preparation and texturization methods. Limitations are the non-ideal position of the conduction band, *i.e.* too large an electron affinity for spontaneous water reduction, low minority carrier diffusion length, surface states that can mediate recombination, low stability in acidic media, and photocorrosion. We have recently fabricated Sn-doped hematite (Fe<sub>2</sub>O<sub>3</sub>) films by aerosol pyrolysis (AP) on fluorine doped tin oxide (FTO). Photosensitivity had an onset around 650 nm and maximum incident photon to electron conversion efficiency (IPCE) was 0.21 at 400 nm. The aim of the present work was to check whether the capping with TiO<sub>2</sub> can be used for corrosion protection of such films.

AP hematite films on FTO were covered by titania films fabricated by spray-pyrolytic coating. Spray pyrolysis of TiO<sub>2</sub> used as precursor a 0.2 M ethanolic solution of titanium di-isopropoxide bis-acetylacetonate. AP hematite layers coated with TiO<sub>2</sub> show that with increasing thickness (increasing number of passes of the spray nozzle) of the TiO<sub>2</sub> coating the photoelectrochemical response decreased. This is due to TiO<sub>2</sub> increasingly

taking part in the solid liquid interface. This is also reflected in the photocurrent onset shifting to more negative potentials. The Faradaic efficiency (*f*) of the photocorrosion reaction in 1 M sulphuric acid decreased from 0.47 % (for an unprotected hematite electrode) to 0.17 % for that covered with spray coated TiO<sub>2</sub> layer (but decreased photoresponse).

10:20am **C4-FrM-8 Multifunctional Coatings for Maritime Applications**, José Castro ([uc2021120076@student.uc.pt](mailto:uc2021120076@student.uc.pt)), University of Coimbra, Colombia; M. Lima, I. Carvalho, M. Henriques, University of Minho, Portugal; S. Carvalho, University of Coimbra, Portugal

The main transportation system in the world commerce are ships and their problems could be critical, affecting the world economy. Corrosion and biofouling are considered like common issues associated to maritime components and those must be prevented to avoid possible damage, pollution or functional performance losses and hence, economical and environmental drawbacks. In this context, some products have been applied to minimize dead times in maintenance in ships, and hence extend its productive time. Tributyltin (TBT) paint was the most used solution before 2008, however it was banned since then. With this lack, multifunctional coatings seem to be a good option to replace TBT. Zirconium (oxy)nitrides doped with Cu obtained by Magnetron Sputtering technology, could gather the desired properties in maritime applications. The films were sputtered over SS316L substrates, material used largely in the naval industry, among others. Cu<sub>x</sub>O<sub>y</sub> and Zr(O)N coatings were deposited as control samples, and these helped to disclose features and mechanisms in Cu-Zr(O)N films. The properties of films were assessed by SEM, EDS, XRD, AFM, and OCA measurements. Also, EIS and potentiodynamic polarization tests were performed in NaCl (3.5% wt.) solution for 24 h to simulate seawater exposure. XPS were done before and after corrosion test to establish the action of copper and its reactivity with artificial seawater. Also, copper ionic release was studied in seawater by ICP-OES. Bacterial inactivity, which is directly related with the antibiofouling surface potential, was evaluated by inhibition halo tests. The results revealed that Cu did not react with Zr(O)N directly during deposition process. This demonstrates the influence of Cu in Zr(O)N was promote gaps among film's columns boundaries, affecting other films properties such as surface energy, roughness, and wettability. Concerning corrosion tests, Cu deteriorates the Zr(O)N chemical strength against seawater. On the other hand, ZrON film exhibited an antibacterial action with the Cu inclusion, though after the chemical activation. The Zr(O)N films were unable to capture enough oxygen to oxides the copper during the deposition process. With the additional availability of oxygen from the chemical activation process, the Cu inside the ZrON film, can react to form CuO. The Cu<sup>2+</sup> ions releasing had no influence on the antibacterial film action. The presence of CuO was vital to get an antibacterial comportment. The obtained results shown the first sight of the potential of Cu-Zr(O)N films to be applied as a unique coating to avoid biofouling and corrosion under seawater exposure and replace TBT paint in maritime components.

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