Thin Films Division
Room 316 - Session TF3+MS-WeM

Simulations and Machine Learning Applications for Thin Films

Moderator: Angel Yanguas-Gil, Argonne National Lab

11:00am **TF3+MS-WeM-10 What an Experimentalist Needs from Computational Materials Science (Including Machine Learning) – Studies in Semiconductor Processing and Metrology***, Rafael Jaramillo,* MIT **INVITED**

I will present a view on computational materials science and machine learning, from the perspective of an experimentalist working primarily on compound semiconductors. I will first present uses of computation within my own group. These include computational thermodynamics to guide materials design and synthesis, atomistic modeling of deep levels in semiconductors, finite-element modeling of mechanical and acoustic phenomena, and machine learning models of optical metrology to improve materials discovery and microelectronics manufacturing. In many cases, our computations are limited by challenges that are beyond our expertise as experimentalists. With these challenges in mind, I will then highlight several outstanding needs from the computational science community, illustrated by ongoing research projects:

(1) We pioneered the synthesis of chalcogenide perovskite thin films by gas-source molecular beam epitaxy (MBE). Our successes pose questions of process optimization, particularly related to connections between precursor selection, processing temperature, and crystal quality. There is a need for multi-scale modeling of crystallization at solid-vapor interfaces, including highly-non-thermodynamic conditions such as plasma processing, to de-risk the development of manufacturing-compatible deposition methods.

(2) We discovered that chalcogenide perovskites have the strongest low-frequency dielectric response among VIS-NIR semiconductors. The only other family of semiconductors with comparable dielectric response are halide perovskites. We also discovered that chalcogenide perovskites have, in common with their halide cousins, slow non-radiative excited-state recombination. These observations pose the question of how, exactly, soft phonon spectra affect Schottky-Read-Hall (SRH) recombination rates. Polarons may be relevant. Exact calculations of SRH capture cross sections for particular materials, coupled to a Fröhlich model of electron-phonon interactions, would shed light on these open questions in solar cell materials physics.

(3) Native oxidation of chalcogenide layered and two-dimensional semiconductors (notably including transition metal dichalcogenides, TMDs) needs to be well understood for microelectronics fabrication, and presents unique opportunities for ultra-scaled logic and memory devices. We have used theory and experiment to describe TMD native oxidation processes. However, reactive molecular dynamics simulations combined with advanced data analytics are needed to accelerate progress towards device technology that would be advanced and manufacturable.

11:40am **TF3+MS-WeM-12 Computational Analysis and Design of Precursors for ALD and CVD of Metals***, S. Elliott, A. Chandrasekaran, S. Tiwari, A. Fonari, D. Giesen,* Schrödinger*; **Casey Brock**,* Schrödinger

Understanding a deposition process depends to a large extent on understanding the chemical and physical properties of the precursor molecules. Volatility, reactivity and thermal stability are the three key precursor characteristics needed for chemical vapor deposition (CVD) and atomic layer deposition (ALD), although properties such as melting point, viscosity, synthetic cost and nucleation behavior are also important. Quantifying these characteristics for known precursors can help trouble-shoot an existing process, and designing novel precursors with optimum characteristics is a robust way to improve a process. We illustrate these points on the example of beta-diketonate-based Pd(II) precursors for the deposition of palladium metal. The aim is to find the optimum ligand combination in both homoleptic and heteroleptic complexes.

Precursor volatility often dictates the lower limits of temperature and pressure at which a process can be run. We use a machine-learning model of volatility to see the effect of ligand identity on this property. Specifically, cyclopentadienyl and allyl ligands are found to lower the evaporation temperature to <100 degrees C in the 1-5 Torr pressure range. The other end of the process window is determined by thermal decomposition. For Pd(hfac)2 and formalin experiments show a narrow ALD window between 200 and 230°C, followed by decomposition at higher temperatures. We therefore use density functional theory (DFT) to assess the thermal stability of candidate complexes. We exclude those heteroleptic complexes that DFT predicts to be impossible to synthesize because of ligand exchange. We find that the poor stability of thd complexes can be overcome by switching to fluorinated ligands. We also present quick and approximate measures of the reactivity towards reduction to metallic Pd, whether by CVD or ALD, and compare these with more time-consuming DFT calculations of the surface chemistry.

The computational tools for these properties have been automated to the level where they can be integrated into a team's R&D workflow for routinely assessing current precursors or discussing new ones, so that lists of molecules can be generated and ranked according to the key characteristics for a particular process and application area.

12:00pm **TF3+MS-WeM-13 Dopant-selective Atomic Layer Deposition of Metals for Bottom-up Nanoelectronics***, Nishant Deshmukh,* Georgia Institute of Technology, USA*; D. Aziz, A. Brummer, M. Filler,* Georgia Institute of Technology

The entirely bottom-up fabrication of nanoelectronic devices promises electronics with an unprecedented combination of performance and scalability. A long-standing challenge has been the bottom-up fabrication of nanoscale features on nanoscale semiconductors. Bottom-up methods can create suitable semiconductor structures, but top-down methods are needed for other important device features, such as contacts or gate stacks. For example, Si nanowire pn diodes can be readily fabricated with the vapor-liquid-solid (VLS) growth method; however, lithography is still necessary to define contacts to the p and n segments. Here, we report a dopant-selective atomic layer deposition (ALD) process to deposit metal thin films suitable for constructing fully bottom-up pn diodes. Briefly, undecylenic acid, a bifunctional self-assembled monolayer (SAM), is blanket attached to the Si surface. Exposure to KOH removes it from the surface of heavily-doped (~10^{20} cm^{-3}) p-type and n-type Si while it remains on lightly-doped (~10^{14} cm^{-3}) Si. Subsequent Pt ALD yields deposition only on the heavily-doped Si. X-ray photoelectron spectroscopy (XPS) shows that the ratio of Pt deposition on the heavily-doped to lightly-doped Si can be as high as 130. We suspect that this high selectivity results from undecylenic acid attaching to lightly-doped Si through its alkene group, and to heavily-doped Si through its carboxylic acid group. This difference in attachment results in KOH being able to remove undecylenic acid only from the heavily-doped Si, thus allowing Pt to deposit.

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