Transmission Electron Microscopy Study of Pseudoperiodically Twinned Zn_2SnO_4 Nanowires

Hanyuan Chen, Jianxiong Wang, Hongchun Yu, Huaixin Yang, Sishen Xie, and Jianqi Li*

Beijing National Laboratory of Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China

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The ternary oxide functional nanomaterial Zn_2SnO_4 has been synthesized by the thermal evaporation method. The products in general contain numerous kinds of nanowires. In the present work, a remarkable type of Zn_2SnO_4 nanowires with a pseudoperiodical twinning structure has been investigated by transmission electron microscopy (TEM). These nanowires with a diameter of about 100 nm grow along the ⟨111⟩ direction. High-resolution TEM examinations suggest that a large fraction of the (111) twin boundaries are extended to a thickness of a few nanometers. The twining plane for the perfect case is localized on the Zn atom layer.

Introduction

Semiconducting oxide nanomaterials, such as ZnO,[1,2] SnO_2,[1,3,4] and In_2O_3,[5] have attracted considerable attention in recent years, due to their potential applications in the development of nanoscale electronic and optoelectronic devices. Certain research has been focused on the synthesis of one-dimensional semiconducting nanocomposites[6−8] that are expected to show desired multifunctionality. Zn_2SnO_4 [9,10] is one of the significant functional materials with high electron mobility, high electrical conductivity, and low visible absorption; these properties allow this functional material to be suitable for application as photovoltaic devices and sensors for detection of humidity and various combustible gases, etc. In our recent works, Zn_2SnO_4 nanomaterials have been synthesized with the zinc oxide (ZnO) and tin oxide (SnO_2) by the thermal evaporation method. Structural investigations reveal that a fraction of Zn_2SnO_4 nanowires in the as-synthesized samples display a marvelous periodic twinning structure. Crystals with face-centered cubic (fcc) structure frequently show well-defined twinning as lately observed in a number of metallic nanocrystals. For instance, twins[11,12] have been observed in copper, gold, and, especially, silver nanowires, in which the 5-fold twinning[13,14] has been analyzed and modeled in detail. As a significant defect structure, twin boundaries could generate positive energy and are expected to have important effects on electronic and mechanical properties.[15,16] Mechanical studies indicate that twin boundaries act commonly as dislocation obstacles to affect the deformation behavior as observed in copper nanomaterials.[17] In the present paper, we will focus on the investigation of the pseudoperiodic zigzag twinning structure of Zn_2SnO_4 nanowires by TEM. This kind of nanowire grows along the ⟨111⟩ direction, and the twin boundaries appear regularly with an average periodicity of 150 nm. The zigzag angle between two twinning nanounits is about 141° (i.e. twice the renowned (111) twining angle of 70.5° for fcc structure).

Experimental Section

About 6 g of ZnO and SnO mixed powders with weight ratio of 2:1 was positioned at the middle of a quartz boat, which was sent to the center of a quartz tube. Some substrates were placed downstream inside the tube. The substrates were 2−4 Ω n-type Si(100) wafers, onto which a layer of Au (about several tens of nanometers in thickness) was evaporated under high vacuum (2×10^{-5} Torr). The tube was then sealed and heated in a furnace at a rate of 10 °C/min to 1000 °C and kept at this temperature for 2 hours. During the experiment, a pure argon flow was introduced through the tube at a flow rate of 50 scccm and the pressure of the tube was sustained to 5×10^{-1} Torr. For transmission electron microscopy (TEM) examination, the powder samples of the as-synthesized Zn_2SnO_4 nanomaterials were dispersed in acetone using ultrasonic device. Acetone containing Zn_2SnO_4 nanowires was dropped to a holey carbon supporting carbon film (or microgrids). High-resolution TEM images and diffraction patterns were obtained by using Tecnai-F20 field-emission electron microscope operating at an accelerating voltage of 200 kV.

