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# Adsorption of Sb on the $\{10\bar{1}0\}$ Facets of ZnO Nanowires

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Zinc oxide nanomaterials with a wurtzite structure are used for various applications including catalysis [1]. ZnO nanowires are of interest due to its high surface-to-volume ratio and thermodynamic stability of non-polar $\{10\bar{1}0\}$ surfaces. Metal particles have been deposited onto the prismatic planes of ZnO nanowires for sensing and photocatalytic applications [2]. The interfacial structure between ZnO $\{10\bar{1}0\}$ surfaces and various metals have been investigated [3]. Kraševec *et al.* reported that an oriented overgrowth of the spinel $Zn_7Sb_2O_{12}$ layers was observed between ZnO surfaces and a thin Sb-rich film [4]. Uniform antimony coating onto the surfaces of ZnO nanowires may provide new functions for applications in sensing, catalysis, energy conversion or nanoelectronics. We report here our recent study of the adsorption of Sb onto the $\{10\bar{1}0\}$ facets of ZnO nanowires.

The Sb/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 $Sb_2O_3$ powders were placed down the stream of the tube furnace and were heated to generate Sb vapor inside the furnace. ZnO nanowires, formed in the high temperature zone, were carried to the low temperature zone where Sb atoms adsorbed onto the surfaces of the ZnO nanowires. By controlling the Sb partial vapor pressure we can control the thickness of the deposited Sb layers. 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 deposited Sb and its relationship with the facets of the ZnO nanowires.

Figure 1a shows a HAADF image of an as-synthesized Sb/ZnO nanowire. The ZnO nanowire is atomically smooth with a diameter of about 20 nm. Analyses of HAADF images revealed that the ZnO nanowire grew along the [0001] axis and was enclosed by the six $\{10\bar{1}0\}$ surfaces. Detailed examination of the HAADF images revealed that the surface atoms of the ZnO nanowire (Fig. 1a and 1b) yielded a brighter image contrast. Furthermore, the brighter atoms only decorated on every other column of the surface Zn atoms. Since such brighter surface atoms have not been observed in ZnO nanowires that have been synthesized without the addition of Sb, we assigned these brighter dots to columns of antimony atoms adsorbed onto the $\{10\bar{1}0\}$ surfaces of the ZnO nanowire. It should be noted that Fig. 1a shows both the $(10\bar{1}0)$ and $(\bar{1}010)$ surfaces of the ZnO nanowire and that Sb only adsorbs onto the "valleys" of the ZnO $\{10\bar{1}0\}$ surfaces.

The proposed structure of the Sb-ZnO $(10\bar{1}0)$ surface is shown in Fig 2. Fig 2a was constructed according to the HAADF image (Fig 1b): Sb atoms occupy the positions of the Zn1 atoms on the $(10\bar{1}0)$ surface. The slightly larger spacing from the next Zn layer may be due to the larger size of Sb and modification of its bonding with the oxygen atoms. Four different Zn and four different O are labeled as 1, 2, 3 and 4. The coordination number of the inner oxygen atoms (e.g. O2) is 4 but that of the surface oxygen atoms (O1) is 3. The distances between any Zn atom and its nearest Sb are all relatively large. Each Sb atom has three nearest oxygen neighbors, one O1 and two equivalent O2. Fig 2b shows the plan

view of an unreconstructed ZnO $(10\bar{1}0)$ surface and Fig 2c illustrates one proposed model to explain the observed image contrast of the Sb atoms. This model is based on a non-reconstructed ZnO $\{10\bar{1}0\}$ surface and the fact that Sb fully adsorbed onto the most favorable sites. With the limited information available, we cannot rule out alternative adsorption models. Our model suggests that the Zn1 atoms on the ZnO $\{10\bar{1}0\}$ surfaces can be completely replaced by the adsorbed Sb atoms [5].

