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Preferential Growth of δ-Bi_2O_3 Layers on the {$11\bar{2}0$} Facets of ZnO Nanowires

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One-dimensional nanostructures have been intensively investigated due to their unique properties and widespread applications [1]. In particular, novel and/or multifunctional properties can be derived from complex nanoscale systems consisting of different materials. With a wide band gap of 3.37eV, semiconducting zinc oxide materials find wide applications in energy harvesting and storage, catalysis, and optoelectronics [2]. On the other hand, bismuth oxides, with special physical properties such as large energy band gap, high refractive index, and high oxygen-ion conductivity, can be used for sensors, optical coatings and photovoltaic cells [3]. In this communication, we report our study of the preferential layer-by-layer growth of δ-Bi_2O_3 onto the {$11\bar{2}0$} nanoscale facets of ZnO nanowires.

The Bi_2O_3/ZnO nanowires were synthesized in a high temperature tube furnace by a standard vapor phase transport process. Mixed ZnO and carbon powders were heated to about 1100°C and Bi powders were placed down the stream of the tube furnace and were heated to evaporate Bi atoms inside the tube furnace. ZnO nanowires, formed in the high temperature zone, were carried to the low temperature zone where Bi atoms were deposited onto the surfaces of the ZnO nanowires. The thickness of the deposited Bi depends on the Bi partial vapor pressure, the deposition temperature, and the flow rate of the carrier gas. 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 synthesized nanostructures.

Figures1a-1c show low and high magnification HAADF images of a representative ZnO nanowire. Layers of atoms with bright image contrast are clearly visible. The Fourier diffractogram shown in the inset of Fig. 1c suggests that the electron beam was close to the ZnO [$10\bar{1}0$] zone axis. Another set of the spots (indicated by the red circles) were identified as originated from the surface over-layers, which are clearly visible in Fig. 1c. These spots originated from the lattice fringes of δ-Bi_2O_3 layers, with the electron beam oriented along the [001] zone axis. The bright row of atoms in Fig. 1b suggests that the first layer of Bi atoms are located on top of the Zn atoms of the ZnO ($\bar{1}2\bar{1}0$) surface. An incomplete second layer of Bi atoms is also observable. Based on these observations, we propose that δ-Bi_2O_3 grows preferentially on ZnO {$11\bar{2}0$} nanofacets with a layer-by-layer growth mechanism, at least for the first few layers, after which highly disordered islands (probably a $Zn_xBi_{1-x}O$ phase) are formed. A good dimensional match exists between the ZnO {$11\bar{2}0$} planes and the δ- Bi_2O_3 {100} planes. The fact that δ-Bi_2O_3 has a high concentration of oxygen vacancies may facilitate to accommodate the superposition of oxygen atoms [4]. Since only a few Bi atoms were observed on the ZnO {$10\bar{1}0$} facets we can conclude that the bismuth or bismuth oxide phases did not nucleate on the ZnO {$10\bar{1}0$} nanoscale facets. Figure 1d shows a schematic diagram illustrating the observations. Detailed analyses of the interfacial structures and the growth mechanisms will be discussed [5].