Results and Discussion

The as-synthesized products were first analyzed using a scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectroscopy (EDXS). Figure 1a shows a typical SEM image illustrating that the as-synthesized sample consists of a large quantity of nanowires and nanobelts with evidently different shapes. Certain nanowires identified as either regular or rhombohedra single crystals have been investigated in our previous work.[18] On the other hand, SEM observations also indicate that a large fraction of the nanowires in the as-grown products display remarkable periodic structural morphologies. The inset of Figure 1a shows an X-ray diffraction (XRD) pattern from a Zn_2SnO_4 sample. Most of the main sharp diffractions in the XRD spectrum can be well-indexed to a face-centered spinel-structured Zn_2SnO_4 with the space group of $Fd\bar{3}m$ and the crystal parameter of $a = 8.65$ Å. Some peaks corresponding to the residual ZnO also exists in this spectrum, as indicated by asterisks. Figure 1b shows the large magnification SEM image of a nanowire with a zigzag shape;certain contrast anomalies arising from planar defects can be recognized as parallel dark lines. This kind of nanowires in general has a diameter of about 100 nm with the length ranging from 10 to 20 μm. To get more information about the three-dimensional

* Corresponding author. Tel: +86-10-82649524. Fax: +86-10-82649531. E-mail: ljq@aphy.iphy.ac.cn.

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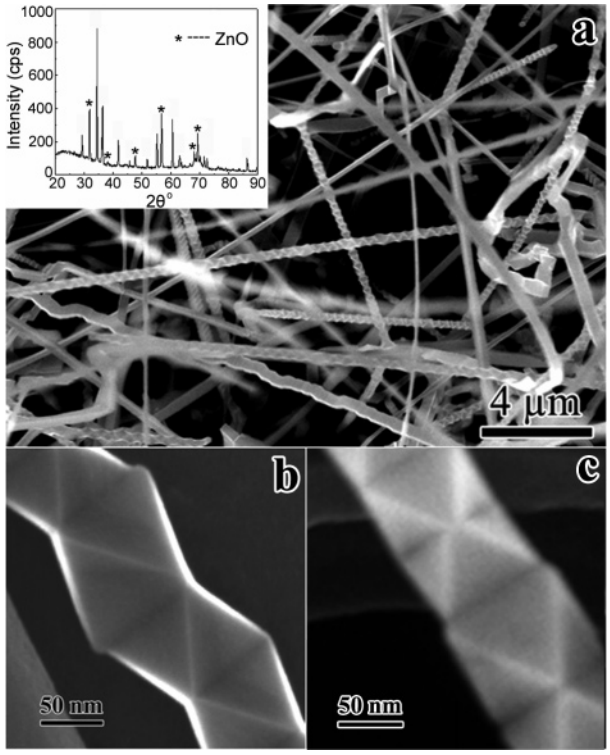

Figure 1. (a) SEM images show the morphology of the as-synthesized products. The inset displays an XRD pattern in which the diffraction peaks can be well-indexed by the fcc Zn_2SnO_4 and the residual ZnO. (b) High-magnification SEM image of a nanowire with a 100 nm diameter and pseudoperiodic structure. (c) SEM image of the other type of notable morphology after an anticlockwise tilting of about 30° from Figure 1b.

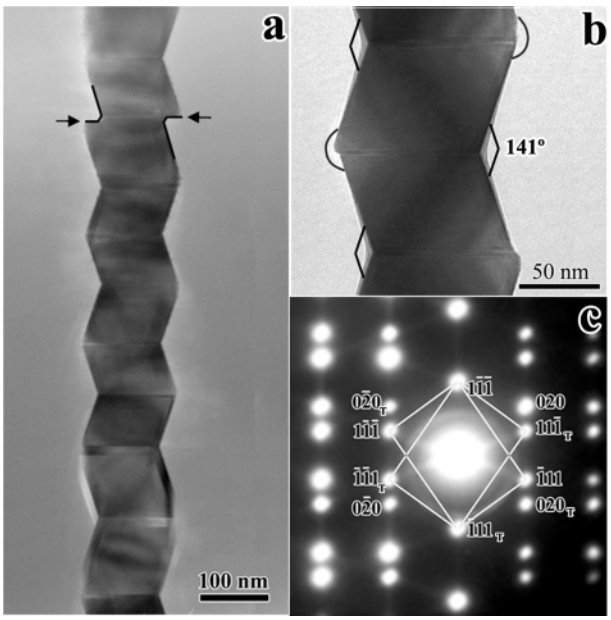

Figure 2. (a) TEM image of a Zn_2SnO_4 twinning nanowire showing the remarkable pseudoperiodic structure. A defective shift on a boundary is indicted by arrows. (b) TEM image of a local part of the Zn_2SnO_4 nanowire, clearly showing the twining turns. (c) Electron diffraction pattern showing the well-defined (111) twining relationship in a Zn_2SnO_4 nanowire.

