Fundamentals and Technology of Multifunctional Materials and Devices

Room Royal Palm 1-3 - Session C3-2

Thin Films for Energy-related Applications

Moderators: Jim Partridge, RMIT University, Martin Allen, University of Canterbury

1:30pm **C3-2-1 P-type Cu_2O Modified by NiO_x as a Photocathode for Efficient Hydrogen Production in Photoelectrochemical Water Splitting**, ***Ching Lin***, *J Ting,* National Cheng Kung University, Taiwan

First, Cu_2O/NiO_x nanoparticles were synthesized using a hydrothermal method with CuCl and NiO as precursors. Second, Cu_2O/NiO_x nanoparticles were made into a thin film by spin coating method. The NiO_x modified the surface of Cu_2O particles seem to be efficient way as a protective layer in order to enhance the efficiency of H_2 production. The core-shell structure of Cu_2O/ NiO_x nanoparticles were examined with a SEM. Due to an appropriate band energy structure, the photogenerated electrons from Cu_2O are easily transferred to the conduction band of NiO. Therefore, the possibility of the electrons and holes recombination is considerably reduced. XPS spectra revealed that the surface species of NiO_x is a mixture of NiO and $Ni(OH)_2$, which enhances charge separation in photoexcited Cu_2O. The role of NiO and $Ni(OH)_2$ is similar and both were suggested to act as a trap for photoelectrons, therefore retarding charge recombination. We demonstrate that a Cu_2O-based electrode for H_2 evolution can be prepared free of noble metals and we show its utilization in a PEC water splitting cell made solely from earth abundant elements.

1:50pm **C3-2-2 High Temperature Resistant Molybdenum Thin Film Metal Mesh Electrode as Replacement for ITO**, ***Niklas Bönninghoff***, National Taiwan University of Science and Technology, Taiwan

Indium tin oxide (ITO) films are still, despite their disadvantages, the main choice for thin film optoelectronic applications. Indium however is steadily increasing in price. One alternative to ITO is the use of a metal mesh. The most important parameters of a meshed thin film for optoelectronic devices to control are transparency, conductivity and compatibility with industrial processes (e.g. high temperature). Generally, the smaller the mesh dimensions (line width and pitch), the better the device, but the higher the costs.

Two different metal mesh patterns (line grid and hexagonal grid) have been fabricated on a glass substrate, using I-line photolithography to create a pattern on a photoresist, which was used to mask the substrate during DC magnetron sputter deposition. The material used is 5N pure Molybdenum. The deposition parameters (working pressure, DC power and substrate temperature) were chosen to gain a high conductivity film (measured by four-point probe), while still achieving acceptable adhesion (measured by scotch tape test), by usage of a bilayer. The grid pitch has been optimized for a specific device with an area of 15 mm^2.

The mesh's line thickness is 2 microns. The pitch is 300 microns for the line grid and 360 microns for the hexagonal grid, which results in a calculated transparency of 97% and 98% respectively. The transparency however decreases with increasing device size.

In conclusion, a metal mesh with good conductivity, high temperature resistance and an excellent transparency has been fabricated.

2:10pm **C3-2-3 Piezoelectric and Pyroelectric Materials and Systems for Energy Harvesting**, ***Chris Bowen***, *M Xie, Y Zhang, D Zabek, J Roscow,* University of Bath, UK **INVITED**

The continuing need for reduced power requirements for small electronic components, such as wireless sensor networks, has prompted renewed interest in recent years for energy harvesting technologies capable of capturing energy from ambient vibrations and heat. This presentation provides an overview of piezoelectric harvesting system along with the closely related sub-classes of pyroelectrics and ferroelectrics [1,2]. These properties are, in many cases, present in the same material, providing the intriguing prospect of a material that can harvest energy from multiple sources including vibration and thermal fluctuations [3-5].

Examples of modelling and experimental investigations of porous materials for harvesting are discussed including novel freeze cast and sandwich layer structures are described. Pyroelectric layers for thermal harvesting are also described with the use of patterned electrodes to enhance thermal fluctuations and the potential to use pyroelectric charge for water splitting discussed.