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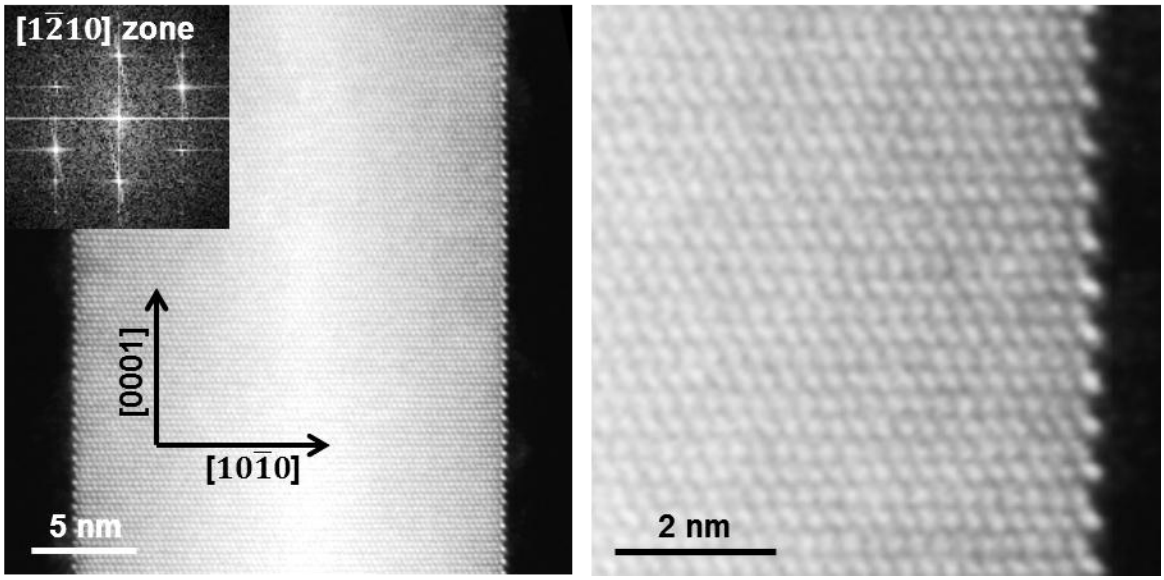


**Figure 1.** Sub-angstrom resolution HAADF images of a ZnO nanowire deposited with Sb on the $\{10\bar{1}0\}$ surfaces. (a) Low and (b) high magnification images.

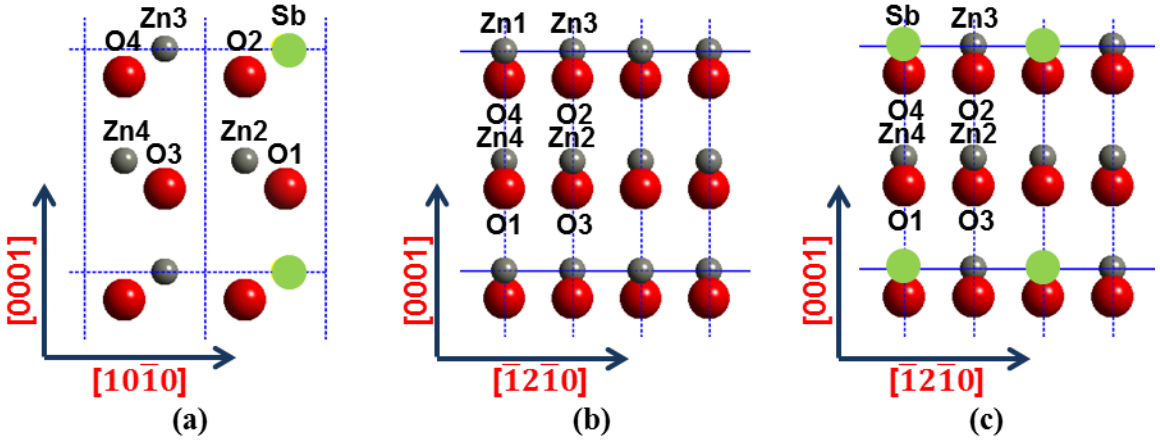


**Figure 2.** Schematic diagrams showing the (a) side view, (b) top view (without Sb) and (c) top view (with Sb) of the surface structure of the ZnO $(10\bar{1}0)$ surface.

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