

Topical Symposium on Sustainable Surface Engineering Room Town & Country D - Session TS4-1-ThM

Coatings and Surfaces for Thermoelectrical Energy Conversion and (Photo)electrocatalysis I

Moderators: Clio Azina, RWTH Aachen University, Germany, Carlos Tavares, University of Minho, Portugal

8:00am **TS4-1-ThM-1 Inorganic Thermoelectric Films for Harvesting Waste Heat Near Room Temperature: Opportunities and Challenges, Rui Shu (rui.shu@liu.se)**, Linköping University, Sweden, USA **INVITED**

The abundance of untapped low-grade heat presents a significant opportunity for sustainable energy solutions. However, current recovery technologies often fall short due to their lack of cost-effectiveness. Effectively harnessing this waste heat holds the promise of fostering a more sustainable society. Notably, inorganic thermoelectric bulk materials have shown promise in capturing waste heat near room temperature, offering potential applications in energy harvesting and thermal cooling.

However, challenges persist, including limited thermoelectric performance when transitioning to thin films and hindered large-scale implementation due to the scarcity and costliness of elemental Te. Adapting high-performance inorganic bulk thermoelectric materials into consistent thin films remains a significant obstacle.

This presentation explores the opportunities and challenges associated with using inorganic thermoelectric films for waste heat recovery at room temperature. Recent research advancements focusing on materials like Mg_3Bi_2 and transition-metal-nitride-based thin films are highlighted. Notably, these materials circumvent the use of scarce and brittle tellurium, with Mg_3Bi_2 -based substitutes showing promise as alternatives to commercially used Bi_2Te_3 . Our study aims to pave the way for the practical utilization of highly efficient inorganic thermoelectric films in energy harvesting applications.

8:40am **TS4-1-ThM-3 Retaining Crystallinity of as-deposited Thermoelectric Fe_2VAl -based Thin Films Grown from DCMS and HiPIMS, Ludwig Enzberger (ludwig.enzberger@tuwien.ac.at)**, TU Wien, Institute of Materials Science and Technology, Austria; S. Kolozsvari, Plansee SE, Germany; P. Mayrhofer, TU Wien, Institute of Materials Science and Technology, Austria

Thermoelectric materials have gained much attention in recent years due to their ability to directly interconvert electrical and thermal energy via the Seebeck/Peltier effect. This can be used to convert waste heat back into usable electrical energy, making thermoelectrics very interesting materials in a world with increasing demand for renewable and efficient utilisation of energy. The efficiency of this process is generally dependent on three parameters - the thermopower S , the electrical conductivity σ and the thermal conductivity λ - which are represented together in the dimensionless Figure of Merit ZT .

Among thermoelectrics, Heusler and half-Heusler materials have shown to be promising candidates, due to their high Seebeck coefficients at room temperature and their high electrical conductivity, while generally higher thermal conductivity is often a drawback in thermoelectric performance.

In 2019, Hinterleitner *et al.* managed to produce magnetron sputtered thin films of $bcc-Fe_2V_{0.8}W_{0.2}Al$ with an exceptionally high Seebeck coefficient, Power Factor and Figure of Merit, but the samples needed to be heat-treated for one week to crystallize from their initially amorphous state.

In this work, we present Fe_2VAl -based full-Heusler thin films retaining their crystallinity during sputter deposition. By tuning deposition temperature, bias potential and pulse on-time we managed to fabricate films of $Fe_2V_{0.8}W_{0.2}Al$ in a W-type bcc-structure on silicon and austenite substrates. These films were analysed using XRD, EDX, electron microscopy and by measurement of transport data (resistivity, Seebeck coefficient). Thermal conductivity of the films was derived from measurements of thermoreflectance and specific heat capacity.

