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Interfacial Atomic Structure of BiO_x Functionalized ZnO Nanowires

J. Xu[1] and J. Y. Liu[2]

[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

One-dimensional nanostructures have been intensively investigated due to their unique properties and widespread applications. In particular, multifunctional properties can be derived from complex nanoscale systems consisting of heterostructures. With a wide band gap of 3.37eV, semiconducting ZnO materials find wide applications in energy harvesting and storage, catalysis, and optoelectronics [1]. On the other hand, Bi_2O_3, with an energy band gap of 2.85 eV, high refractive index, and extremely high oxygen-ion conductivity, can be used for sensors, optical coatings and photovoltaic cells [2]. It is expected that the nanoscale heterostructures consisting of these two oxides will provide unique properties. Following our previous study on the synthesis of BiO_x coated ZnO nanowires (NWs) [3], we report here our investigation of the interfacial atomic structures of BiO_x functionalized ZnO NWs with the goal to tune their nanoscale architectures for targeted applications.

The BiO_x/ZnO NWs were synthesized in a high temperature tube furnace by a standard vapor phase transport process [3]. Aberration-corrected STEM techniques, especially the high-angle annular dark-field (HAADF) imaging mode, were used to investigate the atomic structures of the BiO_x coating layers, the ZnO NWs and the BiO_x/ZnO interfacial regions.

Figures1a-1b show low and high magnification HAADF images of a typical BiO_x/ZnO NW, oriented close to the [10-10] zone axis. The {10-10} surfaces are relatively flat except some steps (indicated by the yellow arrows) near the tip of the NW. The bright edge contrast represents the decoration of the NW by the Bi species as clearly shown in Fig. 1b. The coating layers consist of epitaxially grown (100) planes of the cubic δ-Bi_2O_3 with a spacing of 2.82Å and the Bi-containing amorphous-like islands [3]. It is interesting to note that Bi layers (bright dots in Fig. 1b) "grew" into the ZnO along the (10-10) planes (indicated by the yellow arrow in Fig. 1b). The decreasing brightness of the Bi atoms along the ZnO [-0001] suggests that less and less Bi atoms were found in regions away from the ZnO {10-10} surfaces. Fig. 1c shows a schematic diagram illustrating the relationship between the growth of BiO_x and the ZnO NW. Because of the large differences in their lattice spacings, the presence of the BiO_x layers inside the ZnO NW causes lattice distortion and strain fields. An extra layer of ZnO was observed to accommodate the BiO_x layers. The existence of such unique configuration may be related to the kinetics of the BiO_x/ZnO NW growth processes. Figure 1a also shows the presence of δ-Bi_2O_3 joining two ZnO NWs (indicated by the block arrow). Figure 2 shows the magnified image of this region clearly revealing the epitaxial growth of the faceted δ-Bi_2O_3 on the (0001) surface of the ZnO NW. The epitaxial relationship is identified as δ-Bi_2O_3[1-10](111)//ZnO[10-10](0001). Detailed analyses of the interfacial structures and the growth mechanisms of the BiO_x/ZnO NWs will be discussed [4].

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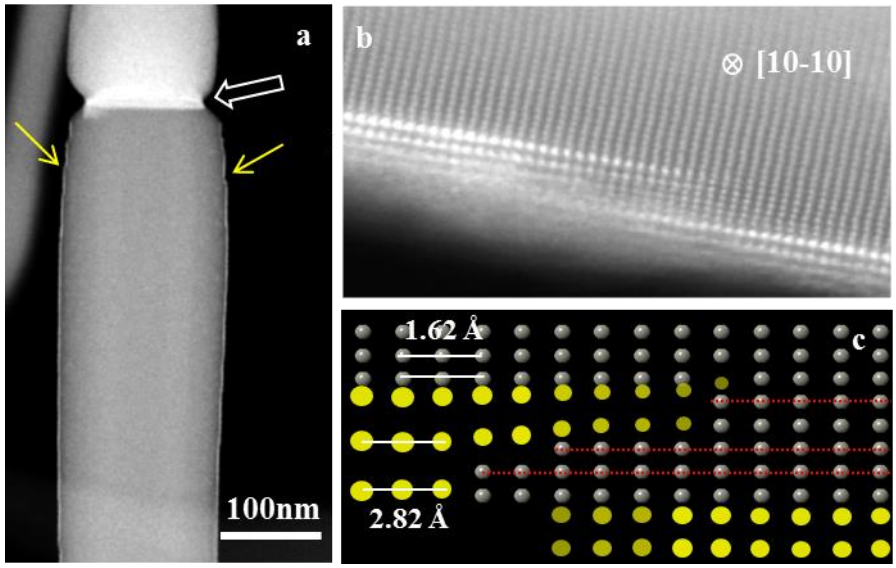

Figure 1. Low (a) and high (b) magnification HAADF images of a typical Bi_2O_3/ZnO NW. Layers of BiO_x were coated onto the ZnO NW. Fig. 1b clearly shows the growth of BiO_x layers into the ZnO NW. Fig. 1c is a schematic diagram illustrating the arrangement of Zn and Bi atoms at the interfacial region.

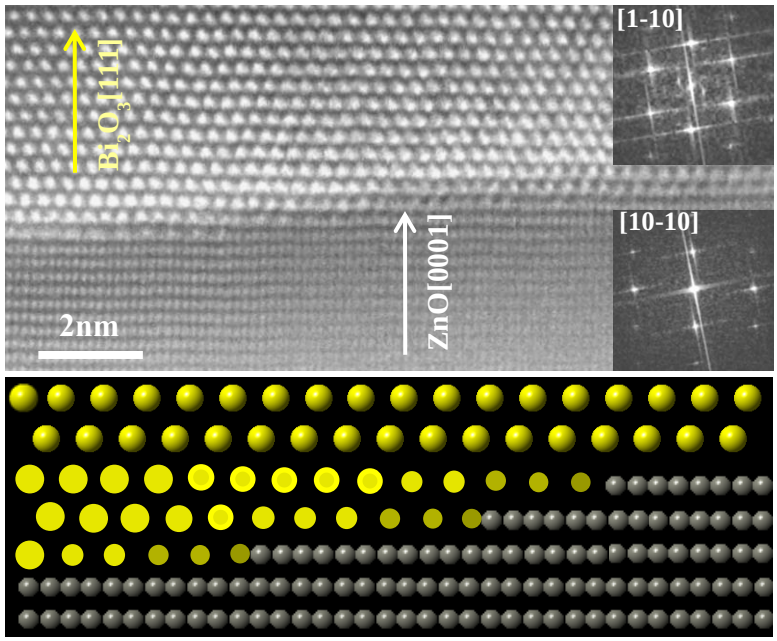

Figure 2. HAADF image of Bi_2O_3 epitaxially grew on the (0001) surface of the ZnO NW shown in Fig. 1a (The δ-Bi_2O_3 connected the two ZnO NWs). The schematic diagram illustrates the atomic arrangement of Bi and Zn atoms in the interfacial region.

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