[1] C. R. Bowen, H. A. Kim, P. M. Weaver and S. Dunn, Piezoelectric and ferroelectric materials and structures for energy harvesting applications, Energy and Environmental Science, 7, 25-44 (2014)

[2] CR Bowen, J Taylor, E LeBoulbar, D Zabek, A Chauhan, R Vaish, Pyroelectric materials and devices for energy harvesting applications, Energy & Environmental Science 7 (12), 3836-3856 (2014)

[3] J Zhang, C Wang, C Bowen, Piezoelectric effects and electromechanical theories at the nanoscale, Nanoscale 6 (22), 13314-13327 (2014)

[4] C. R. Bowen and M. H. Arafa, Energy Harvesting Technologies for Tire Pressure Monitoring Systems, Advanced Energy Materials 5, 1401787 (2015)

[5] J. Roscow, Y.Zhang, C.R.Bowen et al., Porous ferroelectrics for energy harvesting applications, *Euro. Phys. J. Special Topics.,* 224, 2949-2966 (2015)

2:50pm **C3-2-5 Ion-assisted Growth of Compound Thin Films for Energy-related Applications**, ***Tomas Kubart***, *A Aijaz,* Uppsala University, Sweden

Energy-related applications generally require high quality thin film materials. In many cases, low growth temperatures are desired while the performance is still critical. In this contribution, low temperature ion-assisted growth of compound thin films is discussed using piezoelectric AlN and thermochromic VO_2 as examples.

Using ions instead of neutral atoms provides means for additional energy input which can be readily controlled by externally applied electric fields. We use High Power Impulse Magnetron Sputtering (HiPIMS), a sputtering technique in which a very high ionization degree of the material is achieved due to the pulsed mode operation of the discharge. Low frequency operation with a duty cycle of about 1% is typically used, which leads to two orders of magnitude higher electron densities and corresponding increase in the ionization of the deposition flux.

For piezoelectric AlN films, we have demonstrated a significant enhancement of the AlN texture by using the HiPIMS process [1]. Already at room temperature, films with good texture and low FWHM values of the rocking curve were grown directly on silicon without any seed layer. This is attributed to the high flux of low energy Al and N ions formed in HiPIMS as well as high dissociation of N_2 in the dense HiPIMS plasma. Such films are suitable for electroacoustic devices, microelectromechanical systems, or energy harvesters.

The deposition temperature is also an important factor for thermochromic materials. Vanadium dioxide thin films provide means for controlling solar energy throughput and can be used for energy-saving applications such as smart windows. At present, however, the deployment of VO_2 in thermochromic devices is limited by the high growth temperature, typically above 450°C. Using HiPIMS, we have reduced the growth temperature to 300°C [2]. We have varied the ion energy and found and optimum at 100 eV. Strategies to further reduce the deposition temperature are discussed.

References

[1] M.A. Moreira, T. Torndahl, I. Katardjiev, T. Kubart, Journal of Vacuum Science & Technology A 33 (2015) 021518.

[2] A. Aijaz, Y.-X. Ji, J. Montero, G.A. Niklasson, C.G. Granqvist, T. Kubart, Solar Energy Materials and Solar Cells 149 (2016) 137-144.

3:10pm **C3-2-6 Growth and Characterization of Thin Film $CaMnO_3$ and $CaMn_xNb_{1-x}O_3$ Thermoelectrics**, ***Erik Ekström***, *B Paul, F Eriksson, P Eklund,* Linköping University, IFM, Sweden

Thermoelectrics show great promise as waste heat harvesters in power plants, cars and other applications. This places demands on their physical and chemical properties. They should be non-toxic, have a high conversion efficiency and thermally stable.

In this work, thermoelectric thin film $CaMnO_3$ and $CaMn_xNb_{1-x}O$ perovskite oxides on Al_2O_3 (0001), (1-100) and (1-102) have been investigated. The films were deposited by magnetron sputtering followed by annealing at 800 °C in oxygen [1]. Nb was introduced by co-sputtering. The structural properties of the films were assessed using X-ray diffraction (XRD) by performing q-2q scans and by plan-view scanning electron microscopy studies.