9:00am **TS4-1-ThM-4 Thermoelectrical Investigations of TaC-Based Superlattice Protective Coatings, Barbara Schmid (barbara.schmid@tuwien.ac.at)**, S. Lin, T. Schöngruber, N. Koutná, TU Wien, Institute of Materials Science and Technology, Austria; S. Bühler-Paschen, TU Wien, Austria; L. Mitterhuber, Materials Center Leoben, Austria; D. Ingerle, TU Wien, Austria; S. Kolozsvari, Plansee SE, Germany; P. Mayrhofer, TU Wien, Institute of Materials Science and Technology, Austria

Transition metal carbides (TMC) and nitrides (TMN) feature high melting points up to 4000 °C and superior thermal stability and are therefore regarded as ultra high temperature ceramics (UHTC). Those materials are well-established in the realm of protective coatings. Superlattice architecture can impact a plethora of different material characteristics such as mechanical, chemical and electric properties. Inspired by preliminary DFT high-throughput screenings, we developed TiC/TaC and TiN/TaC superlattice coatings exhibiting bilayer periods between 2 and 50 nm via non-reactive DC magnetron sputtering. Those materials exhibit high hardness and fracture toughness and are therefore immaculate choices as protective coatings. These superlattice materials also exhibit decent thermal stability and electrical conductivity, which motivated us to calculate their thermoelectrical properties via DFT using BoltzTraP and VASP. The experimentally determined Seebeck coefficients exhibit a significant bilayer-period-dependence. By conducting Time Domain Thermoreflectance investigations, we also derived their figure of merit (ZT) values.

9:20am **TS4-1-ThM-5 Exploring the Potential and Challenges of Solution-Processed Inorganic Thermoelectric Materials, M. Ibáñez**, Institute of Science and Technology Austria (ISTA), Austria; Tobias Kleinhanns (Tobias.Kleinhanns@ist.ac.at), Institute of Science and Technology, Austria **INVITED**

Over the past few years, there has been a significant surge in interest surrounding solution-based techniques due to their cost-effectiveness and scalability in the production of high-performance thermoelectric materials. This approach involves the synthesis of particles in a solution, followed by their purification and thermal processing to yield the desired dense polycrystalline material. In contrast to traditional methods, solution-based syntheses offer the ability to manipulate particle characteristics, including size, shape, crystal structure, composition, and surface chemistry, to an unprecedented degree. This fine-tuned control over powder properties opens up distinct opportunities for crafting thermoelectric materials with meticulously controlled microstructural attributes.

In this presentation, our primary focus will be on Ag_2Se , an important thermoelectric material for harnessing thermoelectricity at or near room temperature, an area where the selection of high-performing materials is currently limited. While Ag_2Se shows great promise, the main problems are the large discrepancy in the reported thermoelectric properties and difficulties in replicating its exceptional performance. These discrepancies often stem from the intricate control of defects within the material, such as vacancies, interstitial atoms, dislocations, grain boundaries, and precipitates.

We will show that our solution-based synthesis method enables precise defect control, especially avoiding fluctuations in stoichiometry. Additionally, we will illustrate how we can fine-tune microstructural defects, including strain, dislocations, and grain boundary density, leveraging the characteristic phase transition of Ag_2Se during the sintering process. Our results will highlight that besides stoichiometry, the microstructure is crucial for tuning Ag_2Se transport properties and how this control can be provided by our novel synthetic route. Furthermore, we will highlight the sustainability and scalability of our approach, where solvents can be recycled and energy consumption minimized, contributing to a more environmentally friendly production process.

10:20am **TS4-1-ThM-8 3D Nanoscale Spatial Imaging of Doped ZnO and TiO_2 Transparent Thermoelectric Thin Films, J. Ribeiro, F. Correia, H. Faria**, University of Minho, Portugal; A. Welle, T. Boll, Karlsruhe Institute of Technology (KIT), Germany; Carlos Jose Tavares (ctavares@fisica.uminho.pt), University of Minho, Portugal

Transparent thermoelectric materials are a promising technology for touchscreen displays and solar cell applications, rendering a sustainable powering of the device. In order to enhance the thermoelectric performance, the material must have a high Seebeck coefficient and high electrical but low thermal conductivity. This work focuses on the effect of

