

Spontaneous growth and luminescence of zinc sulfide nanobelts

Ying-Chun Zhu,^{a)} Yoshio Bando, and Dong-Feng Xue

Advanced Materials Laboratory, National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan

(Received 18 November 2002; accepted 21 January 2003)

ZnS nanobelts have been synthesized by a simple thermal evaporation method in a N₂ atmosphere containing a small amount of CO and H₂ gases. The synthesized ZnS nanobelts have a width in the range of 40 to 120 nm, a thickness of 20 nm, and a length of several micrometers. The nanobelts are single crystals with a hexagonal wurtzite structure growing along the [001] direction. A vapor–solid process is proposed for the formation of such nanobelts. The as-prepared nanobelts shows two emission bands, around 450 and 600 nm. © 2003 American Institute of Physics.
[DOI: 10.1063/1.1562339]

Zinc sulfide, as a II–IV semiconductor with a band-gap energy of 3.6 eV,¹ has been extensively studied due to its wide applications as phosphors and catalysts. Zinc sulfide as a famous luminescence material shows various luminescence properties, such as photoluminescence (PL),² electroluminescence,³ mechanoluminescence,⁴ acoustic-luminescence,⁵ and thermal luminescence,⁶ which enable wide applications in the fields of displays, sensors, and lasers. Moreover, zinc sulfide is also widely used in photocatalysis.^{7–9} It is reported that ZnS is an effective catalyst for the photo-oxidation and photoreduction of a series of organic substrates.^{7,8}

As is well known, nanoscale semiconductor materials show interesting properties, and great effort has been made to control their sizes, morphologies, and crystallinity in order to tune their physical properties. Besides the zero-dimensional nanoparticles, various structures, such as nanotubes, nanorods, nanowires, and nanobelts, have been achieved from different materials,^{10–13} of which ZnS is one of the widely studied materials. Many attempts have been made to prepare zero-dimensional zinc sulfide. ZnS nanocrystallites have been generally synthesized using colloid chemistry methods, and different particles have been obtained by controlling the reaction conditions, such as the precursor's concentration, the nature of solvents, capping and stabilizing agents.^{14–17} However, there are only few reports on the preparation and characterization of one-dimensional (1-D) ZnS nanostructures.^{18–20} ZnS nanowires have been synthesized by using a template method¹⁸ and by using a silicon substrate with an Au catalyst through a thermal evaporation process.¹⁹ ZnS rods with a diameter of 300 nm have been obtained by the chemical conversion of zinc oxide in the sulfur vapor and H₂S atmosphere.²⁰ ZnS nanobelts have not yet been synthesized so far. In this letter, we report the preparation, structural characterization, and the PL property of zinc sulfide nanobelts obtained from zinc sulfide powders by a simple thermal evaporation process.

A rf induction furnace was used for the synthesis of ZnS nanobelts. Graphite powders and fibers were put into a

graphite crucible with a diameter of 2 cm and a length of 15 cm, above which a graphite disk with zinc sulfide powders was arranged. Some B–N–O powders²¹ were put onto the graphite powders in order to increase the reduction atmosphere. All the components were enclosed in a graphite susceptor, and the susceptor was put in the center of the furnace with a flowing N₂ atmosphere (1.5 l/min.) The temperature of the susceptor was controlled to ensure that graphite powders were heated to 1600 °C, while the zinc sulfide powders were heated to 1150 °C. The N₂/H₂O stream (obtained from bubbling N₂ through distilled water) was managed to pass through and react with the graphite powders at 1600 °C for the generation of CO and H₂ gases. Next, the N₂ stream, together with the CO and H₂ gases, passed through zinc sulfide powders. After the process was conducted for 1.5 h, the furnace was cooled down. At the cooling stage, the N₂/H₂O stream was stopped, but the N₂ flow lasted until the furnace cooled down to room temperature. After the synthesis, a white product was formed on the surface of zinc sulfide precursors. After the product was dispersed into ethanol, it was transferred onto a copper mesh. The specimen was then characterized using a JEM-3000F (JEOL) field-emission high-resolution transmission electron microscope (HRTEM) operated at 300 kV, which was attached with an energy dispersive x-ray spectrometer (EDS). PL measures were taken at room temperature using a He–Cd laser line of 325 nm as the excitation source.