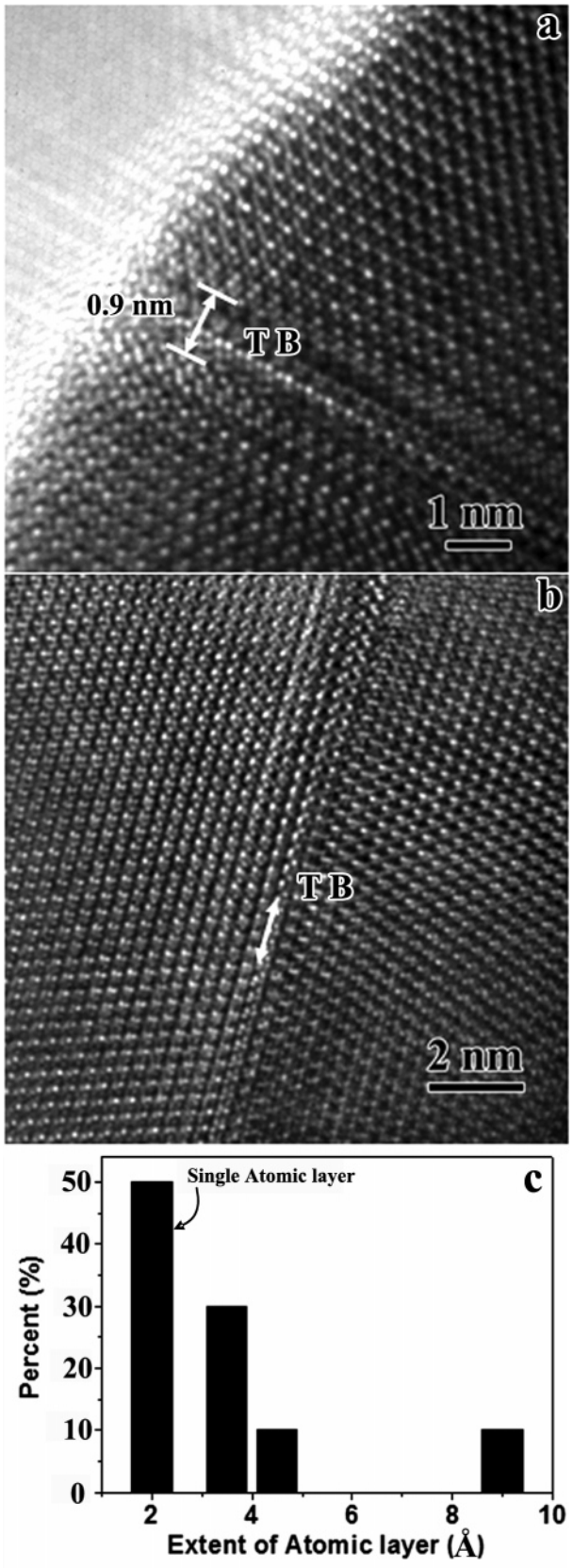

Figure 3. (a) A HRTEM image displaying a twinning boundary about 0.9 nm in the width. (b) A HRTEM image displaying a sharp twinning boundary. (c) The brief statistical data for thickness of the twin boundaries in this kind of nanowire.

structural feature of this nanowire, we tilted the wire anticlockwise about 30° round the long axis to another notable position. As shown in Figure 1c, this image again shows a clear pseudoperiodic contrast arising from planar defects. Actually, according to our experimental observations, this kind of nanowires has a marvelous, but complex, three-dimensional structure with remarkable symmetric properties. A systematical

