Wednesday, May 13
Facility-specific Workshops

APS Workshop 8
In situ X-ray Characterization of Microstructure during Manufacture

Location: Bldg. 401, Room A5000

Organizers: Don Brown and John Carpenter (Los Alamos National Laboratory)

Recent years have seen tremendous advances in the ability to monitor materials microstructure, in both spatial and temporal resolution, at third-generation synchrotron x-ray sources. Concurrently, in an effort to rebuild manufacturing capability in the United States toward lower cost, more efficient production, "advanced manufacturing" techniques are being developed. Because of this timing, a marriage between manufacturing and characterization techniques is possible. Indeed, because of the particularly simple geometry of many of the characterization techniques, such as high-energy diffraction, small angle scattering, and radiography, it is natural to explore *in situ* x-ray characterization measurements during manufacturing.

The purpose of this workshop is to bring together both researchers who have already initiated *in situ* manufacturing programs and those who could benefit from such work. The intent is to draw scientists interested in either materials (including polymers, electronics, metals, and ceramics) or manufacturing processes (from traditional casting to simple heat treatments to the most modern advanced manufacture techniques) or both. The session will consist of several talks to sample the state of the field, followed by discussion of instrumentation needs (e.g., power or water needs) necessary to enable continued advancement of capabilities.

8:30 – 8:40 Welcome & Introductory Remarks

8:40 – 9:20 Amy Clarke (Los Alamos National Laboratory)
Multi-scale Prediction and Control of Metal Alloy Solidification Dynamics to Achieve Advanced Manufacturing

9:20 – 10:00 Jon Emery (Argonne National Laboratory)
A Portable, Modular Reactor for in situ *Synchrotron X-ray Investigation of Atomic Layer Deposition Processes*

10:00 – 10:30 Break

10:30 – 11:10 Ruipeng Li (Cornell University)
Evolution of Organic Thin Film Transistors Controlled by Blade-coating Method

11:10 – 11:50 Aaron Stebner (Colorado School of Mines)
A Novel in situ *Planar Biaxial Experiment*

11:50 Wrap Up

WK8

Multi-scale Prediction and Control of Metal Alloy Solidification Dynamics to Achieve Advanced Manufacturing

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Metal alloy solidification provides the first opportunity to affect structural, chemical, and defect evolution that dictates mechanical performance. Because solidification is multi-scale, we use state-of-the-art synchrotron x-ray and proton imaging to study solidification dynamics and inform advanced computational models. At the microscopic scale, we control thermal gradient and solid-liquid interface velocity during directional solidification to manipulate microstructural and chemical evolution. We quantitatively compare our x-ray imaging of a dilute aluminum-copper alloy with three-dimensional phase-field simulations. We are able to successfully predict microstructural characteristics with phase-field, but only if solutal convection — a key factor identified from our experiments — is incorporated. At the mesoscopic scale, the evolution of dendritic arrays in aluminum-based alloys is compared to dendritic needle network modeling. We also predict casting mold filling and local thermal gradients and solid-liquid interface velocities with continuum-scale process modeling to yield microstructural predictions within a casting. Our multi-scale integration of *in situ* characterization, modeling, and controlled processing will enable the prediction and control of microstructural evolution during solidification and advanced manufacturing of metal alloys.

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A Portable, Modular Reactor for *in situ* Synchrotron X-ray Investigation of Atomic Layer Deposition Processes

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Atomic layer deposition (ALD) is a thin film growth technique that utilizes alternate self-limiting surface reactions of vapor-phase precursors. The self-limiting growth process afforded by ALD provides unique advantages that are unavailable through other vapor-phase deposition methods. Specifically, ALD excels at: 1) growth of highly uniform and conformal films on large area substrates or high aspect ratio nanostructures and 2) precise and accurate control over thin film coating thickness (sub-nanometer) and composition (atomic-scale). These characteristics are particularly applicable in, for example, manufacturing processes for microelectronics, catalysis, and solar energy conversion and storage. Ultimately, to best understand ALD processes, *in situ* monitoring of structural and chemical properties during deposition is required. This is particularly important during the early stages of deposition — a growth regime that critically influences the films' morphology, crystallinity, and composition. Furthermore, as ALD is increasingly applied in ultrathin film applications (< 10 nm), the early-cycle ALD nucleation behavior, which often deviates from linear, steady-state growth modes, begins to dominate film properties and has critical influence for device applications.

Synchrotron characterization techniques provide some of the most powerful tools for the study of film structure and chemistry. The brilliance and tunability of the source at the APS allow us to access scattering and spectroscopic techniques unavailable with in-house laboratory setups and provide us with the opportunity to probe various ALD processes *in situ* starting at the very first deposition cycle. Here, we present the design and implementation of a portable ALD reactor that possesses a modular reactor scheme that enables simple experimental switchover between various characterization techniques and beamlines. As first examples, we present *in situ* results for 1) x-ray surface scattering and reflectivity measurements of epitaxial ALD of ZnO on sapphire, 2) grazing-incidence small angle scattering of ALD-related sequential infiltration of trimethylaluminum and water into PS-*b*-PMMA block copolymer lamellar thin films, and 3) grazing-incidence x-ray absorption spectroscopy of nucleation-regime growth of Er_2O_3. Importantly, the *in situ* ALD reactor is designed to serve a broad user base with diverse experimental requirements and objectives, and is available for use to researchers upon request.

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Evolution of Organic Thin Film Transistors Controlled by Blade-coating Method

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Solution-processed organic thin film transistors (OTFTs) have attracted considerable attention due to their high performance, low cost and easy manufacture. Achieving high performance requires that the microstructure and morphology of solution-cast thin films — that develops via nucleation and growth processes — exhibit a high degree of crystallinity with two-dimensional in-plane π-stacking, a low density of grain/domain boundaries exhibiting low crystallographic misorientation. Efforts to tune the microstructures and morphologies of solution-cast thin films have been hampered by the lack of understanding and control over the nucleation and growth of the thin films as the molecules cystallize from the solution phase under highly non-equilibrium conditions.

Here, we demonstrate *in situ* characterization of the structural variation of the organic transistors cast by the doctor-blading coating process through microbeam Grazing Incidence Wide Angle X-ray Scattering (GIWAXS) at D-line in CHESS, Cornell University. The crystallization process is monitored for various coating speeds to control the evolution from anisotropic to isotropic films, which provides a full characterization of the nucleation evolution in the doctor-blading coating process. The results reveal the relationship between the microstructure, morphology and the device performance and direct fine tuning of coating parameters for future roll-to-roll processing of organic electronics devices.

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A Novel *in situ* Planar Biaxial Experiment

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Advanced alloys, such as lightweight metals and shape memory alloys, are becoming increasingly important to the advancement of many industries. They often possess complex microstructures that result in anisotropic and asymmetric behaviors, often due to twinning and phase transformation of low symmetry crystal structures. Because of this, their three-dimensional mechanical properties and mechanisms of deformation cannot be fully understood through uniaxial characterization and processing studies. To elucidate these behaviors, a custom planar biaxial load frame capable of *in situ* x-ray and neutron diffraction experimentation has been built. The instrument was designed to study any arbitrary plane-stress loading condition, in addition to load path change events. Thus, the micromechanics of full plane stress yield and transformation loci may be quantified in addition to path-dependent behaviors. We will review the new experimental capabilities, sample designs, and discuss implications for improving processing models of advanced alloys.