Isothermal annealing was performed in high vacuum using an in situ XRD furnace to study the phase evolution up to 1100 °C. The annealing was done in 100 °C steps, doing a measurement for each step. The structure of the film after the 3 h post deposition heat treatment was orthorhombic

$CaMnO_3$. This structure remained stable up to 700 °C, while above 800 °C it decomposed into cubic $Ca_xMn_{1-x}O$. The cubic structure is stable at 800 °C, but at 900 °C the phase changes to orthorhombic MnO_2 and Ca rich cubic $Ca_xMn_{1-x}O$. Additionally, the structure decomposed into a multitude of phases at 1100 °C. X-ray diffraction was also recorded while cooling down, showing that the structure obtained at 1100 °C remained to room temperature.

Scanning electron microscopy revealed that by changing the Ca composition in the rangepower on the Ca magnetron changes the surface structure of the films. A low Ca content resulted in Mn-rich nano-inclusions which are also visible in the XRD. Increasing the Ca content reduces the amount of inclusions and at the ideal composition they disappear. When increasing the Ca content the grain size decreases laterally as seen in SEM and decreases vertically as indicated by an increasing peak width.

Four point probe measurements at room temperature show a decrease in resistivity for the alloyed samples compared to the un-alloyed ones and it is also observed that substrate orientation influences the resistivity. The lowest resistivity for un-alloyed films is 1.70 Ωcm, 1.80 Ωcm and 0.69 Ωcm for (0001), (1-100) and (1-102) orientation, respectively. Having an Nb content of x = 3 results in the lowest resistivity of 0.46 Ωcm, 0.06 Ωcm and 0.10 Ωcm for (0001), (1-100) and (1-102) orientation, respectively. The reduction of resistivity is due to an increase in carrier concentration which has been observed in other studies [2].

1 Paul et al Advanced Electronic Materials **1,** 1400022 (2015).

2Xu et al Solid State Ionics **171,** 147 (2004).

3:30pm **C3-2-7 3D-Painted Solid Oxide Fuel Cells: A New Approach to Functional Multi-Ceramic Construct Fabrication***, **Nicholas Geisendorfer**, A Jakus, H Wang, Z Gao, S Barnett, R Shah,* Northwestern University, USA

The fabrication and assembly of solid oxide fuel cell (SOFC) components into an integrated structure, including both support and functional layers, remains one of the primary challenges preventing the widespread adoption of SOFCs as an energy conversion technology. We present an efficient and highly scalable multi-material process for fabricating SOFCs using a combination of 3D-Painting (a room-temperature, liquid extrusion-based 3D-printing process) and dip-coating of particle-laden, liquid-based 3D-inks. 3D-printing is used to sequentially deposit anode and cathode functional layer materials, nickel oxide-yttria stabilized zirconia (NiO-YSZ) and lanthanum strontium manganite (LSM), respectively, without the need to alter printing parameters, allowing unprecedented control over gas channel geometries. Depositing layers thinner than 100 µm using 3D-printing is impractical, so these inks, designed for 3D-printing, are repurposed for the production of mechanically robust, controllably thick, multi-material films via dip-coating to be used as YSZ electrolytes and strontium lanthanum titanate (SLT)/LSM interconnect bilayers. The inks used for both 3D-printing and dip-coating are synthesized through simple, room-temperature mixing of a combination of organic solvents, a biomedical elastomer binder (~10-40 vol.%) and powders of interest (~60-90 vol.%). Vol % powder controls shrinkage and porosity during firing; tailoring the powder vol % for each ink is vital to preventing warping and cracking during cell co-firing and to ensure optimal performance of each component. Fully assembled fuel cell structures are co-fired in air at 1250°C for 4 hours. The microstructural and electrochemical characteristics of fired cells are analyzed and compared with cells produced entirely using tape-casting techniques. We demonstrate that this technique is highly scalable and useful for fabricating monolithic, planar SOFCs of various sizes without the need for cumbersome support materials.

