

XANES and XEOL Study of SnO₂ nanowires

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Introduction

Tin oxide is a wide bandgap (3.6 eV) semiconductor that is currently generating a lot of research interest since SnO₂ nanostructures can be easily produced by a wide variety of methods. It is currently being investigated for potential applications in battery [1] and fuel cell electrodes [2], photovoltaic cells [3], gas sensors [4], etc. Specific interest in SnO₂ nanowires owes mainly to unique surface properties including light emission and environmentally sensitive

resistivity. Although there has been considerable progress in these areas, many issues such as the effect of the substrate on the morphology and the origin of the luminescence are still not very well understood.

In this study we prepared and characterized the structure, electronic and optical properties of 1-dimensional SnO₂ nanostructures grown on various substrates using X-ray Excited Optical Luminescence (XEOL) and X-ray Absorption Near Edge Structures (XANES) at the Sn $M_{5,4}$ and O K absorption edges. XANES is a technique which probes the unoccupied electronic density of states above the Fermi level via electronic dipole transitions. XEOL is an X-ray photon-in, optical photon-out technique that monitors the optical response of light emitting materials excited by the absorption of X-ray photons, often across the absorption edge of interest.

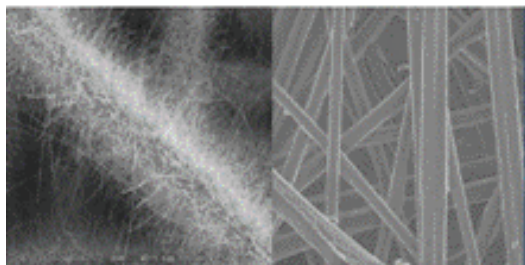


Figure 1: SnO₂ grown on a TiO₂(100) substrate.

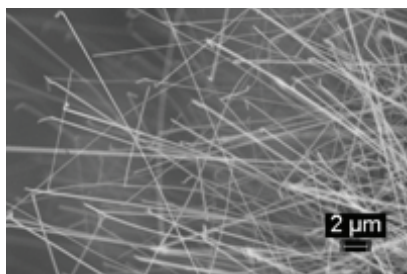


Figure 2: SEM of SnO₂ nanowires grown on carbon fibre

Experimental Results and Discussion

The nanowires were prepared by Chemical Vapor Deposition (CVD) of Sn powder at elevated temperature in a horizontal tube furnace under a mixture of flowing argon (carrier gas) and oxygen (reagent gas). A number of substrates including carbon paper, Si(100), TiO₂(100) and TiO₂(110) rutile were used. The resulting SnO₂ nanowires were examined using Scanning Electron Microscopy (SEM, LEO 1530) in the Nanofabrication Lab at the University of Western Ontario. X-ray absorption and XEOL experiments were conducted on the Spherical Grating Monochromator (SGM) beamline 11ID-1. As shown by the SEM (Figures 1 and 2) the as-grown nanowires are on the order of 100 nm in diameter and many tens of micrometres long. The nanowires are very straight and gold catalyst material can be seen at the tips. Those grown on single crystal substrates tend to exhibit a texture whereas on carbon paper SnO₂ NW tends to grow on the surface of the carbon fiber (Figure 2).

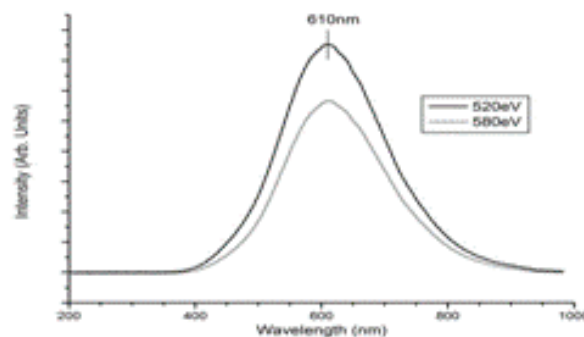


Figure 3: XEOL spectra of SnO₂ nanowires

Figure 3 shows the room temperature XEOL spectra of SnO₂ nanowires grown on TiO₂(100) substrate excited with soft X-ray photons below and above the oxygen

K-edge (520eV and 580 eV respectively). The spectra show a strong emission band from 400-900 nm, centered on 610 nm. No band-gap emission was observed at the expected 344 nm wavelength (3.6 eV). It has been shown that the near band-gap emission can be quenched by the surface or defect states in the band-gap [5]. Absent from these results, as well, is a second luminescence shoulder centered on 498 nm which has been previously been reported in SnO₂ nanoribbons. This could be due to the difference in morphology (wire vs. ribbon).