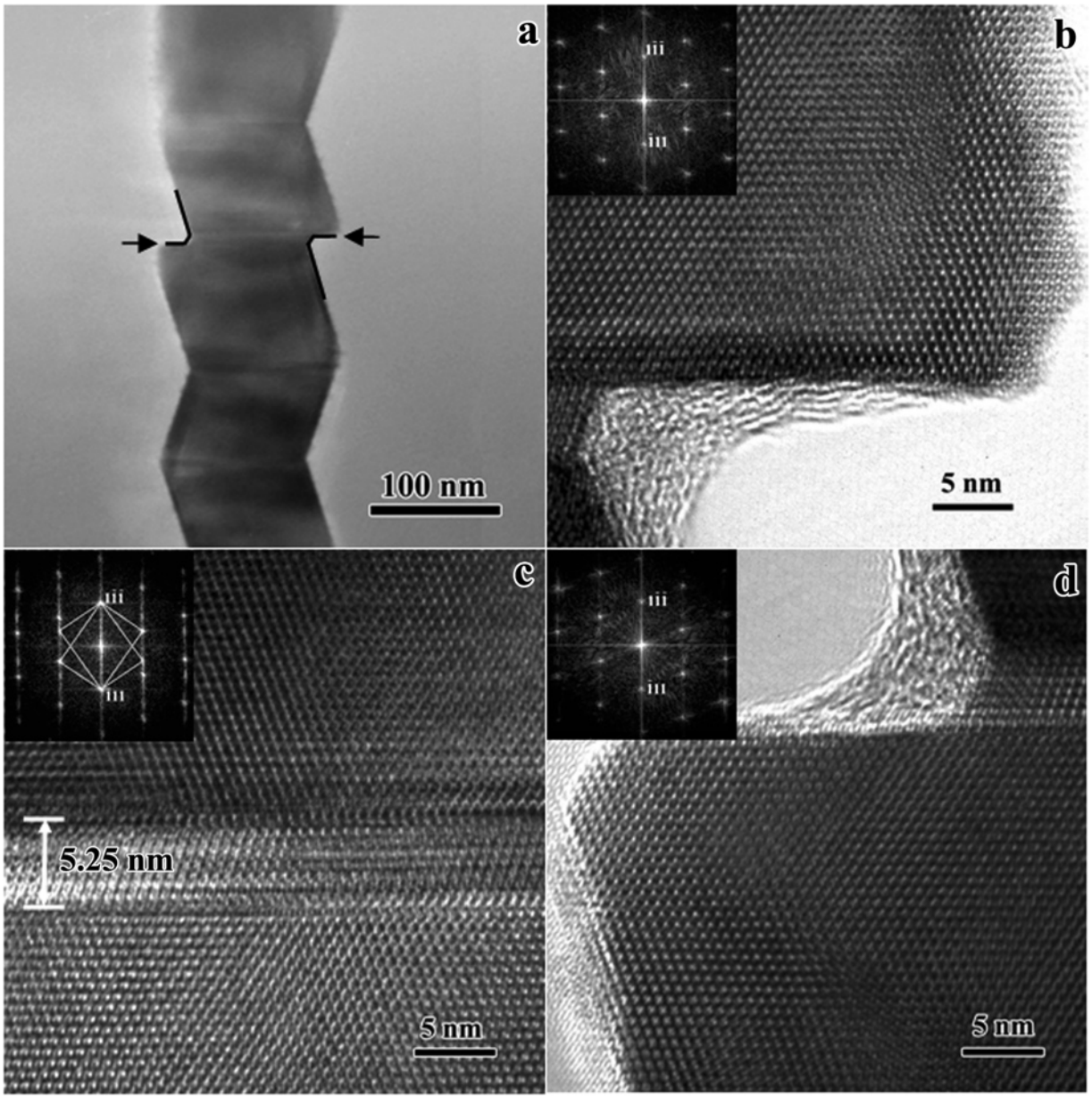

Figure 4. (a) TEM image shows a common type of defect structure in Zn_2SnO_4 nanowires. (b) HRTEM image and the FFT pattern (inset) of the right area of this dislocation. (c) HRTEM image of the defect structure showing the presence of a twining transition layer. (d) HRTEM image of the left area of the dislocation.

investigation for modeling the nanowire, by means of electron tomography, is still in progress. We herein will mainly discuss the typical periodic properties of the zigzag Zn_2SnO_4 nanowires observed along the direction as shown in Figure 1b.

To characterize the basic crystal structure and defects in connection with the pseudoperiodic morphology, we have carried out an extensive study on the as-synthesized samples. Figure 2a−c shows the bright TEM images and the corresponding diffraction pattern taken along the direction along which the zigzag structure features are clearly visible. The Zn_2SnO_4 nanowire shown in Figure 2a has a diameter of about 100 nm, and each subunit of the zigzag crystal has a parallelogram shape. The electron diffraction pattern shown in Figure 2c arises unambiguously from the (111) twinning structure commonly appearing in the fcc systems. All diffraction spots in present pattern can be easily indexed by twinned nanocrystals. The frequent and regular appearance of twins directly suggests that the (111) twins are energetically favorable in this kind of nanomaterial. The zigzag structures presented in Figure 2a,b result from the periodic appearance of twin boundaries; therefore, the growth of the nanowires is driven by the alternative appearance of different twining variants, as illustrated in Figure 2c. The turning points in general coincide with the twin boundaries and yield a series of parallelogram-shaped nanounits. The periodicity of this zigzag structure ranges from 150 to 250 nm as revealed in our experiments. Figure 2b presents the bright-field TEM images showing the morphologic properties of twin boundaries. It is known that the (111) twined crystals have a relative rotational angle of 70.5°; therefore, the inside zigzag angles as indicated by the broken lines can be given as 141°, in good agreement with the theoretical estimation. On the other hand, the outside turnings, as indicated by arc lines, depart obviously away from the twin boundary positions with an average distance of 3 nm, and structural defects and surface disorder are frequently visible in these areas. In addition to the twining structure, a notable structural feature shows up as a clear shift between the neighboring subunits at the twin boundaries commonly appearing in this kind of nanowire (see

