STEM Cathodoluminescence Mapping of Surface Traps in ZnO Nanowires.

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ZnO is an attractive material for electronic and optoelectronic applications due to its wide bandgap, large exciton binding energy, highly efficient emission, and chemical stability [1]. While a variety of different nanostructure morphologies have been reported, the large surface area-to-volume ratio means surface defects often deteriorate performance. Understanding the spatial distribution of surface traps and how to minimize their concentration is critical to engineering future nanoscale ZnO devices.

Unlike photoluminescence, cathodoluminescence (CL) can probe the emission properties of individual nanostructures, since CL uses a nanometer scale probe. SEM-CL has been used to study defect emission in individual ZnO structures previously, with studies showing, for example, green emission associated with Zn vacancies [2] and a blueshift in the near-band-edge emission with decreasing particle size[3]. However, the large interaction volume of the electron beam in an SEM limits the possible CL resolution. We have the potential to achieve higher spatial resolution by performing our CL measurements in a scanning transmission electron microscope.

Figure 1 shows an HRTEM image of an individual ZnO nanowire grown via gold-catalyzed molecular beam epitaxy. The nanowires are high quality, wurtzite structure, and have their growth axes along the 001 direction.

As shown in Figure 2, we use hyper-spectral STEM-CL imaging to show that defect emission in ZnO nanowires emanates from the surface. Figures 1b and 1c are constructed by integrating the CL intensity over the indicated energy range. A comparison of the resultant maps with the HAADF image (Figure 1a) reveals emission around 3.3 eV is strongest in the nanowire core, and emission between 2.0-3.0 eV is strongest on the edges of the nanowire. The 3.3 eV emission corresponds to the bandgap, and the broad emission between 2.0-3.0 eV is related to defects [1]. At the edges of the nanowire the electron beam-surface interaction is maximized; thus Figure 1c shows surface defects are responsible for the broad emission. Further analysis demonstrates that higher energy defect emission within the 2.0-3.0 eV range is more tightly confined to the surface.

Similar measurements on ZnO nanowires with ternary ZnMgO shells show no detectable emission below 3.0 eV. The lack of any defect emission indicates the ZnMgO shell passivates the surface, which represents a critical step towards improving conductivity in ZnO nanowires [4].

References:

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[2] F Fabbri *et al*, Scientific Reports **4** (2014), p. 5158.
[3] CW Chen *et al*, Applied Physics Letters **88** (2006), p. 241905.
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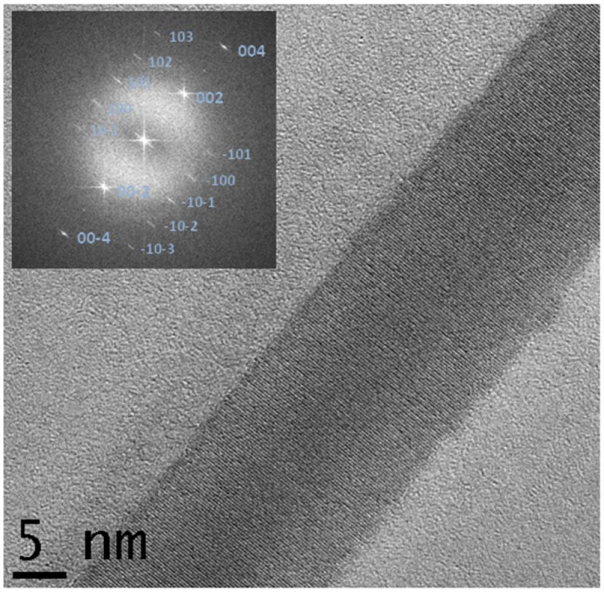

Figure 1. HRTEM image of a ZnO nanowire. The inset is the Fourier transform, where Bragg reflections are labeled with the *hkl* indices of wurtzite ZnO.

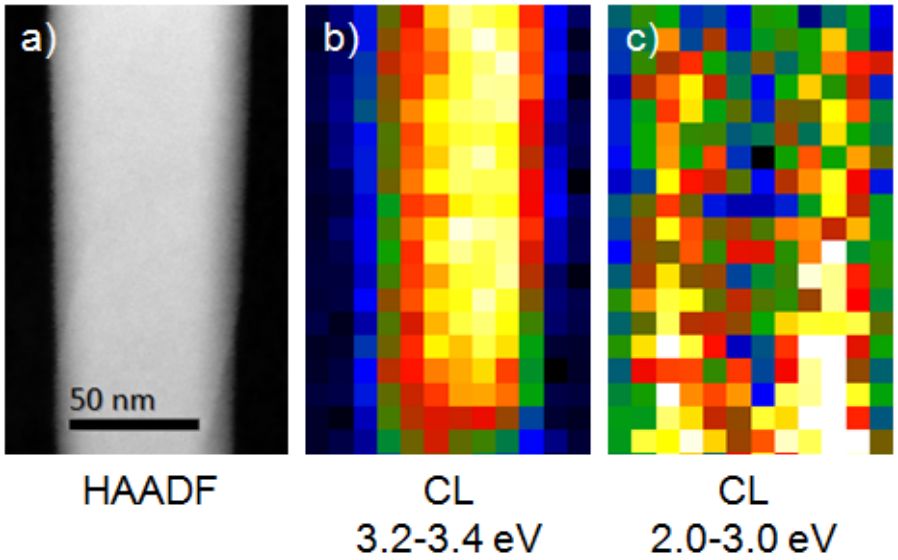

Figure 2. (a) HAADF image of a ZnO nanowire. (b) CL map of the 3.3 eV bandgap emission. (c) CL map of the 2.0-3.0 eV defect emission. Each pixel in a CL map contains a CL spectrum; (b) and (c) are generated by integrating the spectra over the indicated energies, and are normalized to each map's maximum intensity.