# Coherent X-ray measurement of local step-flow propagation during polycrystalline organic semiconductor thin film growth with desorption

Randall L. Headrick [1*], Xiaozhi Zhang[1], Jeffrey G. Ulbrandt [1], Peco Myint [2], Andrei Fluerasu [4], Lutz Wiegart [4], Yugang Zhang[4], Christie Nelson[4], and Karl F. Ludwig, Jr. [2,3]
*Email: rheadrick@uvm.edu
[1] Department of Physics and Materials Science Program, University of Vermont, Burlington, Vermont 05405 USA
[2] Division of Materials Science and Engineering, Boston University, Boston, Massachusetts 02215 USA
[3] Department of Physics, Boston University, Boston, Massachusetts 02215 USA
[4]National Synchrotron Light Source II, Brookhaven National Lab, Upton, NY 11967, USA.

Step flow dynamics during vapor deposition is investigated in real-time by utilizing 9.65 keV X-rays from the CHX coherent hard X-ray synchrotron beamline at NSLS-II. X-ray Photon Correlation Spectroscopy (XPCS) is performed in the Grazing Incidence Small Angle X-ray Scattering (GISAXS) mode to achieve surface-sensitive conditions. Local step-flow during $C_{60}$ deposition on a graphene-coated surface is monitored through the observation of oscillatory correlations in the later stages of growth after crystalline mounds have formed. In conditions where mounds form, the surface is too rough to observe layer-by-layer oscillations. While this greatly limits the type of information that can be obtained from conventional experimental techniques that employ low-coherence X-rays or electrons, an important aspect of this work is that coherent X-rays do not average over complex structures, so that local phenomena such as step flow can be monitored in real time. The experimental results for $C_{60}$ thin film growth shows that the step-flow velocity is nonuniform, and we model the X-ray wavevector-dependent velocity as being a simple function of the step-edge terrace lengths above and below.[1] This model predicts that the steps become almost stationary near the edges of the mounds where the local terrace length is very small, and the average slope of the surface is large. The sensitivity to local step-flow is increased due to coherent heterodyne mixing of X-rays scattered from the average mound structure with those scattered from the step array. This work shows that the use of coherent X-ray scattering provides an approach to understand surface dynamics and fluctuations during crystal growth.

We have also extended these measurements to additional materials systems, including the growth of organic semiconductor small molecules with a lower symmetry than $C_{60}$, such as diindenoperylene (DIP) vapor deposition on thermally oxidized silicon surfaces. Results for DIP growth show that desorption of deposited species plays a role in determining the evolution of surface morphology during crystal growth when the desorption time constant is short compared to the time to diffuse to a defect site, step edge or kink. XPCS measurements reveal local step flow within mounds, and we find that there is a novel terrace-length-dependent behavior of the step edge dynamics. Numerical analysis based on a 1+1-dimensional model suggests that terrace-length dependent desorption of deposited ad-molecules is an essential cause of the step dynamics, and it influences the morphology evolution. At high temperatures, the grooves between the mounds tend to close up leading to nearly flat polycrystalline films.

[1] R.L. Headrick et al. Coherent X-ray measurement of step-flow propagation during growth on polycrystalline thin film surfaces. Nature Communications. 2019; 10: 2638.