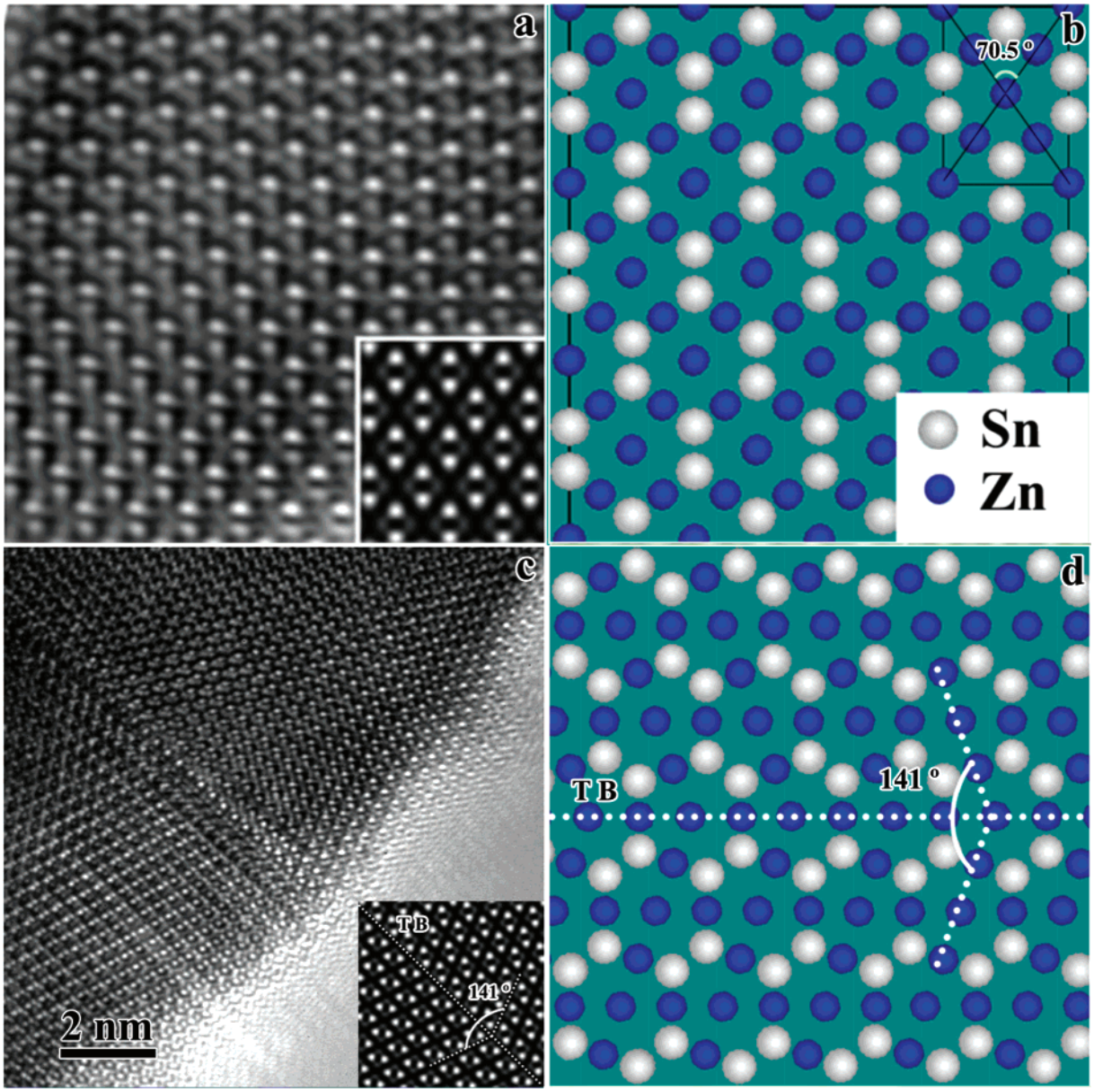

Figure 5. (a) HRTEM image displaying clearly the atomic structure in the (011) plane. The inset shows a HRTEM simulation image in good agreement with the experimental one. (b) A schematic structural model showing the arrangement of Sn and Zn atoms in a single fcc Zn_2SnO_4 crystal; white dots represent Sn atoms, while black dots denote Zn atoms. O atoms are omitted. (c) HRTEM image of a twinning boundary. The inset is the theoretical simulation image. (d) A structural model of a sharp twin boundary showing the Zn atoms on the twin boundary.

the arrow in Figure 2a). This phenomenon is considered to be important for understanding the formation of twining structure and the growth of nanowires as discussed below.

