

ANALYSES OF DEFECTS IN ZINC OXIDE BIPOD PARTICLES

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Introduction

Zinc oxide (ZnO) is an interesting and important II–VI semiconductor for both, applications and basic researches, owing to its unique physical and chemical properties. It is a material with great potential for a variety of practical applications, such as piezoelectric transducers, varistors, phosphors, chemical and gas sensors and UV-light emitters¹.

A variety of ZnO nanostructure morphologies, such as rods, wires, tetrapods, and microspheres, have been reported². An unusual feature of the prepared ZnO samples, visible as a crack perpendicular to the length, in the middle of the particle, and sometimes also along the length, with rare occurrences of a well-separated splitting, was reported by Oliviera et al.³. Wang et al.⁴ reported that the mechanism of the formation of bipod crystals was based on an already existing nucleus in solution, and the growth of crystallite twins takes place along the polar *c*-axis by the incorporation of growth units on the growth interfaces. Hu et al.⁵ reported the formation of linked ZnO rods with various morphologies, where the formation of bipods can be controlled by an oriented attachment mechanism. In the literature, planar defects in the middle of ZnO particles (bipod) was seen on many micrographs, but in most cases were not commented or even noticed. In this work we are presenting a detailed characterization of the planar base-plane and prismatic defects obtained in the hexagonal ZnO bipod particles with electron microscopy for samples prepared by precipitation method in a mixture of water/ethylene glycol.

Experimental

In a typical experimental procedure, zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Sigma-Aldrich, 98%) and urea (Sigma-Aldrich, 99%) were dissolved in MilliQ water. The chemicals were analytical reagents and used without any further purification. Two types of sample preparation were performed. The first sets of experiments (marked as Samples A) were carried out under constant stirring (200 rpm) in 250-ml open reactors at 90 °C for 0.5 hours. The concentrations of Zn^{2+} ions and urea were 0.01 M and 0.05 M, respectively. A reaction mixture of water/EG with the volume ratio 1/1 was used. The second sets of experiments (marked as Sample B) were carried out in the 40-ml Teflon-lined autoclave, which was placed in an oven preheated at 90 °C. The experiments were performed in a mixture of water/ethylene glycol (EG,

Merck) with the volume ratio 1/3 and with concentrations of Zn^{2+} (0.001 M) and urea (0.005 M) after 72 hours. The as-prepared solids were filtered off, washed with water and dried in air.

The structures of the samples were studied using the Jeol 2010 FEG STEM and Jeol 2100 TEM microscopes operating at 200 KV, equipped with EDX detectors for the compositional analyses. In the case of small particles (up to 100 nm) a fraction of the particles in the form of a suspension in ethyl alcohol was transferred to a lacy, carbon-coated Ni or Cu grid and examined in the microscope.

In the case of larger particles (in the μm range) the crystals were crushed in a mortar and the resulting powder was subsequently embedded in phenol-formaldehyde resin and thoroughly mixed. The mixture was placed in a die, pressed (0.5 MPa) and cured at 150 °C. High-resolution TEM (HRTEM), selected-area electron diffraction (SAED) and convergent-beam electron diffraction (CBED) were employed to examine the structure of the materials. The simulated CBED patterns, used for the polar-axis orientation, were calculated with the EMS program code.

The morphologies of the samples were characterized by scanning field-emission electron microscopy (FE-SEM, Zeiss Supra 35 VP with an EDS analyzer).

Results and Discussion

We prepared ZnO particle with shape such as rod-like, needle-like and ellipsoidal. Shape was strongly dependent on the experimental parameters. Rod-like particles were prepared in an open reactor (Fig 1a) while needle-like particles (Fig. 1b) were obtained in an autoclave. FE-SEM images show the presence of rod-like and needle-like hexagonal particles. The aspect ratio of differently shaped particles varies, but all samples have very distinct symmetrical, twin (bipod) structure with planar defect in the middle.

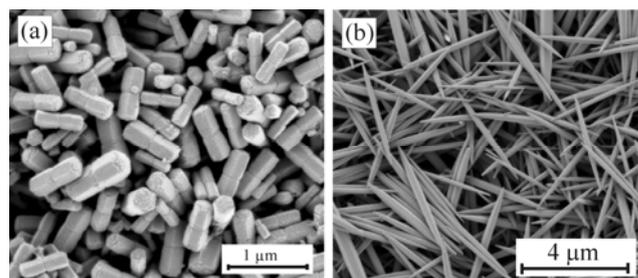


Figure 1: FE-SEM micrographs of: (a) – Sample A prepared in the open reactor and (b) – Sample B prepared in the autoclave

