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Analytical Electron Microscopy of ZnO Bipods Grown from Solutions

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Zinc oxide is wide band gap semiconductor (3.37 eV) with unique properties which can be tuned by varying the size and morphology of the particles. It can be used in various applications such as transparent electrodes, UV light emitting devices, piezoelectric devices, gas sensors, solar cells and as active material in photocatalysis [1,2]. The preparation of nano-to-submicrometer particles from solutions is low-cost technique and lately attracted a lot of interest due to the low temperature needed for the synthesys (85-95 ^{o}C). In this work zinc oxide crystals were prepared by homogeneous precipitation method using urea and zinc nitrate as raw materials.
ZnO particles in a rod-like shape with regular twin (bipod) structure (Fig. 1) were prepared in an open reactor whereas needle-like shape structures (Fig. 2) were obtained in an autoclave. ZnO rod-like particles had an aspect ratio of 3.2 and very distinct planar defect in the middle. TEM/EDXS analysis revealed that these defects contain small amount of silicon. It was estimated that around one atomic layer of silicon is present at the defect. From convergent beam electron diffraction patterns it was found that these planar defects are inversion domain boundaries (IDB) with head-to-head orientation of polar axis. Sides of the crystals were found to be much smoother than the terminal ends (basal planes) of the particles. Lee and Wiederhorn [3] reported that in polycrystalline ZnO the grain growth in c- direction is much slower than the growth in c+ and prismatic directions. Daneu and Recnik [4, 5] explained the anisotropic growth of ZnO grains with inversion domain boundaries where orientation of polar axis at the IDB is head to head and the growth rate in prismatic direction is faster than in c- [000-1] direction, meaning that grains are elongated in the direction parallel to the IDB. In our case the situation is different. Obviously grain growth in [000-1] direction is faster than in the prismatic directions. 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). 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.
ZnO particles prepared with precipitation in autoclave had much higher aspect ratio (20±5) and had needle-like morphology. Inside those particles beside IDB on basal planes also prismatic inversion domain boundaries were found. These boundaries again contain small amount of silicon. 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. The influence of deliberate silicon addition was also tested. In the case where 100 ppm of silicon was added the number of basal IDBs drastically increased.

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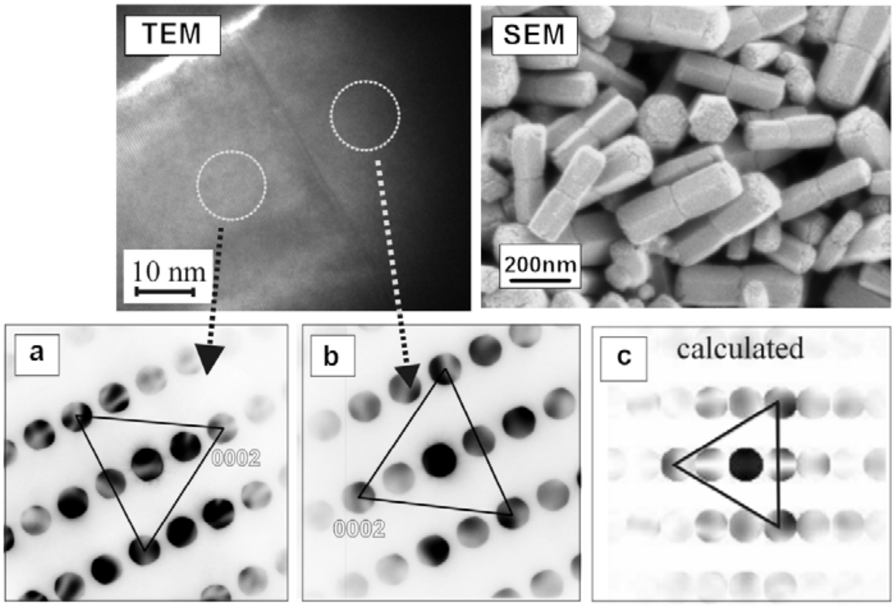

FIG. 1. TEM and SEM micrographs of ZnO bipods. Convergent-beam electron diffraction patterns from indicated areas near the inversion-domain boundary (a and b) and calculated pattern (c) where polar axis (c+) are indicated with triangles. In IDB at the middle of the bipod the "head-to-head" orientation of polar axis was confirmed.

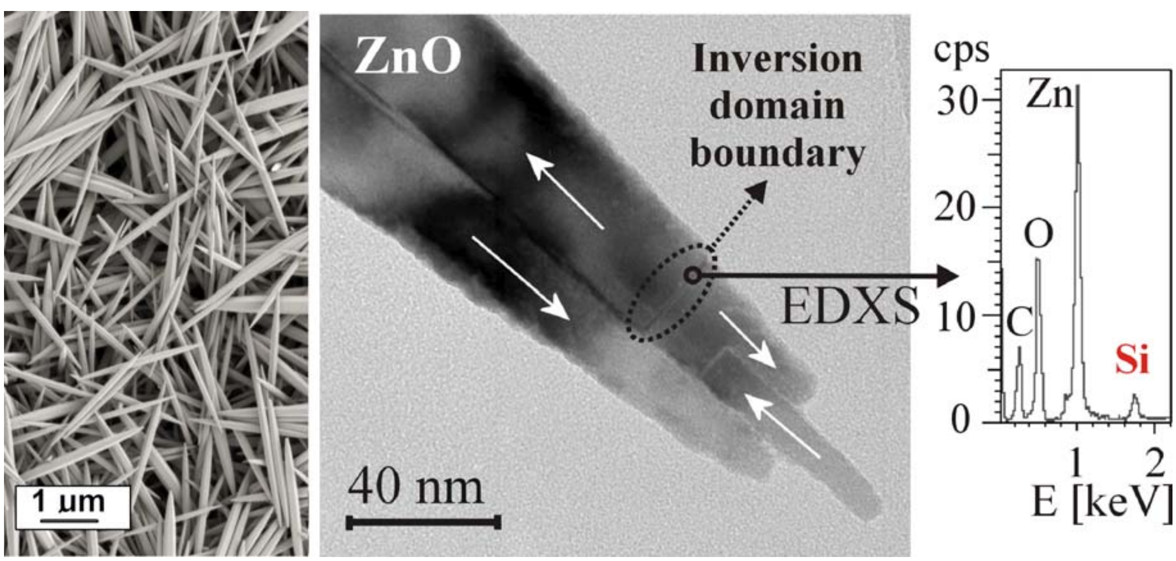

FIG. 2. SEM (left) and TEM (middle) micrographs of needle-like ZnO particles. Planar features inside the particles were identified as inversion domain boundaries (IDB). EDXS spectrum (right) from IDB showing that around one atom layer of Si is present at the planar defect. White arrows indicate the polar axis.

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