

Influence of Bismuth Additive on the Growth of ZnO Nanostructures

J. Xu¹ and J.Y. Liu²

¹ School for Engineering of Matter, Transport and Energy, Arizona State University, Tempe, Arizona 85287, USA

² Departments of Physics, Arizona State University, Tempe, Arizona 85287, USA

Semiconducting ZnO nanostructures have broad technological applications in optoelectronics, photovoltaics, energy harvesting and storage, sensing and catalysis [1]. Among many available techniques to fabricate ZnO nanostructures, the vapor phase transport method has its advantages such as generation of high-purity materials, no use of aqueous chemicals, and the modular addition of various materials to form compound nanostructures. We report here our recent investigation of the effect of Bi additive on the nucleation and growth of ZnO nanostructures.

The Bi₂O₃/ZnO nanostructures were synthesized in a high temperature tube furnace by a standard vapor phase transport process. The products were characterized by a FEI XL-30 scanning electron microscope (SEM) for observation of the general morphology of the different Bi₂O₃/ZnO structures. The JEOL JEM-ARM200F aberration-corrected scanning transmission electron microscope (STEM), with a nominal image resolution of 0.08 nm in the high-angle annular dark-field (HAADF) imaging mode, was used to investigate the atomic structure of the Bi₂O₃/ZnO structures.

To produce ZnO nanowires, mixtures of ZnO and carbon powders are usually heated to high temperatures (e.g., 1000°C) to generate Zn/ZnO molecular species within the tube furnace; upon cooling down, these molecular species nucleate and grow ZnO nanowires. When Bi powders were placed downstream and were heated to generate high Bi vapor pressure the morphology and the structure of the final product depends on the degree of mixing between the Bi vapor and the Zn/ZnO molecular species. By changing the amount of Bi additive and controlling the Bi partial vapor pressure, we can adjust the morphology and composition of the final products.

Fig.1 (a)-(f) shows the morphology variations of the Bi₂O₃/ZnO compound nanostructures when the Bi partial vapor pressure is decreased. With high Bi vapor pressure, big particles consisting of both Bi₂O₃ and ZnO were produced. When the Bi vapor pressure was decreased, thick and segmented microwires were produced. In backscattering electron images, Bi₂O₃ and ZnO phases were separated and some Bi₂O₃ grew on the outside of the ZnO microwires, forming a core/shell structure (Fig.2). With further reduction of the Bi vapor pressure, ZnO nanowires started to form (Fig. 1e). When the Bi vapor pressure was extremely low and did not mix with the Zn/ZnO molecular species, regular ZnO nanowires were produced (Fig. 1f). However, aberration-corrected STEM images revealed that the surfaces of the ZnO nanowires were coated with single Bi atoms or small clusters of BiO_x. Based on these observations, we propose that the presence of Bi or BiO_x species modifies the nucleation and growth of the ZnO micro- and nano-structures; they facilitate the growth of ZnO on surfaces other than the {0001} surface, resulting in modified micro- and nano-structures. It has been reported that liquid bismuth oxide significantly promotes the ZnO grain growth and recrystallization [2]. Detailed analyses of the synthesis conditions and the effect of Bi additive on the growth of ZnO nanostructures will be discussed [3].

References:

- [1] C. Jagadish, S. Pearton (Eds.) Zinc Oxide Bulk, Thin Film and Nanostructures. Elsevier (2006).
 [2] J. Wong, J. Appl. Phys. **51** (1980), p.4453.
 [3] This research was funded by Arizona State University. We gratefully acknowledge the use of facilities within the LeRoy Eyring Center for Solid State Science at Arizona State University.

