Imaging Domain Structures in Nanocrystals using Coherent X-rays

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Domains play a central role in determining the electrical and mechanical properties of crystals and especially relevant in semiconductors. Our group has developed a powerful synchrotron-based X-ray method, Bragg Coherent Diffraction Imaging (BCDI), for imaging domains in three dimensions inside crystals with ~20nm resolution. The method relies on Shannon-oversampling of the diffraction pattern, so is restricted to looking at nanocrystals, which give strongly-fringed diffraction patterns. The oversampling allows a mathematically overdetermined solution of the crystallographic "phase problem", using iterative and Machine Learning algorithms adopted from the optics field [1].

This talk will introduce the BCDI method and demonstrate its utility in understanding the significant enhancement of the dielectric constant of Barium Titanate (BTO) in nanometer-sized grains. These lead-free dielectric materials perform three times better than macroscopic materials in Multilayer Ceramic Capacitors, which are commercially widespread. Various models have been proposed for the enhancement. Here we use BCDI to understand the "microstrain" defined by the classical Williamson-Hall analysis of neutron or X-ray powder diffraction data. While classical XRD shows the material is cubic, X-ray pair distribution function measurements clearly show the local structure is lower symmetry than cubic. 3D BCDI of selected nanocrystals, shown in Fig 1, reveals the existence of ~50 nm- sized domains, interpreted as tetragonal twins, which cause the average crystalline structure to appear cubic [1]. The ability of these twin boundaries to migrate under the influence of electric fields explains the dielectric anomaly for the nanocrystalline phase.

To understand the role of these domain boundaries in the electrical and mechanical properties of crystals, we have performed ultrafast time-resolved diffraction experiments at the X-ray Free-electron Laser (XFEL) facility in Pohang, Korea. By analyzing the evolution of the diffraction lineshape, we established separate roles for the electron and phonon contributions to the melting dynamics of polycrystalline gold and palladium thin films, concluding that melting is highly heterogeneous, commencing at the domain boundaries [2,3]. The localized electrical and mechanical properties are intimately connected with the short time-scales accessible in diffraction experiments using XFELs.

As a first attempt to apply this to semiconductor research, we the performed a pump-probe (PP) study of the (222) forbidden Bragg peak of Silicon [4]. A "device layer" silicon wafer-bonded to a silicon substrate was specially fabricated by MEMC with a Si(100) substrate and a 170 nm Si(100) film rotated at ~45 degrees for crystallographic isolation. We also looked at a second sample, RIE-etched down to 50 nm. The critical idea is that the 222 reflection sees exclusively the covalent bonds and not the symmetric core electrons, so is able to detect the separate contributions

of these electrons to melting. The XFEL experiment showed that the covalent bonds were extinguished on femtosecond time scales, while the electron-phonon coupled acoustic response was determined by the device thickness, in the mid picosecond time range. This behavior is consistent with the "two temperature model" of heat transfer from the electrons to the phonons in this system.

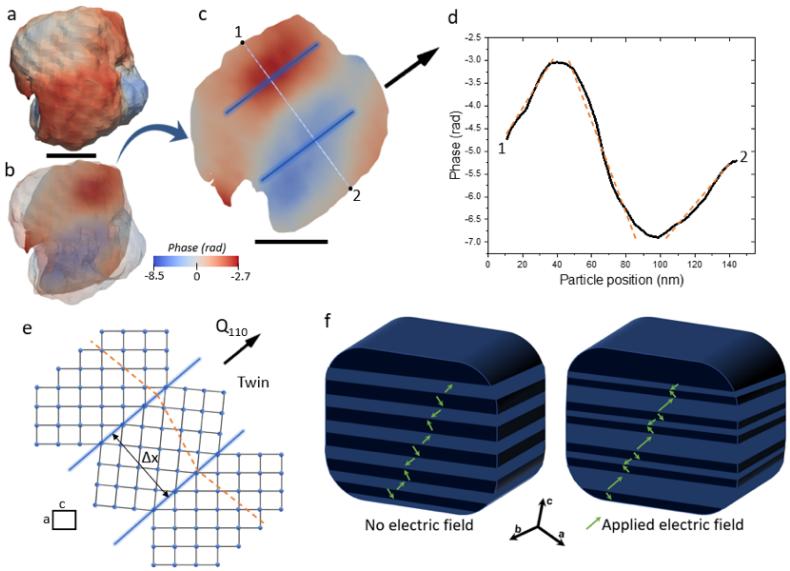

Figure 1. Twin domain model of $BaTiO_3$ (BTO) nanocrystal structure from the Bragg Coherent Diffraction Imaging analysis. (a-c) 3D reconstruction (d) Phase line plot along the white line shown in (c). (e) Schematic of twin domains with the c/a ratio exaggerated ten times (f) Schematic model of the dielectric response as field-induced migration the domain walls.

References

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