

Correlative STEM-Cathodoluminescence and Low-Loss EELS of Semiconducting Oxide Nano-Heterostructures for Resistive Gas-Sensing Applications

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Recent advances in resistive-type oxide gas sensors have been made primarily by the combination of multiple materials into nano-heterostructures that often show enhanced or unique properties compared to each pure material constituent [1,2]. It has been shown to be especially useful to use highly crystalline one-dimensional nanorods and nanowires decorated with either discrete oxide particles or a continuous coating generating a core-shell structure [3]. The operating principle of these sensors is simply measuring a change in resistance of a film deposited between two or more electrodes, which varies with the number of charge carriers accepted or donated between the surface and the nearby gas molecules. Two different resistance-dominating mechanisms exist in these sensors when the nanowires are deposited as a random network film [1]. In both mechanisms a depletion layer is formed at the surface and a larger depletion layer creates a higher resistance. The first mechanism considers the potential energy barrier at the interface between two nanowires that an electron must overcome to move through the film. The second mechanism considers electrons moving along the axis of a nanowire and the constriction of the cross-sectional area that does not lie in the depletion region. This can be equated to pushing a current through a smaller diameter wire, which increases the resistance. The second axial mechanism can be engineered through decoration or coating of, for example, p-type Cr₂O₃ onto an n-type SnO₂ nanowire. The p-n junctions created can affect this mechanism greatly, enhancing the sensor response and even making the material more selective toward specific gases and reducing cross-interference.

There has been little attempt to characterize the electronic interactions of the core and coating materials. Choi et al. have shown that the selection of a coating material with a higher or lower Fermi energy than the core in n-n and p-p junctions can make SnO₂ nanowires more selective to oxidizing or reducing gases, respectively [3,4]. Still, no direct evidence exists to show how well the band edges and defect states (shallow and deep levels) near the heterojunction interface agree with bulk measurements taken over a large sample area. Direct evidence of the electronic structure at a high spatial resolution would enhance the currently over-simplified models and allow better bottom-up design and materials selection.

In this study single-crystal n-type SnO₂ nanowires have been coated by magnetron sputtering and chemical vapor deposition with n-type TiO₂, WO₃, ZnO, Nb₂O₅, and MoO₃ as well as p-type Cr₂O₃, Co₃O₄ and NiO. Coating thickness and continuity is also varied. Each nano-heterostructure material is tested for gas-sensing performance toward several reducing and oxidizing gases as a random network film as well as single-nanowire sensors fabricated via Pt deposition in a dual-beam FIB. Initial results have shown that the random network film switches from n-type to p-type response when a thick enough p-type coating is applied. However, single nanowire measurements show only n-type behavior no matter the coating thickness. These effects are likely due to choice of conduction paths through the nanostructures. These sensor measurements form the basis for the study but direct characterization of the electronic structure can greatly aid in the explanation of the results.

A monochromated FEI Titan 80-300 S/TEM equipped with a Gatan Vulcan cathodoluminescence (CL) detector and a Gatan Tridiem EELS system has been used for high spatial resolution mapping of defect states and band edges, respectively. Knowledge of the defect states is essential when evaluating a material for gas sensing applications because the surface defects control the reaction with the gases. CL studies performed in the SEM of SnO₂ powders and nanowires assigned peaks to a number of different oxygen vacancies and structural defects but many aspects remain uncertain [5]. The SEM-CL spatial resolution results in sampling many particles or nanowires at once. In contrast, the STEM-CL system allows spatial mapping of CL spectra from specific nanowire facets that can be correlated to the surface defects on each crystalline plane. Furthermore, the electronic defect states present in the coating materials in nanocrystalline form can be mapped and compared to bulk materials. This information adds fundamental knowledge to the behavior of these materials as they exist in this widely-used nano-heterostructure form and helps refine the models of gas-surface reactions. As the CL data does not include full band-gap transitions, monochromated EELS was used to map the band edge onsets across the heterojunction interface in order to draw a more realistic heterojunction band diagram. These measurements can be correlated with the CL data to help predict charge carrier movement across the heterojunction interface and therefore the behavior of the depletion region between the two materials.

The single-nanowire electrical measurements show non-linear and sometimes asymmetric behavior and can be used to draw information about the built-in voltage at the heterojunction interface. I-V curves taken in different gas atmospheres and varied elevated temperatures also help to draw information about how the depletion region and built-in voltage behave during real sensor tests. The future challenge remains to correlate this high-resolution electronic structure information to the resulting gas sensor behavior [6].

References:

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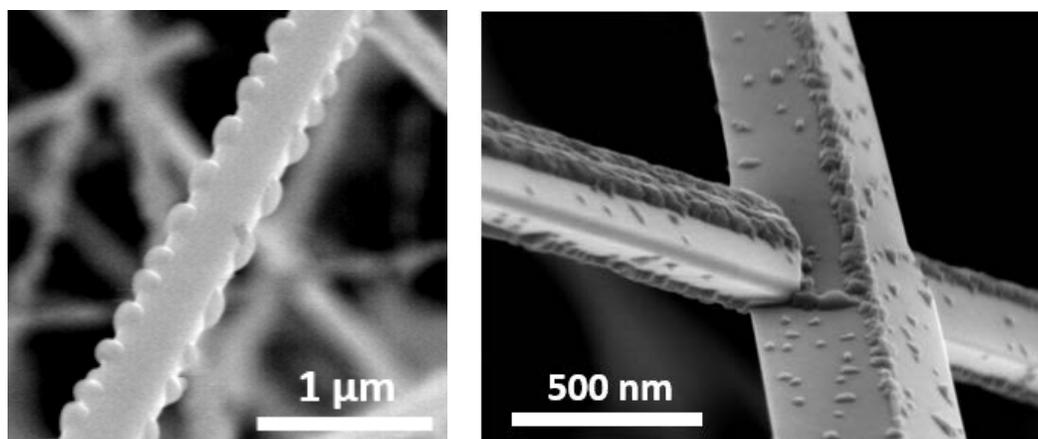


Figure 1. SEM images of nano-heterostructures characterized showing Co₃O₄ nanoislands decorating SnO₂ nanowires (left) and Cr₂O₃ nanoislands and strips decorating SnO₂ nanowires (right).