The TEM analysis shows that as-prepared products have a strip-shaped structure with widths from 40 to 120 nm and lengths of several micrometers. Figure 1(a) shows the arrays of zinc sulfide nanobelts. The representative TEM image of a single nanobelt [Fig. 1(b)] reveals that the nanobelt has a thickness of 20 nm and a width of 50 nm. The thickness-to-width ratio of the nanobelt is about 1:2.5. The nanobelt has a perfect morphology, as can be seen from its sharp edges, indicated by arrows in Fig. 1(a). The EDS analysis shows that the sample is composed of Zn and S elements, as illustrated in the inset of Fig. 1(b), where Cu peaks were generated from the supporting Cu meshes.

Figure 2 shows the HRTEM image and electron diffraction (ED) pattern of a straight ZnS nanobelt [Fig. 2(a)]. The ED pattern [inset, Fig. 2(b)] was taken from the nanobelt

^{a)}Author to whom correspondence should be addressed; electronic mail: yczhu2010@yahoo.com.cn

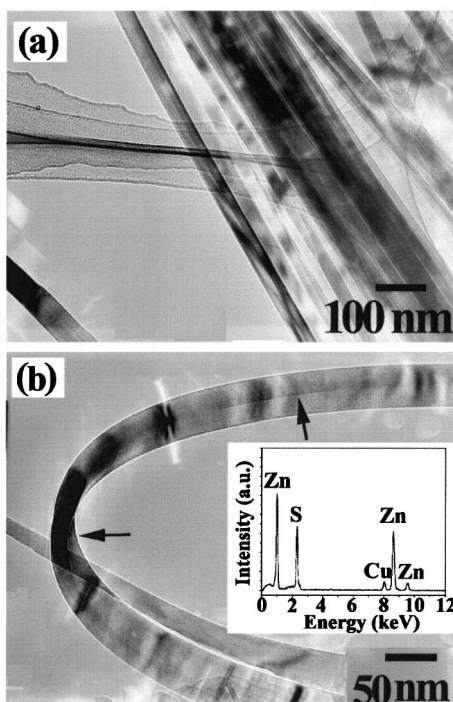


FIG. 1. TEM morphology of ZnS nanobelts. (a) Arrays of nanobelts. (b) A typical TEM image of a single nanobelt. Inset in (b) is the EDS spectrum of the nanobelts.

shown in Fig. 2(a). The ED pattern can be indexed as a hexagonal wurtzite phase with lattice constants of $a = 0.38$ nm and $c = 0.62$ nm, recorded from $[010]$ zone axis. The measuring d -spacings of (100) and (001) planes are 0.33 and 0.62 nm, respectively, which are consistent with the ideal values of wurtzite ZnS (JCPDS Card: 36-1450). The axis direction of the as-prepared ZnS nanobelts is generally along $[001]$, as confirmed by the ED pattern and HRTEM image. The perfect diffraction pattern and lattice fringes [Fig. 2(b)] indicate that the nanobelt is a single nanocrystal.

A vapor–solid mechanism is proposed for the formation of ZnS nanobelts. ZnS powders evaporated into vapors during the heating process. The temperature of the ZnS precursor was controlled just below the sublimation point of ZnS ($\approx 1180^\circ\text{C}$), so that ZnS vapor can be solidified again on the precursor's surface. Nanobelts then nucleated and elon-

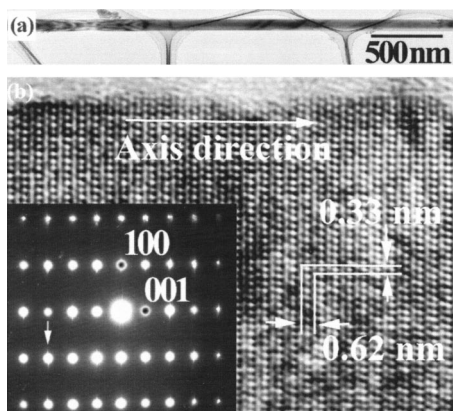


FIG. 2. TEM and HRTEM images of ZnS nanobelt. (a) TEM image of a straight nanobelt. (b) HRTEM image of the nanobelt in (a). The inset in (b) is its ED pattern with $[010]$ incidence.