3:50pm **C3-2-8 Nanoengineering Periodically Structured SiCu Thin Film Anodes for Rechargeable LIBs***, **Billur Deniz Polat Karahan**, B Bilici,* Istanbul Technical University, Turkey*; O Eryilmaz,* Argonne National Laboratory, USA*; K Amine,* Argonne National Laboratory, USA, United States of America*; O Keles,* Istanbul Technical University, Turkey

In the quest for a radically better lithium-ion battery, a promising direction is suggested so-called “silicon (Si) composite” anodes, in which the negative electrode contains a higher proportion of Si with another material. In the current technology, while the Si composite electrodes have the potential to have far higher energy density, long cycle life and high reversibility are still not satisfactorily provided due to intrinsic properties of Si such as low electrical conductivity and high volumetric changes upon cycling.

Therefore, in this work, to create electron conduction pathway in the electrode and to increase the ductility of the film 10%at. Cu atoms are co-deposited with Si. Then to induce homogeneously distributed interspaces in the electrode structured composite thin film has been engineered by glancing angle electron beam deposition (GLAD) method. This process enables to deposit coatings of any materials without a need of binders or any conductive additives. Plus, various structures from nanocolumns to helices might be deposited by optimizing the evaporation rate of source materials, the incident angle and the azimuthal rotation rate of the substrate.

An innovative approach involving adaptation of ion assistance to GLAD has been also proposed in this study. The well adherent composite nanostructures are expected to provide large reaction area with Li, facile stress relaxation (to prevent electrode pulverization or delamination), effective electrical contacts with the substrate and short Li diffusion distances.

To evaluate the electrochemical performances of the structured composite films, two samples have been deposited on Cu collector with different evaporation rates: quartz crystal microbalances of Cu and Si show 0.4-4 Å/s and 0.9-10 Å/s for Samples 1 and 2, respectively. The morphological analyses show that depending on the evaporation rates of sources the structure of the film changes which affects their performances in cycling.

4:10pm **C3-2-9 A Mesoporous CuAlO2 Hole Transport Layer for Perovskite Solar Cell***, **Wei-Jie Sun**, J Ting, P Chen,* National Cheng Kung University, Taiwan

Mesoporous CuAlO2 (CAO) has been investigated for use as a hole transport layer in perovskite based solar cells (PSC) having a p-i-n heterojunctions configuration. CuAlO2 nanopowders (NPs) was first synthesized using a sol-gel method with Cu(NO3)2 and Al(NO3)3 as the precursors. The obtained CuAlO2 NPs were spinning-coated onto indium-tin oxide substrate to form a hole transport layer. The obtained CuAlO2 NPs and layers were examined for the material characteristics, in particular, photoelectrical properties. Effects of the synthesis conditions of these characteristics are addressed and discussed. PSCs having a CuAlO2 transport layer were fabricated. The cell performance was evaluated to demonstrate the advantages of using CuAlO2 as a hole transport layer.

4:30pm **C3-2-10 Fabrication of Hybrid Perovskite Solar Cells based on Low Temperature Solution Process***, **Tzung-Wei Tsai**, Y Yu, C Teng,* Ming Chi University of Technology, Taiwan

Organic–inorganic perovskite solar cells have recently emerged at the forefront of photovoltaics research due to its dual electron and hole mobility. Organo-metal halide perovskites were composed of an ABX3 (e.g. $CH_3NH_3PbI_3$) structure in which A represents a cation, B a divalent metal cation (e.g. Pb^{2-}) and X a halide (e.g. F, Cl, Br, I). We used two different materials such titanium dioxide (TiO_2) as the perovskite electron transport layer of the solar cell in this study. The titanium dioxide colloid was prepared by using a ball-milling process with the 50 micrometer zirconia balls in a SiC pot for 8~10h. Then, the titanium dioxide powders were prepared after annealing. The effects of annealing temperature on the properties of perovskite thin film were also investigated. The organic–inorganic perovskite solar cells with structure ITO/TiO2/Perovskite/Spiro-OMeTAD/Ag were fabricated. The best performance of the prepared solar cells had a photo conversion efficiency of 6.4%, J_{sc} of 12.11 mA/cm^2, V_{oc} of 0.96V, and fill factor of 0.56, respectively.

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