

## Thin Film Division

### Room A105 - Session TF2+AP+SE+SS-WeM

#### Controlling Microstructure and Accessing Non-Equilibrium Phases in Thin Films

**Moderators:** Robert Grubbs, IMEC Belgium, Richard Vanfleet, Brigham Young University

11:00am **TF2+AP+SE+SS-WeM-10 Stabilizing Polar Polymorphs of Scandium Ferrite for Photovoltaics**, *M. Frye, Lauren Garten*, Georgia Institute of Technology **INVITED**

Metastability is no longer synonymous with unstable or unattainable, but further work is needed to enable the next generation of electronics and photovoltaics. In this talk I will discuss the development of a stabilization route for the P63cm phase of ScFeO<sub>3</sub> through precursor control and interface engineering. The P63cm phase has potential for lead-free piezoelectric, photo-ferroic, and ferroelectric applications. Unfortunately, this phase is in competition with four other known polymorphs that are similar in structure and energy and there is not a well matched epitaxial substrate. So we took a different approach by controlling the atomic layering of the precursor structure and the deposition timing to stabilize the P63cm phase under conditions that previously lead to the ground state. The film structure is verified by transmission electronic microscopy and x-ray diffraction. Ab initio calculations confirm that layered growth stabilizes the metastable phase and highlights the importance of the variable oxidation state of iron, the high activation energy against diffusion, and the surface termination of the substrate in designing a stabilization approach. This work highlights routes to access similar polymorphs on an array of different substrates, opening up new materials and new device architectures.

11:40am **TF2+AP+SE+SS-WeM-12 The Role of Thermal Vibrational Disorder in the Structural Phase Transition of VO<sub>2</sub> Probed by Raman Spectroscopy**, *Aminat Oyiza Suleiman*, Institut National de la Recherche Scientifique, Canada; *S. Mansouri*, Institut National de la Recherche Scientifique, Canada; *N. Émond*, Massachusetts Institute of Technology, Canada; *T. Bégin, J. Margot*, Université de Montréal, Canada; *C. Mohamed*, National de la Recherche Scientifique, Canada

Vanadium dioxide (VO<sub>2</sub>) is a typical correlated electron material which exhibits a first-order metal-insulator transition (MIT) at a near-room temperature of about 340 K. Upon heating, VO<sub>2</sub> switches from an insulating monoclinic phase (M1 or M2) to a metallic tetragonal rutile phase (R). The mechanism behind the MIT in VO<sub>2</sub> is still controversial: Is it a structure driven Peierls transition mechanism or a Mott transition where strong electron-electron correlations drive charge localization and collapse the lattice symmetry? By directly comparing the electrical and lattice-dynamic properties of VO<sub>2</sub>, useful information about the MIT/SPT in VO<sub>2</sub> can be obtained.

Herein, we therefore present a detailed Raman study of undoped (M1) and Cr-doped (M2) VO<sub>2</sub> thin films as a function of temperature. The studied VO<sub>2</sub> films with different thicknesses are deposited on c- and r-sapphire substrates. While their structural properties and morphology are examined by XRD and AFM techniques, respectively, Raman measurements are correlated to four-point probe resistivity measurements, giving an insight into the coupling between VO<sub>2</sub> structural phase (SP) and MI transitions. By distinctively combining the Raman data with information from reported EXAFS data, a relationship between the Raman intensities and the mean Debye-Waller factors ( $\sigma^2$ : the mean-square relative displacements) is established. The temperature dependence of the vanadium dimers Waller factor ( $\sigma_R^2(V-V)$ ), as calculated from the Raman intensity, was found to follow the temperature profile of the  $\sigma_{EXAFS}^2(V-V)$  obtained from the reported EXAFS data. These findings provide an evidence on the critical role of the thermal vibrational disorder in VO<sub>2</sub> phase transitions, demonstrating that by correlating Raman data with EXAFS analysis, both lattice and electronic structural dynamics can be probed.

12:00pm **TF2+AP+SE+SS-WeM-13 Interplay of Lattice Distortion and Electronic Structure in Metastable Brookite TiO<sub>2</sub>**, *Pritha Biswas*, Oregon State University; *M. Choi, K. Koirala, M. Bowden, L. Strange*, Pacific Northwest National Laboratory; *H. Zhou*, Argonne National Laboratory; *J. Tate*, Oregon State University; *Y. Du, T. Kaspar, D. Li, P. Sushko*, Pacific Northwest National Laboratory

Controlling the coupling between lattice distortions and electronic properties is one of the promising routes toward enhancing the performance of materials used in energy technologies, such as photocatalysis, photovoltaics, and energy storage. Oxide semiconductors that exhibit polymorphism represent a convenient class of systems to study this coupling by investigating the effect of external stimuli on transition pathways between polymorphs. Among the oxide semiconductors, earth-abundant TiO<sub>2</sub> exists in several polymorphic forms, including rutile, anatase, and brookite, with distinctly different structural symmetries. Compared to the common rutile and anatase polymorphs, metastable brookite TiO<sub>2</sub> is the least studied one due to the difficulties associated with its synthesis in a phase pure form. At the same time, mechanisms of its transformation to the more stable anatase and rutile polymorphs are promising to provide a rich insight into the relationships between the character of the lattice deformations, defect content, and electronic structure. We have developed a recipe for phase selective TiO<sub>2</sub> polymorph formation, where tuning of oxygen vacancy concentration drives the crystallization of amorphous TiO<sub>2</sub> thin films towards a specific polymorphic structure. In this study, thermal treatment was used to control the evolution of as-deposited, sputtered amorphous TiO<sub>2</sub> thin films towards the brookite lattice. The crystallinity and phase purity of the resulting structures were investigated by lab-based grazing incidence XRD, synchrotron XRD, and transmission electron microscopy. The dependence of structural variations present in the sample on the details of the annealing treatments was evaluated using Rietveld refinement analysis. X-ray photoelectron spectroscopy (XPS), confocal Raman spectroscopy, and high-resolution transmission electron microscopy (HRTEM) were used to understand the effect of local deformation on the electronic structure of brookite. We found a correlation between the degree of lattice parameter deviation, shifts of the Raman vibrational modes, and the position of the brookite valence band. The effect of these lattice distortions at the atomic scale on the photocatalytic activity of brookite will be discussed.

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