doping on ZnO and TiO₂-based thin films deposited by DC magnetron sputtering. The properties of the films depend strongly on the dopant type and concentration. On the one hand, it has been documented that Al and Ga doping can improve the electrical properties in ZnO, as can Nb doping in TiO₂. On the other hand, introducing heavier elements (such as Bi, Sb or Nb) into the metal-oxide matrix hinders phonon-mediated heat conduction, and consequently reduces the thermal conductivity, which is a promising approach. Atom Probe Tomography and Time-of-Flight Secondary Ion Mass Spectrometry are powerful tools to determine the composition and inherent homogeneity within the thin films, as well as to investigate the cation and anion segregations to interfaces and grain boundaries. For the ZnO-based films, Al and Ga dopants are homogeneously distributed within the crystals, with the exception of Bi, which is not incorporated in the ZnO wurtzite cell and segregates at the grain boundaries and at the triple junctions. Thus, Bi contributes to grain boundary scattering of phonons and contributes less to the reduction of the thermal conductivity, in comparison to Ga-, Al-, and Sb-doping in ZnO. For the Sb-doped ZnO thin films, a larger Zn content was registered at the triple junctions of the grain boundary. As for the Nb-doped TiO₂ thin films, Nb is homogeneously distributed into the TiO₂ matrix and no grain boundaries are visible. However, the composition varies depending on the deposition conditions, where the Nb content inside the film changes depending on the oxygen content controlled through the reactive O₂ flow during the sputtering depositions.

10:40am **TS4-1-ThM-9 Ni-B-based Polyalloy Electrocatalyst Coatings Deposited by MSPVD for Efficient Oxygen Evolution Reaction**, *Kubilay Sahin (ahink@uni.coventry.ac.uk)*, Institute for Clean Growth and Future Mobility, Coventry University, Department of Metallurgy, University of Mons (UMONS), UK; *V. Vitry*, Department of Metallurgy, University of Mons (UMONS), 23 Place du Parc, B-7000 Mons, Belgium., Belgium; *A. Cobley*, Institute for Clean Growth and Future Mobility, Coventry University, Priory St, Coventry, CV1 5FB, UK.; *J. Graves*, *G. Pourian Azar*, Institute for Clean Growth and Future Mobility, Coventry University, UK

Molecular hydrogen has been considered as one of the best green energy sources due to its high energy density¹. Water splitting is a highly promising approach to generate molecular hydrogen without any damage to environmental health. However, electrocatalyst materials, which are generally expensive noble elements, are required to complete the reactions efficiently and sustainably. Due to their excellent features such as low cost, high abundance, high corrosion resistance and durability, catalytic activity, and good synergistic effect with other elements, Nickel-based electrocatalysts have been reported as one of the most valuable alternatives to expensive noble metals². Electrodeposition, electroless plating, hydrothermal deposition, and physical vapour deposition are some of the used techniques to synthesize Nickel-based electrocatalysts. Electroless nickel-boron plating is a remarkably beneficial technique to produce Ni-B coatings with outstanding features such as hardness, wear resistance, and corrosion resistance. In recent studies, Ni-B coatings have also demonstrated encouraging catalytic activity with remarkable stability³. While Ni-B coatings have been extensively studied for various applications, there is not enough research on their catalytic applications. Furthermore, there is no existing literature regarding the deposition of Ni-B coatings utilising a technique other than electrodeposition or electroless plating. However, the Magnetron Sputtering Physical Vapour Deposition (MSPVD) technique has the capability of producing Ni-B coatings with porous and tunable structures together with easy alloyability to further improve the electrochemical performance.

The current study is designed to investigate the electrocatalytic performance of Ni-B-based polyalloy coatings produced by MSPVD. Polyalloy coatings were co-deposited using a Ni-B and transition metal targets such as Fe, Co, and Mo. The coatings were deposited at different deposition parameters such as chamber pressure, substrate type and different chemical compositions. The electrocatalytic performance of the coatings was compared to see the effect of boron, alloying elements, morphology and crystal structure for the Oxygen Evolution Reaction. Superior features like low overpotentials, high stabilities, and high surface areas were obtained after the electrochemical analyses such as Linear sweep voltammetry, cyclic voltammetry, chronoamperometry and electrochemical impedance spectroscopy under alkaline conditions. The results showed promising efficiencies and stabilities for highly tunable, cost-effective Ni-B-based electrocatalyst coatings.

11:00am **TS4-1-ThM-10 Role of Grain Boundaries in the Stress Corrosion Cracking of Nanoporous Gold Thin Films**, *Aparna Saksena (a.saksena@mpie.de)*, Max-Planck Institut für Eisenforschung GmbH, Germany; *A. El-Zoka*, Imperial College London, UK; *A. Saxena*, *E. Hatipoglu*, Max-Planck Institut für Eisenforschung GmbH, Germany; *J. Schneider*, RWTH Aachen University, Germany; *B. Gault*, Max-Planck Institut für Eisenforschung GmbH, Germany

