Energy Harvesting & Storage
Room Naupaka Salon 6-7 - Session EH-ThM

Batteries

Moderator: Ludvik Martinu, Polytechnique Montréal

8:20am **EH-ThM-2 Real-Time TEM Observation of Electrochemistry and Failure in Battery Materials**, ***Reza Shahbazian-Yassar,*** University of Illinois at Chicago

Electrodes in rechargeable batteries undergo complex electrochemically-driven phase transformations upon driving Li ions into their structure. Such phase transitions in turn affect the reversibility and stability of the battery. This presentation gives an overview of the PI's research program on in-situ transmission electron microscopy (TEM) of ceramic battery materials. In-situ TEM has been shown to be a very powerful technique in shedding light to some of the mysteries in electrochemical performance of new materials. Various anode materials including SnO_2 and MnO_2 were subjected to lithiation process and the transport of Li ions was visualized within their atomic structure. For SnO_2 nanowires, it was observed that the Li ion transport results in local strain development preferably along (200) or (020) plans and [001] crystallographic directions. The lithiation behavior in the presence of twin boundary defects was completely different compared to pristine state with no twin boundary defect. We showed that twin boundaries in general provide a more accessible pathway for Li ion transport. Anisotropic plastic deformation was also observed along [010] directions of MnO_2 nanowires. Sb-based intermetallics which have been proved to be promising anode materials for Li-ion batteries, are also capable of storing of sodium ions. We investigated the microstructural changes and phase evolution of such intermetallic nanowires using in-situ TEM. These alloys also exhibit a new cubic alloying phase that form by intermixing of the ABAB atomic ordering in hexagonal lithiated phase due to Li inclusion in their lattices. Our results indicate that the reaction between these alloys and sodium proceeds through a different pathway during the first compared to the subsequent cycles.

8:40am **EH-ThM-3 Reactive Ion Beam Etching of Piezoelectric ScAlN and LiTaO3 for RF Filter Applications**, ***Robinson James***, *Y Pilloux, H Hegde,* Plasma Therm

Etching piezoelectric Scandium Aluminum Nitride (ScAlN) and lithium tantalate (LiTaO3) films with controllable profile angle and very smooth surface is required for next generation Bulk Acoustic Wave (BAW) and Thin Film Surface Acoustic Wave (TF SAW) RF filter applications respectively. First part of the paper reports the facile etching of ScAlN with 15% Scandium concentration by Reactive Ion Beam Etching (RIBE) with very smooth surface of less than 5 nm average roughness and controllable profile angle between 60 to 80 degrees. Recent studies indicate that incorporating high concentration Sc into AlN improves the piezoelectric response of the device by five times and the band width of RF filters also improved. However, etching highly Sc doped ScAlN using traditional RIE and ICP based methods are extremely difficult. Moreover RIE and ICP etching methods exhibit low etch rate and results in rough surfaces when Sc concentration increases more than ~ 8% in ScAlN. Reactive Gas/Ar based RIBE processes were developed with highly controllable profile angle from 60 to 80 degrees, improved etch rate (~ 36 nm/min) and selectivity to photoresist mask (0.7:1), in comparison to conventional IBE. ScAlN selectivity to photoresist was improved significantly when using Reactive Gas/Ar compared to pure Ar based etching. Second part of the paper reports the optimization of LiTaO3 etching with either RIBE or IBE. LiTaO3 etch rate and selectivity were optimized by varying the Reactive gas/ Ar ratio and wafer tilt. LiTaO3 etch rate of ~ 80 nm/min, 1.25: 1 selectivity to PR and a very smooth surface with roughness of ~ 2 nm was achieved. Further improvements in etch rate, selectivity are under investigation. Etching ScAlN and LiTaO3 were characterized using scanning electron microscope (SEM) and white light interferometer (WLI) was used for measuring surface roughness. By varying wafer tilt, Reactive Gas/Ar ratio, beam voltage and current we achieved desired profile angle, etch rate, selectivity and smooth surface. This research has significant importance in fabricating ScAlN based BAW and LiTaO3 based TF SAW RF filters for next generation mobile and wireless applications.

9:00am **EH-ThM-4 Lead-free Epitaxial Ferroelectric Heterostructures for Energy Storage and Harvesting Applications**, ***Amrit Sharma,*** Center for Materials Research, Norfolk State University

Fast and rapid depletion of natural resources such as fossil fuel and coal is driving researchers to focus continuously on the development of new technologies and exotic materials having high energy density and efficiency for both harvesting and storage of clean and green energy. In United States, nearly 68% of the primary energy produced is wasted as a heat each year. Energy harvesting for low power electronic devices using ferroelectric materials is one of the emerging areas of research because they possess excellent piezoelectric and pyroelectric coefficients. These materials are unique as they only sense time dependent temperature change to generate electric power. Temperature change can be obtained through different ambient sources such as waste-heat, solar radiation etc. We have grown lead free $BaZr_{0.2}Ti_{0.8}O_3$ (BZT)/ $Ba_{0.7}Ca_{0.3}TiO_3$ (BCT) multi-layer hetero structures and studied the structural, dielectric, ferroelectric, pyroelectric and energy density characteristics. The BZT/BCT multiplayer epitaxial hetero-structures were grown on La Sr MnO (LSMO) buffered SrTiO (STO) single crystal substrate by optimized pulsed laser deposition technique. The ferroelectric phase transitions have been probed above room temperature with relaxor behavior. These heterostructures show large polarization change and high energy density characteristics due to interface effect even at low applied field and small temperature fluctuation which may be useful for both high energy storage density and thermal harvesting applications.

9:20am **EH-ThM-5 Direct Electrodeposition of High-Performance Li-ion Battery Electrodes**, ***Paul Braun,*** University of Illinois at Urbana-Champaign, USA **INVITED**

Lithium-ion battery electrodes are nearly universally formed via tape casting of a slurry containing a mixture of active material, binder, and conductive carbon. However, the electrochemical and mechanical properties of slurry cast electrodes are often limited by weak interconnections between particles and between the particles and the substrate. We suggest conformal electrodeposition of high-quality electrode materials would provide opportunities to enhance battery performance (energy density, power density, and flexibility) and broaden the scope of available electrode form factors (size, shape, porosity, and 3D integration). We have now made considerable advances in the direct electrodeposition at modest temperatures of high performance tin-based Li-ion anodes and $LiCoO_2$, $NaCoO_2$, $LiMn_2O_4$, and Al-doped $LiCoO_2$-based Li-ion cathodes. The electrolytically active materials were formed either as solid films, or where significant volume changes upon cycling are present, via a templating process, as a 3D mesostructured film. The capacities are near-theoretical, and in the case of the electroplated oxides, the crystallinities and electrochemical capacities of the oxides are comparable to powders synthesized at much higher temperatures (700 ~ 1000°C). The electrodeposition method significantly broadens the scope of battery form factors and functionalities, enabling a variety of highly desirable battery properties including microbatteries, and high energy, high power, and flexible designs.

Author Index

Bold page numbers indicate presenter

— B —
Braun, P: EH-ThM-5, **1**
— H —
Hegde, H: EH-ThM-3, 1
— J —
James, R: EH-ThM-3, **1**
— P —
Pilloux, Y: EH-ThM-3, 1
— S —
Shahbazian-Yassar, R: EH-ThM-2, **1**
Sharma, A: EH-ThM-4, **1**