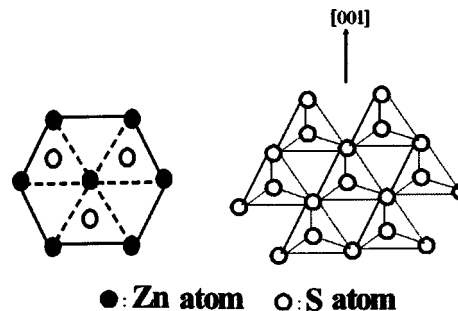


FIG. 3. Crystal lattice and the stacking of $\{\text{ZnS}_4\}$ tetrahedra in $[001]$.

gated along the $[001]$ direction. The growth axis of the nanobelts is consistent with its crystallographic characteristics. As shown in Fig. 3, the hexagonal ZnS crystal can be regarded as a stacking of $\{\text{ZnS}_4\}$ tetrahedra by sharing their common corners. The growth direction of ZnS crystal is determined by the relative stacking rate of the constituent tetrahedra in various crystal faces, and the stacking rate is strongly dependent on the bonding force of atoms in the tetrahedra at the interface. The atom at the corner of a tetrahedron has the strongest bonding force ($s = 2$ v.u.) comparing with the atoms at other positions.^{22,23} As for the interface of ZnS, each tetrahedron has a corner in $[001]$ direction, which favors the growth of ZnS nanobelts along $[001]$ axis.

The atmosphere is an important factor for the formation of ZnS nanobelts. Recently, there have been some reports on the preparation of ZnO nanowires and nanobelts by thermal reaction methods.^{24–28} However, very few reports can be found on ZnS nanowires and no report can be found on ZnS nanobelts, although ZnS has the same structure as ZnO. The problem in preparing 1-D ZnS nanostructures is that ZnS is easily oxidized into ZnO at high temperatures, even at an inert atmosphere with traces of oxygen. An inert gas with a high purity and a tightly sealed apparatus are needed to prevent ZnS from being oxidized at high temperatures.²³ When reductive agents are used, Zn nanobelts and wires are obtained.^{27,29} In this work, the atmosphere was controlled by mixing N_2 with a small quantity of reductive agents CO and H_2 produced from the reaction between C and H_2O steam. In the special atmosphere, ZnS nanobelts were prepared during the heating process.

The PL of ZnS nanobelts presents two emission bands around 450 and 600 nm, as shown in Fig. 4. The emission band around 450 nm is associated with defect-related emis-

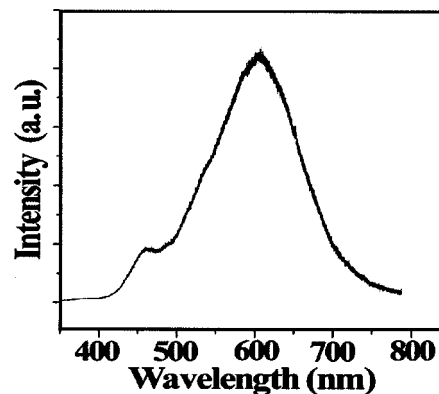


FIG. 4. Luminescence spectrum of ZnS nanobelts.

sion of the ZnS host.^{30–32} The strong orange emission around 600 nm should be assigned to the emission from traces of Mn²⁺ impurity, which is incorporated during the synthesis process. Mn²⁺-doped ZnS shows the orange emission originating from the transition between ⁴T₁ and ⁶A₁ states of Mn²⁺ impurity sites.^{6,7} ZnS is a widely used phosphor, and the role of ZnS is mainly as a host, absorbing energy and transferring the excited electron to the dopants, from which the emission with various colors occurs. The defect-related emission of the ZnS host is not strong, as can be seen in Fig. 4 and often cannot be observed in the doped case.³

In summary, ZnS nanobelts were synthesized by heating ZnS powders in N₂ atmosphere with a small amount of CO and H₂. The as-prepared ZnS nanobelts have a hexagonal wurtzite structure and grow along the [001] direction. The formation of these nanobelts is a spontaneous growth process through the evaporation of a precursor followed by the nucleation and growth. The PL of the nanobelts shows a weak emission band at 450 nm and a strong emission band around 600 nm.

This work was supported by the Japan Science Promotion Society (JSPS) fellowship at the National Institute for Materials Science, Tsukuba, Japan.

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