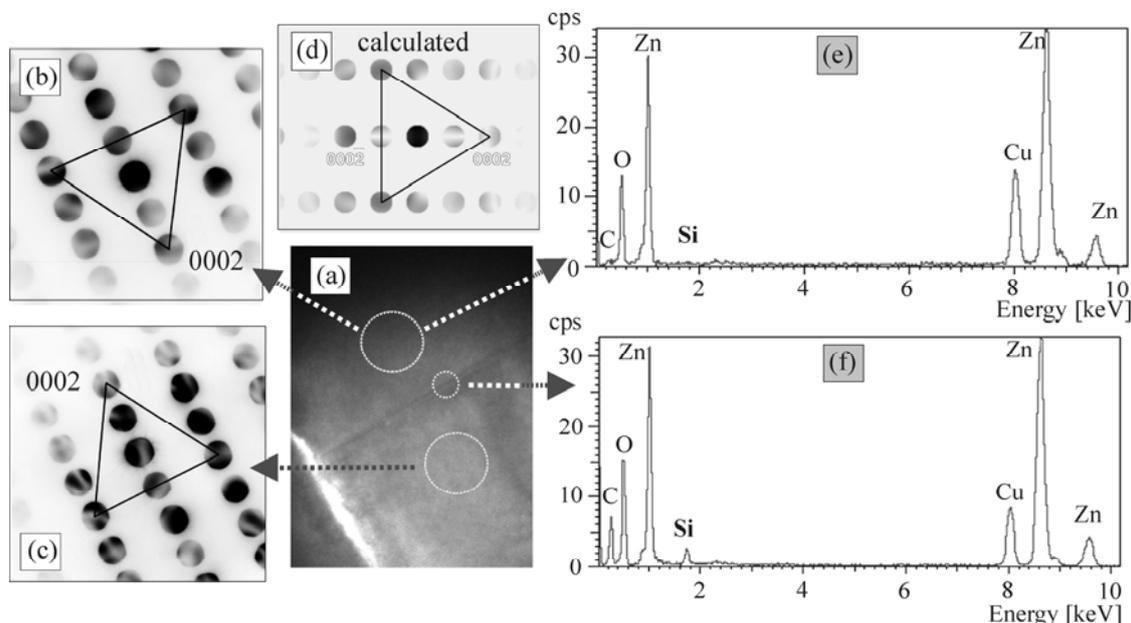


Figure 2: Sample A prepared in the open reactor: (a) – HRTEM image across the IDB with labelled areas where the CBED patterns were recorded, (b) and (c) – experimental CBED patterns at the indicated areas, (d) – calculated CBED pattern where the polar axis (head) is indicated with a triangle (simulated using a 50-nm-thick foil), (e) – EDXS spectrum of the bulk particle and (f) – EDXS spectrum of the planar defect.

Using FEGTEM/EDXS analysis we found that these defects contain small amount of silicon (Fig 2). It was roughly estimated that one atomic layer of silicon is present at the defect. We propose that the central planar defect is nucleated at the very beginning, due to Si which is present as impurity and most probably enters in the system from glassware. The difference in roughness of terminal and side parts of the bipods could lead to a tentative explanation of the growth: crystals grow with attachment and simultaneous crystallization of charged, amorphous, around 6 nm sized particles which attach preferentially to terminal basal planes (c- direction).

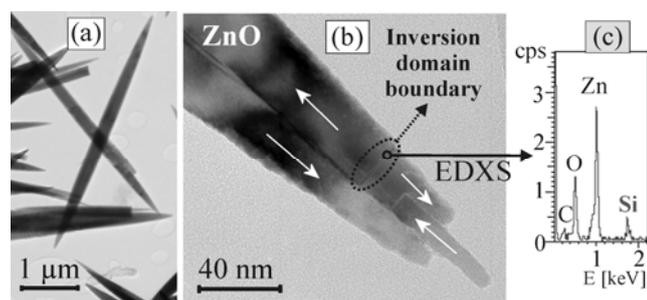


Figure 3: Sample B prepared in the autoclave: (a) – TEM image of needle-like ZnO bipods, (b) – close-up of one part of a bipod where the prismatic and basal IDBs are clearly seen. Arrows indicate the polar axis [0001], (c) – EDXS spectrum collected at IDB.

We assumed that planar defects are inversion domain boundaries (IDBs). To confirm this assumption and to find how the domains are oriented (head-to-head or tail-to-tail) we performed convergent-beam electron-diffraction (CBED) experiments. From CBED patterns we found that these planar defects are

inversion domain boundaries (IDB) with head-to-head orientation of polar axis.

ZnO particles prepared with precipitation in autoclave had much higher aspect ratio (20 ± 5) and had needle-like morphology (Fig. 3a). Inside those particles beside IDB on basal planes also prismatic inversion domain boundaries were found (Fig. 3b). These boundaries again contain small amount of silicon (Fig. 3c). The mechanism of the formation of prismatic IDB was proposed to be the overgrowth of one part of the bipod over another. In this case not just head-to-head arrangement of polar axis but also tail-to-tail was observed.

Conclusion

In the paper we discuss the defects in ZnO bipods that contain very thin (most probably a single atomic) layer of silicon. The observed defects are formed at the very beginning of the crystal growth and therefore play a crucial role in determining the growth and shape. In addition, the characterization of the particles' defects in the basal and prismatic planes was made very transparently. From convergent-beam electron-diffraction patterns we found that the planar defects are inversion domain boundaries (IDBs), with mostly a head-to-head orientation, but in specific cases also in a tail-to-tail orientation of the polar axis.

References

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