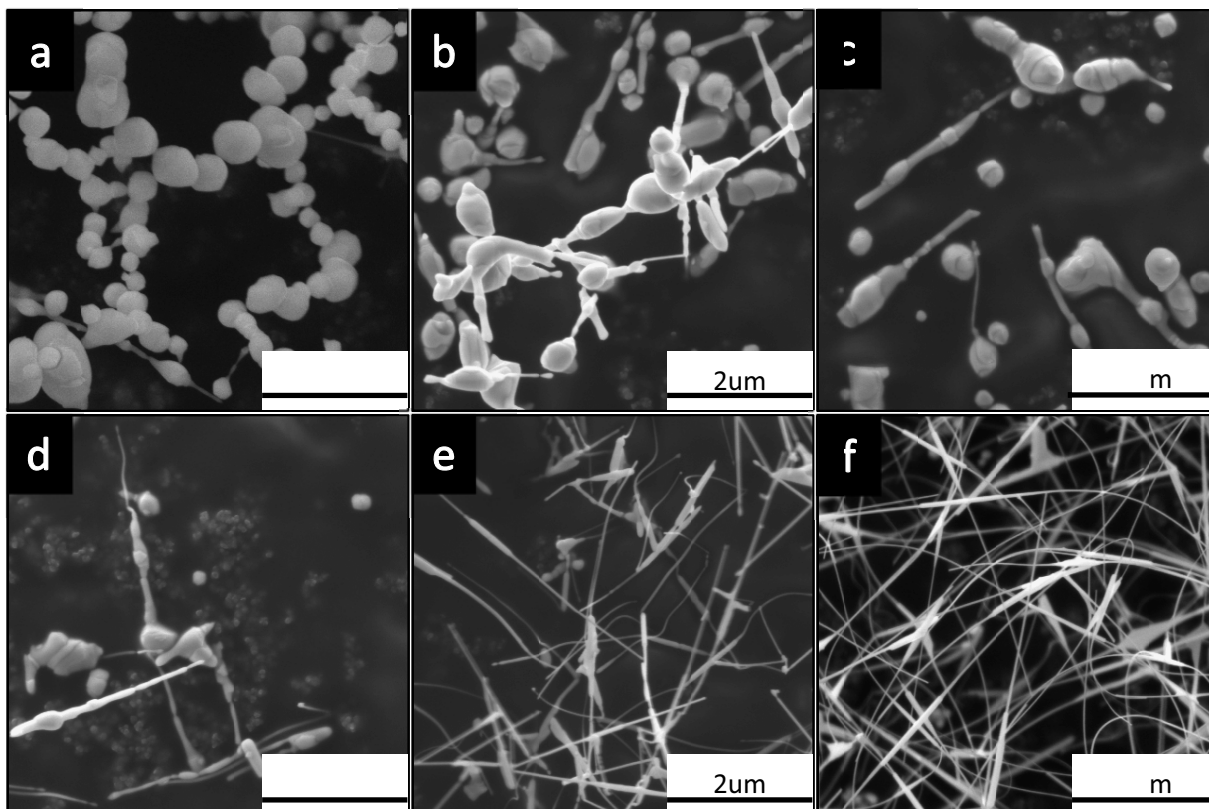


Fig.1. SEM images of $\text{Bi}_2\text{O}_3/\text{ZnO}$ nanostructures formed with decreasing Bi partial vapor pressure.

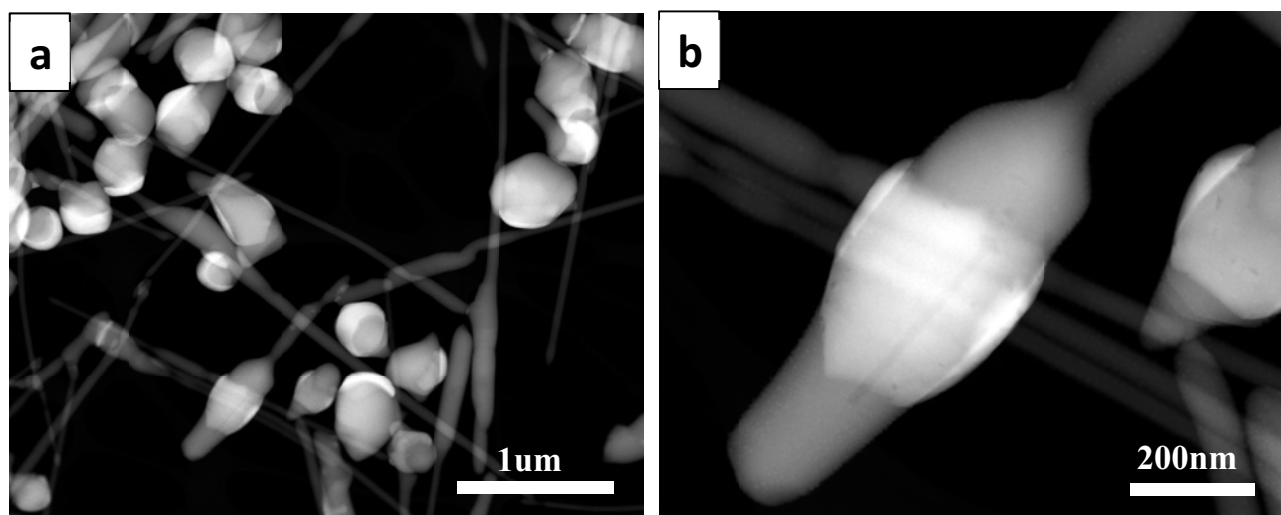


Fig.2. High-angle annular dark-field images of representative $\text{Bi}_2\text{O}_3/\text{ZnO}$ nanostructures clearly show the bismuth oxide phase (brighter image contrast) and their spatial relationship with the ZnO particles or nanowires.