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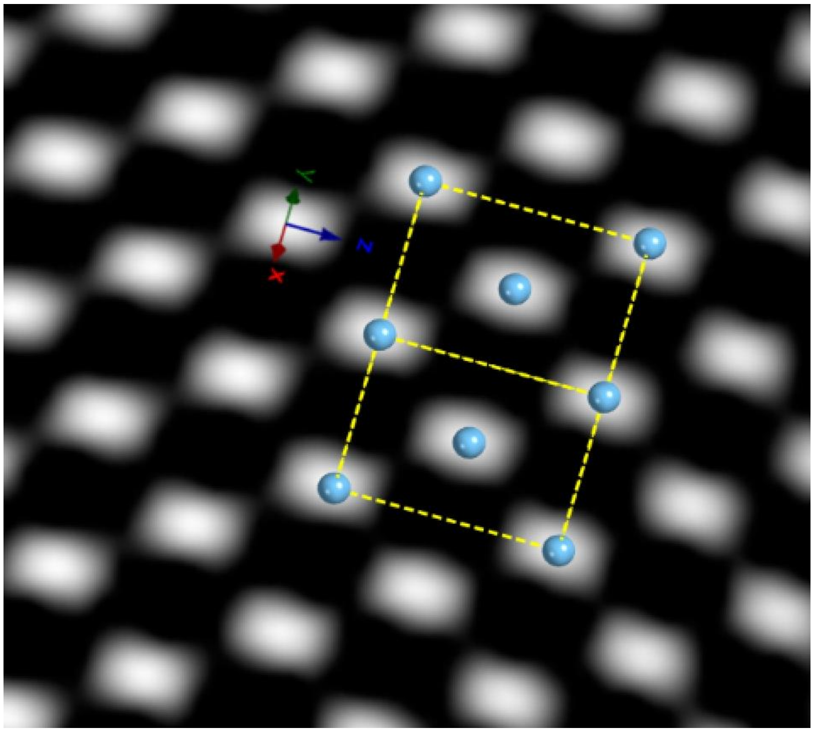
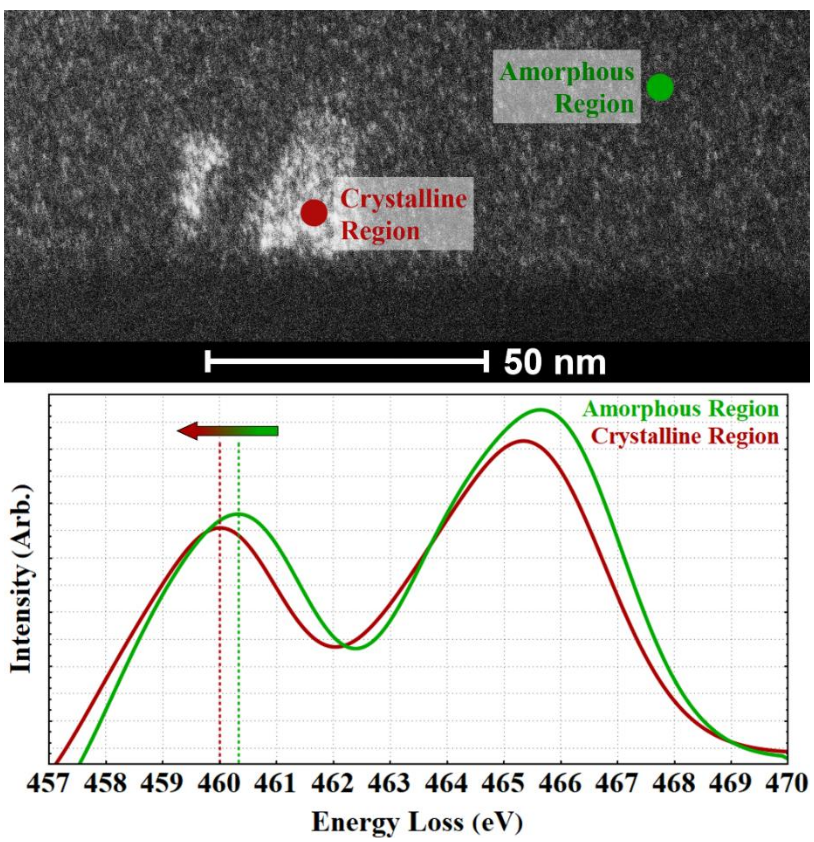
As mentioned in my initial proposal for the Goldstein Scholar award, we were interested in fully characterizing the chemical and crystallographic identity of nanocrystallites found in pulsed laser deposited amorphous titania thin films. Their unique presence in films that have been shown to preferentially crystallize the metastable brookite TiO_2 polymorph made them of particular interest. They were first discovered using the FEI Talos TEM at the Colorado School of Mines. However, the lack of EELS instrumentation for chemical analysis and aberration correction for high-resolution imaging halted the investigation of these crystalline regions. With the expertise of Jim LeBeau and Beth Dickey and the additional capabilities of the FEI Titan microscope at North Carolina State University, characterizing these nanocrystallites was made possible.

With TEM specimens prepped prior to traveling to NC State University, time spent on the microscope was maximized. One proposed theory is that these embedded nanocrystallites create a local coordination and/or strain environment due to oxygen deficiency that acts as a nucleation point for brookite crystals forming in the surrounding amorphous material. Acquisition of EELS spectra from the crystalline region as well as surrounding amorphous region displays a shift in the Ti-$L_{2,3}$ edges to lower energy loss, indicating a decrease in the average titanium valence state – a sign of increasing oxygen deficiency. Based on calculations from some of our collaborators, we expect the brookite structure to become increasingly more stable with respect to its polymorphic counterparts as the local O : Ti ratio decreases. Consistency between theory and experiment is always a great result!

Furthermore, a series of high-resolution STEM micrographs were acquired from an area of the as-deposited film that showed signs of crystallinity in the convergent beam electron diffraction pattern. A slight amount of crystallinity and lattice fringes were visible in these micrographs. Unfortunately, due to the size of these nanocrystalline regions (1-20 nm) in comparison to the thickness of the TEM specimen (60-100 nm), much of the crystalline area of interest was obscured by the surrounding amorphous material. However, Fourier filtering of these high-resolution STEM micrographs still clearly displayed the underlying atomic arrangement, which we found to agree strongly with the cubic TiO structure. This conclusion is consistent with indexing of selected area electron diffraction patterns acquired from the same crystalline regions. With guidance from those at NC State University, we also determined that preparing the TEM specimens by mechanical wedge polishing, as opposed to focused ion beam, would provide much thinner and higher quality cross-sections for direct imaging of the nanocrystallites. As a result, we spent some time in the specimen preparation lab at NC State so I could learn this process of TEM prep. This was perhaps one of the most worthwhile experiences during my time at NC State because I gained the tools and knowledge to continue the efforts of directly imaging the nanocrystallites when I return to the Colorado School of Mines.



Fourier filtered high-resolution STEM micrograph from crystalline region showing the overlaid cubic TiO unit cell.



Noticeable energy loss shift in the EELS spectrum from amorphous to crystalline regions.