

X-ray excited optical luminescence studies of ZnS and ZnO nanostructures

R.A. Rosenberg,¹ G.K. Shenoy,¹ F. Heigl,² S.-T. Lee,³ L.-C. Tien,⁴ D. Norton,⁴ S. Pearton,⁴ P.-S. G. Kim,⁵ X.-T. Zhou,⁵ X.H. Sun,⁵ and T.K. Sham⁵

¹Argonne National Laboratory, Argonne, IL 60439

²Canadian Synchrotron Radiation Facility, Stoughton, WI 53589

³COSDAF and Department of Physics and Materials Science,
City University of Hong Kong, Hong Kong SAR, China

⁴Department of Material Science and Engineering, University of Florida, Gainesville, FL 32611

⁵Department of Chemistry, University of Western Ontario, London, ON, Canada

Introduction

Due to their potential as optoelectronic devices, luminescing nanostructures have been among the most studied in the recent past [1]. Room-temperature UV lasing has been demonstrated in ZnO nanowires. For highly asymmetric wurtzite structures, the orientation of the emitting luminescent dipole with respect to the excited state polarization can play a role in the luminescence yield. ZnS is an important, wide bandgap ($E_g = 3.54$ eV for the thermodynamically stable zinc blende form at room temperature) II-VI semiconductor. It has been developed for a number of applications including UV light-emitting diodes, injection lasers and phosphors. In this presentation we will discuss results of a study on ZnS nanostructures using synchrotron-radiation-based, x-ray-excited optical luminescence (XEOL). Results on ZnO will be presented elsewhere [2].

Methods and Materials

The experimental approach has been described previously [3,4]. All measurements were performed on beamline 4-ID-C at the Advanced Photon Source. Samples were prepared by a high-temperature growth technique described previously. Briefly, ZnS powder was placed in the center of a horizontal alumina tube upstream of a Si wafer, which was covered with 2 nm thiol-capped gold nanoparticles (used to catalyze the growth). The tube was heated to 1000° C while an Ar/H₂ gas mixture flowed through the tube. This process resulted in the formation of nanoribbons of lengths in the range 10-100 μ m and widths less than 100 nm. The samples were characterized by high-resolution TEM images, which showed large areas of hexagonal wurtzite structure interspersed by nanosized regions with cubic sphalerite structure.

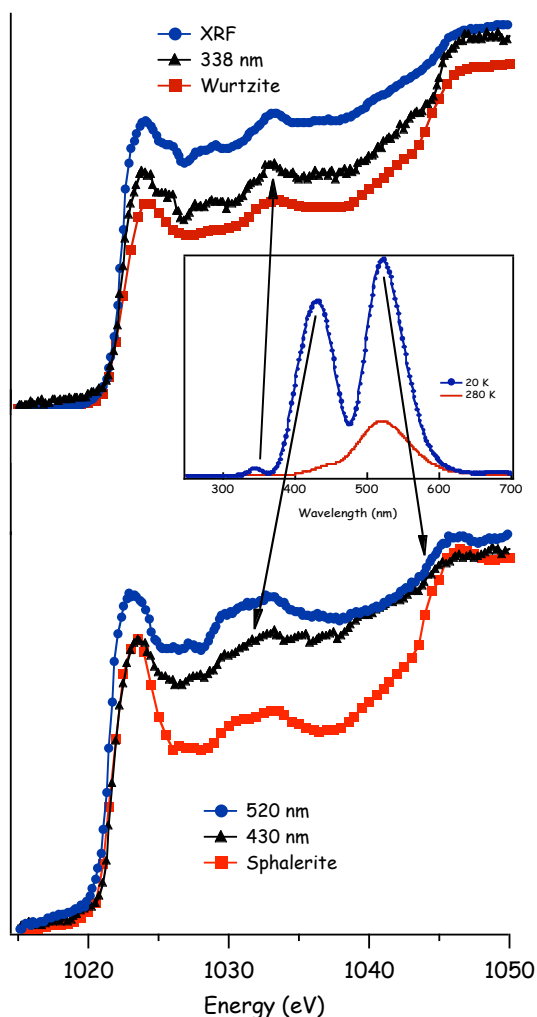
Results and Discussion

Using XEOL, we have determined the local phase of the luminescing sites in ZnS nanowires. The inset of the accompanying figure shows the temperature-dependent optical spectrum obtained when exciting the nanowires with 1100 eV x-rays. There are three main peaks: a band-edge, exciton state at 338 nm, a defect-related emission at 430 nm, and a Au-related feature at 520 nm. (Au is used as a catalyst to grow the wire.) By monitoring the yields of each of these peaks as a function of energy at the Zn L edge, we are able to determine the phase associated with them. The x-ray fluorescence (XRF) and 338 nm peak has a wurtzite signature, while the 430 and 520 nm curves resemble sphalerite. These results show that the 338 nm exciton state originates in the dominant, wurtzite phase of the wire, while the other two peaks occur in dilute (~0.1%) regions of sphalerite.

Acknowledgments

This work was performed at the Advanced Photon Source and was supported by the U.S. Department of Energy, Office of

Science, Office of Basic Energy Sciences under Contract No. W-31-109-ENG-38. Work at UWO was supported by NSERC.



References

- [1] Z.L. Wang, J. Phys. Condens. Matter **16**, R829 (2004).
- [2] R.A. Rosenberg, G.K. Shenoy, L.-C. Tien, D. Norton, S. Pearton, X.H. Sun and T.K. Sham, submitted to Appl. Phys. Lett.
- [3] R.A. Rosenberg, G.K. Shenoy, F. Heigl, S.-T. Lee, P.-S. G. Kim, X.-T. Zhou and T.K. Sham, Appl. Phys. Lett. **86**, 263115 (2005).
- [4] R.A. Rosenberg, G.K. Shenoy, F. Heigl, S.-T. Lee, P.-S. G. Kim, X.-T. Zhou, and T.K. Sham, Appl. Phys. Lett. **87**, 253105 (2005).