XANES spectra (Figure 4) were recorded across the Sn $M_{5,4}$ and O K -edges simultaneously in total electron yield (TEY), X-ray fluorescence yield (FY), and zero order photoluminescence yield (PLY). From the spectra in Figure 4, we clearly see two

main peaks near the oxygen *K*-edge. There is also a strong shoulder before the absorption edge. These features are characteristic of SnO₂ nanostructures as reported previously [5]. The Sn *M*_{5,4}-edge features are much weaker than the O *K*-edge features due to the relatively small Sn *M*_{5,4}-edge cross-section with respect to the oxygen *K*-edge. The Sn *M*_{5,4}-edge region has been magnified in Figure 4. The TEY spectrum show a pre-edge resonance peak 'A' before the Sn *M*₅-edge which is absent in bulk SnO₂. This peak has been previously attributed to surface states caused by unsaturated coordination of surface Sn ions due to oxygen vacancies [5]. A matching peak corresponding to the Sn *M*₄-edge is hidden by the regular bulk SnO₂ resonance in peak 'B'.

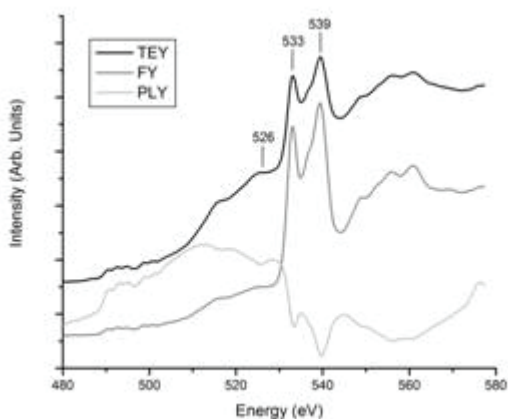


Figure 4 - Sn *M*_{5,4} and O *K*-edge XANES

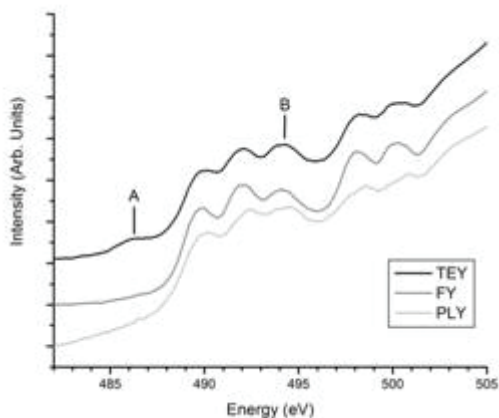


Figure 5 - Sn *M*_{5,4}-edge XANES, peaks A and B are surface states.

A comparison between the surface sensitive TEY and bulk sensitive FY of the Sn *M*_{5,4} spectrum shows that the peak is absent at A and noticeably reduced at B in the FY. This supports the claim that these peaks are due to surface states. Since these peaks are also missing from the PLY spectrum it demonstrates that the production of luminescence is dominated by bulk absorption and subsequent energy transfer through the lattice and not by absorption by surface atoms []. Most interesting is the PLY where the Sn *M*₅-edges exhibit a normal jump and the O *K*-edge is inverted, indicating a significant drop in luminescence efficiency above the O *K*-edge.

Conclusion

SnO₂ nanowires have been synthesized by chemical vapour deposition. The morphology of the SnO₂ nanostructure thus obtained has been characterized by SEM. XANES and XEOL have been used to characterize the electronic and optical properties. The XEOL has been found to be sensitive to the morphology of SnO₂ nanostructures, which depends somewhat on the substrate.

Acknowledgements

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References

1. Ying, Z., Wan, Q., Cao, H., Song, Z. T., Feng, S. L. 2005. Characterization of SnO₂ nanowires as an anode material for Li-ion batteries. *Applied Physics Letters*, 87(11), 113108(3).
2. Saha, Madhu Sudan, Li, Ruying, Cai, Mei, Sun, Xueliang. 2007. High Electrocatalytic Activity of Platinum Nanoparticles on SnO₂ Nanowire - Based Electrodes. *Electrochemical and Solid-State Letters*, 10(8), B130-B133.
3. Zhang, Fengyan, Barrowcliff, Robert A., Hsu, Sheng Teng. 2007. Photovoltaic structure with a conductive nanowire array electrode. U.S. Pat. Appl. Publ., 8pp.
4. Baratto, C.; Comini, E.; Faglia, G.; Sberveglieri, G.; Zha, M.; Zappettini, A. 2005. Metal oxide nanocrystals for gas sensing. *Sensors and Actuators, B: Chemical*, B109(1), 2-6.
5. Zhou, X.T., Heigl, E., Murphy, M.W., Regier, T., Coulthard, I., Blyth, R.I.R., Sham, T.K. 2006. Time-resolved x-ray excited optical luminescence from SnO₂ nanoribbons: Direct evidence for the origin of the blue luminescence and the role of surface states. *Applied Physics Letters*, 89, 213109
6. Zhou, X.T., Murphy, M.W., Ko, J.Y.P., Zhou, J.G., F. Heigl, E., Regier, T., Blyth, R.I.R., Sham, T.K. In press. The Effect of the Surface of SnO₂ nanoribbons on their luminescence using x-ray absorption and luminescence spectroscopy. *Journal of Chemical Physics*.