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Characterization of Sub-Bandgap Energy States in $CuIn_xGa_{(1-x)}Se_2$ and Transparent Conducting Oxides with Electron Energy-Loss Spectroscopy

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Information on bandgaps, defect states, and other electronic transitions, is essential for understanding performance and degradation of semiconductor materials and devices. High-resolution imaging using aberration-corrected scanning transmission electron microscopy (STEM) provides a path for elucidating the physical structure of defects and microstructure, but obtaining electronic structure information, particularly with respect to details of sub-bandgap energy states, has proved more challenging. While electron energy-loss spectroscopy (EELS) provides electronic structure information, limited accessible energy resolution and spurious low-loss signals, like those related to the generation of Cherenkov radiation, make extraction of such information in semiconductors significantly more complex. Nonetheless, recent progress in monochromation for STEM-EELS and extensive research in conditions for limiting Cherenkov radiation in semiconductors have helped position EELS as a viable technique for the characterization of sub-bandgap energy states [1]. In this contribution, we will present results from our research on the use of low-loss EELS for the characterization sub-bandgap defect states in $CuIn_{1-x}Ga_xSe_2$ (CIGS) photovoltaic materials and low energy (near-infrared, NIR) plasmons in multiple transparent conducting oxides (TCOs).

Spatially-resolved characterization of electrically active defects with energy levels within the bandgap is a significant challenge in CIGS (and many semiconductor materials, in general). Such defects can limit/prevent achievement of maximum device performance. The challenge is to be able to correlate these defect energy levels with specific structural features. To this end, we will present recent work on the energy- and spatially-resolved detection of sub-gap defect levels (carrier traps) within two different CIGS samples with two different trap energies (E_V + 0.43 eV and E_V + 0.56 eV). Low-loss EELS is shown to not only enable spatially-resolved detection of these states, but is also found to provide identical energies as those obtained using conventional and accurate deep level transient spectroscopy (DLTS). Furthermore, correlation between a novel scanned probe DLTS method and low-loss EELS show accurate correlation in both spatial localization and sub-gap energy position. Taken together, these results indicate the potential of high-resolution low-loss EELS for the accurate nanoscale characterization of important electronic structure details and properties that can be correlated with various other characterization techniques.

TCOs are known to exhibit sub-bandgap plasmon resonances, typically in the NIR spectral region, which can prove detrimental to their use in some photovoltaic applications [2]. To our knowledge, investigation of these low-energy plasmons via STEM-EELS has not previously been reported, most likely due to aforementioned limitations. Here, we demonstrate the identification of sub-bandgap signals in two different TCO materials commonly used in the fabrication of solar cells: Al-doped ZnO (AZO) and F-doped SnO (FTO). Using Hall-based carrier concentration measurements and optical absorption spectroscopy, plasmons in these materials were determined to reside at 0.49 eV and 0.76 eV, respectively. Low-loss EELS analysis reveals distinct signals in these materials at 0.49 eV and 0.71 eV, respectively, consistent with the external measurements. Interestingly, in the FTO sample, and additional, even stronger and broader peak at 0.50 eV is also observed, the origin of which is under further investigation.

References:

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