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 pioneeredZnO: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.[1,2]To realize flexible and photo-switchable magnets, we have combined nanoscale layers of the rarest trivalent iron oxide polymorph ε-Fe_2O_3 exhibiting giant coercive field values with azobenzene layers undergoing reversible trans-cis-trans isomerization reactions upon successive UV and visible light irradiations.[3,4] 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_2, for the targeted lithium ethyl carbonate films.[5] Finally, for the Li-organic microbattery application, our new active-material arsenal comprises various intriguing intercalated-type layered Li-organic materialsthat experience minimal changes in crystal structure upon the electrochemical Li^+-ion intercalation.[6]

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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_2 by deliberately introducing defects can enhance its properties to a great extent, while a cationic doping of TiO_2 has been documented to improve its electrical conductivity [2]. This work reports the production and characterization of optically transparent Nb-doped TiO_2 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 $W \cdot m^{-1} \cdot K^{-1}$ and a maximum absolute Seebeck coefficient of 223 $mV \cdot K^{-1}$. The resulting maximum thermoelectric power factor is 60 $mW \cdot K^{-2} \cdot m^{-1}$ 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. Andritschky,* 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_3-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^{3+} and Bi^{3+} ions in the ZnO wurtzite structure produces a distinct effect on the thin film microstructure. The substitution of Zn^{2+} ions by smaller Ga^{3+} ions introduces a static disorder to the thin film structure, which is evidenced by an increase in the mean-square relative displacements (MSRD) σ^2(Zn-O) and σ^2 (Zn-Zn). At the same time, large Bi^{3+} 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_x (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.

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