500 CD
DOI: 10.1017/S1431927606062362

Microsc Microanal 12(Supp 2), 2006

Ordered Zinc-Vacancy Induced $Zn_{0.75}O_x$ Nanophase Structure

Yong Ding, Rusen Yang and Zhong Lin Wang*

School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0245 USA

ZnO is a wide bandgap semiconductor of 3.4 eV, which has many applications in optics, optoelectronics, sensors and actuators. The as-synthesized ZnO nanostructures are usually *n*-type semiconductor [1]. The excess electrons may be introduced by the presence of hydrogen, Zn interstitials and/or oxygen vacancies [2, 3]. Furthermore, the n-type character typically introduces compensating acceptor defects, such as Zn vacancies and oxygen interstitials. Identification and quantification of these point defects are important for their electronic and optoelectronic applications. However, what are the relevant native defects of this oxide is still controversial [4, 5].

In this works, a new $Zn_{0.75}O_x$ superstructure grown on ZnO one-dimensional nanobelts has been discovered, which is induced by the ordered Zn vacancies. Figure 1 (a) and (b) are the ZnO nanobelt with large surface as *c* plane and $(01\bar{1}0)$ plane, respectively. The energy dispersive X-ray spectroscopy results in Figure 1(c) indicate that no impurity exists in the belts. After carefully examining the electron diffraction patterns in Figure 1(d) and (e), recorded from the nanobelts shown in Fig. (a) and (b), respectively, the superstructure can be fit as an orthorhombic structure. The lattice parameter measured from the electron diffraction patterns can be identified as $a' = 2a$, $b' \approx \sqrt{3}a$ and $c' = c$, where $a = 3.25Å$ and $c = 5.21$ Å are the lattice parameters of the wurtzite structured ZnO.

The high-resolution transmission electron microscopy (HRTEM) image in Fig. 2 was recorded from Figure 1(a). Image simulations suggest that the defect area in the HRTEM image of Fig. 2 is induced by high-density Zn vacancies. Assuming the existence of Zn vacancies in the defect area and not considering the oxygen vacancies, an atomic model of the superstructure has been built up. The simulated image was inserted in Fig. 2, which match the experimental image very well. The HRTEM image in Fig. 3 was recorded from the nanobelt shown in Fig. 1(b), the incident electron beam is along $[01\bar{1}0]$ direction in stand of [0001] direction in Fig. 2. The experimental image in Fig. 3 also matches the simulated image based on the model shown in Fig. 3.

Regardless of whether oxygen vacancies exist or not, our TEM study on the superstructure and the ZnO nanobelt matrix reveals that the Zn vacancies are abound in this material and a new phase of $Zn_{0.75}O_x$ is formed. This discovery shows that the ZnO nanobelts can have up to 25% of Zn vacancies at least at a local area.

[1] F. A. Kröger, The Chemistry of imperfect crystals (North-holland, Amsterdam, 1974).
[2] D. H. Hofmann, A. Hofsteatter, F. Leiter, H. Zhou, F. Henecker, B. K. Meyer, S. B. Orlinskii, J. Schmidt, and P. G. Baranov, Phys. Rev. Lett. 88, 045504-1 (2002).
[3] A. F. Kohan, G. Ceder, D. Morgan, and Chris. V. Van de Walle, Phys. Rev. B 61, 15019 (2000).

[4] W. Göpel and U. Lampe, Phys. Rev. B 22, 6447 (1980).
[5] D. C. Look, J. W. Hemsky, and J. R. Sizelove, Phys. Rev. Lett. 82, 2552 (1999).

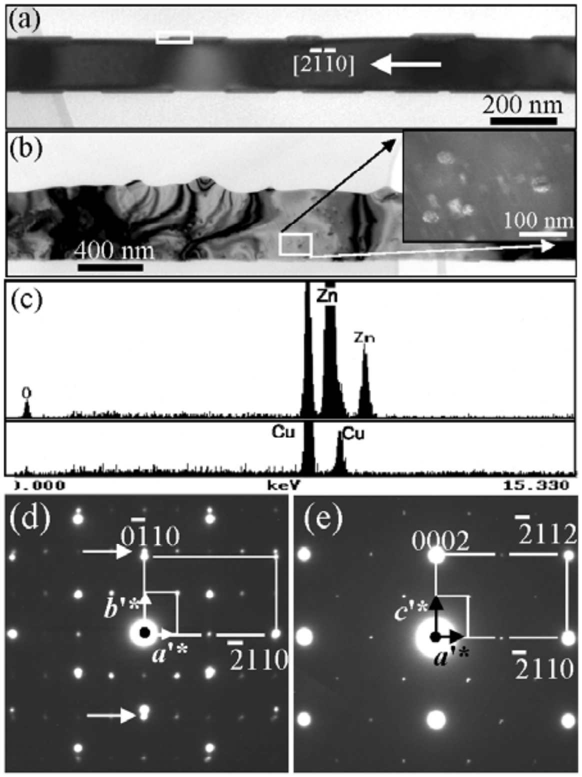

Figure 1. (a) and (b) bright-field TEM images of ZnO nanobelts, showing a superstructured phase at the side and top/bottom surfaces of the wurtzite ZnO nanobelts. EDS spectra in (c) shows no impurities in the belts. (d) and (e) SAED patterns from the nanobelts in (a) and (b), respectively.

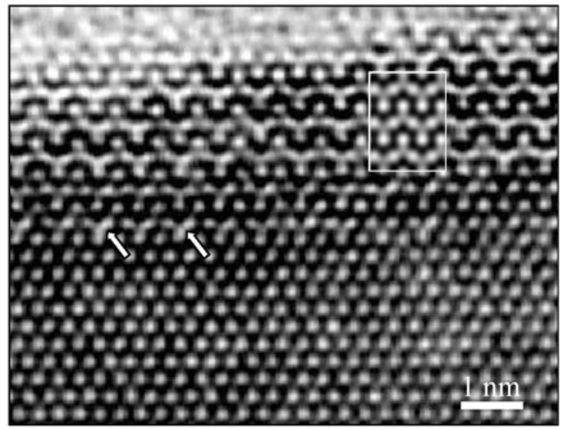

Figure 2. HRTEM image recorded from the rectangle-enclosed area in Fig. 1(a). The inset is a simulated image based on the proposed model.

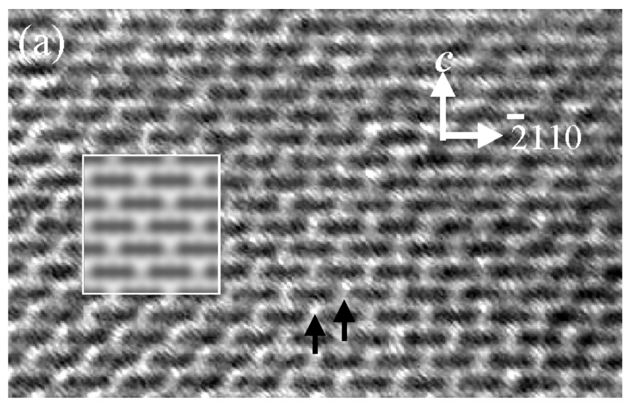

Figure 3. HRTEM images recorded from the nanobelt shown in Fig. 1(b): The inset is a simulated image based on the proposed model.

https://doi.org/10.1017/S1431927606062362 Published online by Cambridge University Press