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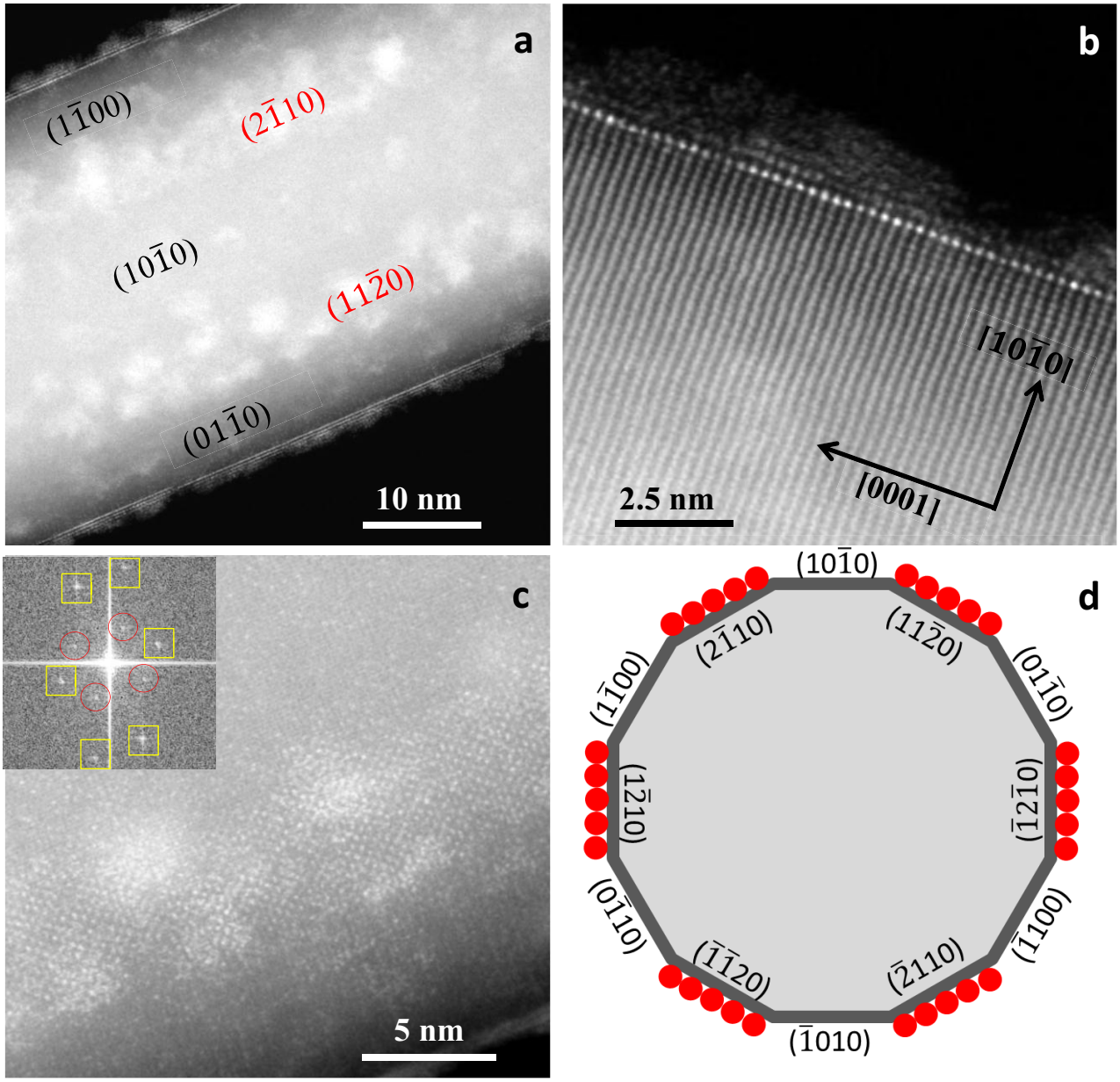

Fig.1. Low (a) and high (b, c) magnification HAADF images of a representative Bi_2O_3/ZnO single nanowire, revealing the preferential growth of Bi_2O_3 layers on the ZnO {11$\bar{2}$0} facets. Figure 1b clearly shows that the Bi atoms are positioned along the rows of Zn atoms on the {11$\bar{2}$0} surfaces. The inset in Fig. 1c is the Fourier diffractogram: The red circles represent spots originated from the Bi_2O_3 layers ([001] zone axis) on top of the ZnO {11$\bar{2}$0} surfaces; the yellow squares represent spots from the ZnO nanowire with the electron beam oriented close to the ZnO [10$\bar{1}$0] zone axis. Figure 1d schematically illustrates the 12 nanofacets of the ZnO nanowire and the preferential growth of Bi_2O_3 layers (red spheres) onto the ZnO {11$\bar{2}$0} facets.

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