Figure 3a,b presents the high-resolution TEM images showing the distinct properties of twin boundaries in the nanosystem. Certain boundaries as typically illustrated in Figure 3a are not very sharp with a clear transition region of ~0.9 nm in width. This kind of extended twin boundaries exhibits remarkable lattice distortion on the boundary vicinities. Figure 3b shows a sharp twin boundary obtained from a thin area, demonstrating the well-defined twining relationship and the well-coherent lattice cross the boundary. On the basis of our TEM observations, we summarized briefly our statistical result as seen in Figure 3c on the boundary widths. It is apparent that most boundaries have a width from 0.2 to 0.4 nm showing up as sharp twin boundaries. About 50% of the twin boundaries contain incoherent lattice structure without clear interfaces. Careful analysis indicated that the local structure on the extended boundary can be well-understood by a distorted fcc structure. No other interfacial phases are observed in our experiments.

We now go on to discuss the local structure of the areas with the evident shift between subcrystals. Figure 4a shows a bright field TEM image of the area with a clear displacement. Careful examinations suggest that there is a very narrow transition layer, and the up-unit and the down-unit keep the same directional parallelogram morphologies. Figure 4b shows the local HRTEM image of the up-unit, and the inset is the FFT pattern, which is consistent with the diffraction pattern of the single crystal (011) plane in the fcc system. Figure 4c is the HRTEM image demonstrating the presence of a transition layer with a thickness of about 5.2 nm. The FFT pattern (see the inset) reveals a well-defined twinning relationship in this local area. The local enlarged HRTEM image of the down-unit is shown in Figure 4d, and the FFT pattern in the inset exhibits totally similar structural features as in Figure 4b. Hence, the evident shift between two subcrystals arises from the presence of the

undersized transition twining units with an average thickness of a few nanometers.

To understand the atomic structural feature nearby the twin boundaries, we have further performed a theoretical analysis in comparison with experimental observations. Figure 5a shows a HRTEM image with a large magnification clearly displaying the atomic structure of the spinel Zn_2SnO_4 crystal projected along the [110] zone axis direction. The simulated image is obtained for the sample thickness of 18 nm and the defocus value of 110 nm, which gives rise to the Sn atoms positions as white dots and Zn atoms as dark contrast. Sn atoms form a diamond structure, while Zn atoms compose tetrahedra. The simulated HRTEM image superposed in Figure 5a is in good agreement with the experimental one. Figure 5b shows the schematic structural model of the fcc spinel Zn_2SnO_4 projected along the [110] direction; the cross angles of two lines of Zn atoms is 70.5°. To facilitate the comparison, only Zn and Sn atoms are presented in the structural model. Figure 5c shows a HRTEM image obtained from a thin area in a Zn_2SnO_4 nanowire with a clear twin boundary, and the inset is the theoretical simulation result based on the structural model of Figure 5d. Carefully examining the experimental image for the twin boundaries, we suggest that the twin boundary is localized on the Zn atomic plane, as illustrated in the structural model present. The Zn atom layers cross the boundary, exhibiting a 141° twinning angle, consistent with our experimental observations.

Conclusions

Ternary Zn_2SnO_4 nanomaterials synthesized by the thermal evaporation method consist of numerous kinds of nanowires. A remarkable type of Zn_2SnO_4 nanowire, as demonstrated by TEM observations, shows a pseudoperiodic twinning structure. These nanowires, with the diameter of about 100 nm, grows along the ⟨111⟩ direction with notable periodic morphologies. Systematical experimental analyses suggest that a large fraction of the (111) twin boundaries are extended to a thickness of a few nanometers. High-resolution TEM study in combination with theoretical simulation demonstrates that the twining plane in general is localized on the Zn atom layer. It should be emphasized that the presence of regular twinning structure might induce certain specific physical properties in this nanomaterial that are desirable in forthcoming technologic applications.

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