For its potential as catalyst, nanoporous gold (NPG) prepared through dealloying of bulk alloys has been extensively investigated. NPG thin films can offer ease of handling and better tunability of the chemistry and microstructure of the nanoporous structure. They are however prone to intergranular cracking during dealloying, limiting their stability and potential applications. Here, we systematically investigate the grain boundaries in Au₂₈Ag₇₂ (± 2 at.%) thin films. We observe that a sample synthesized at 400 °C is 2.5 times less prone to cracking than one synthesized at RT. This correlates with a higher density of coincident site lattice (CSL) grain boundaries, especially coherent Σ3, increased, which appear resistant to cracking. Nanoscale compositional analysis of random high-angle grain boundaries reveals prominent Ag enrichment up to 77 at.%, whereas Σ3 coherent twin boundaries show a Au enrichment of up to 30 at.%. The misorientation and the chemistry of grain boundaries have a crucial role in their dealloying behavior, which controls the cracking. Our results provide a target for optimizing the longevity application of NPG thin films for possible applications.

11:20am **TS4-1-ThM-11 Metal/Oxide Heterostructure as Hydrogen Evolution Reaction Electrocatalyst**, *Thi Y Phung Nguyen (phungnguyen0398@gmail.com)*, National Cheng Kung University (NCKU), Taiwan, Viet Nam; *J. Ting*, National Cheng Kung University (NCKU), Taiwan

In response to the growing demand for sustainable energy sources, there has been a concerted effort to develop efficient electrocatalysts for the hydrogen evolution reaction (HER). Previous researches indicate the need to improve consistent efficiency and stability at high current densities (≥ 500 mA/cm²) over 100 hours. In this study, we have investigated metal/oxide heterostructure HER electrocatalysts. The heterostructure is noble-metal free and synthesized using a hydrothermal method followed by thermal reduction for controlling the alloy/oxide ratio. Various characterization techniques, including scanning electron microscopy, transmission electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, and in-situ Raman spectroscopy are used to examine the obtained heterostructures. Furthermore, the electrochemical performance is evaluated using linear sweep voltammetry, electrochemical impedance spectroscopy, cyclic voltammetry, and electrochemical specific surface area analyses. We demonstrate highly efficient and stable heterostructure HER electrocatalyst. This work contributes to cost-effective and sustainable hydrogen production, with significant implications for renewable energy integration.

11:40am **TS4-1-ThM-12 Copper-Based Porous Surfaces for Electrocatalytic CO₂ Reduction**, *Maria José Lima (mjlima@fisica.uminho.pt)*, *S. Viana*, University of Minho, Portugal; *J. Castro*, *S. Carvalho*, University of Coimbra, Portugal

The United Nations (UN) has identified carbon dioxide (CO₂) as a greenhouse gas (GHG) that is present in the atmosphere as an environmental issue in Goal 13 for climate action.

Decreased CO₂ emissions and participation in a circular economy are crucial to achieving these goals. To include CO₂ in a circular economy, capture and electroreduction of CO₂ into long-chain hydrocarbons or alcohols (C₂+) can be the solution. From a material perspective, copper-based catalysts are active and selective cathodes capable of producing hydrocarbons, increasing the Faradaic efficiency of the CO₂:RR to C₂+ molecules.

Enhancing electrochemical active sites can be an additional strategy to improve CO₂:RR. Different strategies can produce porous electrodes, thus increasing the electrochemical active surface area (ESCA) and the CO₂-catalyst interaction. One technique that produces porous materials is the anodization process, an electrochemical process capable of producing a thin oxide layer at the metallic surface.

In this work, we systematically optimized the anodization parameters of metallic copper (Cu) to develop Cu_xO_y porous electrodes. Different anodization parameters were studied, such as voltage, time, electrolyte concentration, and distance between the anode and the cathode.

Materials characterization was made by SEM, EDS, and XRD, where it was possible to observe a higher porosity and Cu₂O crystalline phase obtained using 0.1 M of K₂CO₃ and applying 25 V for 15 min. In fact, lower applied

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potentials show a compact surface with cracks. Increasing the potential to 25 V favors the formation of hollow tubes, whereas a further increase to 50 V results in structure compaction.

Electrochemical analyses, such as linear sweep voltammetry and cyclic voltammetry, will be shown to discuss the involved redox reactions of organic and inorganic species. The ESCA calculation of each electrode material will permit an understanding of how it correlates with morphology.

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