Ultrafine ZnS Nanobelts as Field Emitters**

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1D nanostructures, such as nanotubes,[1] nanowires,[2] and nanobelts,[3] have become of interest because of their potential value for leading to an understanding of fundamental physical concepts and constructing nanoscale electric and optoelectronic devices.[4] ZnS, an important semiconductor compound of the II–VI group, has a wide band gap energy of 3.7 eV (1 eV = 1.602 × 10–19 J) at 300 K. ZnS is one of the first semiconductors discovered and probably one of the most important materials in the electronics industry.[5] Recently, various ZnS 1D nanostructures have successfully been synthesized.[6] Among them, ZnS nanobelts are one of the most interesting objects. Nanobelts of different widths, ranging from tens of nanometer to several micrometers, have been prepared and studied in detail.[7] Ultrafine ZnO nanobelts proved to be of particular interest for the general study of size-induced electrical and optical properties of functional oxides.[8] Thus the synthesis and novel property exploration of ultrafine ZnS nanobelts are indispensable. However, large-scale ZnS nanobelt synthesis, especially for small (width < 20 nm) belts, is still a challenge.

In this communication, we describe the synthesis of ultrafine ZnS nanobelts by controlling evaporation and agglomeration rates. The range of the belt widths was 5–30 nm, and peaked at 10–20 nm. The belt thickness varied with width and was typically of only several nanometers. The regarded ultrafine ZnS nanobelts not only showed a pronounced quantum-confinement effect (a blue-shift of ca. 0.45 eV compared to bulk ZnS materials), but also possessed good field-emitting characteristics: a low turn-on field of 3.47 V/μm and a high field-enhancement factor (over 2000). Although the work function of ZnS (7.0 eV) is larger than that of Si (5.6 eV), AlN (3.7 eV), SiC (4.0 eV), C nanotubes (5 eV) or ZnO (5.3 eV), the field-emission (FE) properties of the present tiny ZnS nanobelts are comparable or even better than those of many other 1D nanostructures because of a characteristically high aspect ratio. Therefore, ultrafine ZnS nanobelts may be attractive as field emitters and highly useful in novel nanoscale electric and optoelectronic devices.

Figure 1 shows FE scanning electron microscopy (SEM) images of the as-grown nanobelts. A low-magnification SEM image in Figure 1a reveals that the nanobelts are several to tens of micrometers in length. The corresponding high-magnification SEM image in Figure 1b shows that each nanobelt has a uniform width over its entire length. The typical belt width is in the range of 10–20 nm. A high-magnification SEM image in Figure 1c clearly indicates that a product exhibits numerous beltlike structures. Figure 1d and e shows typical high-magnification SEM images of individual nanobelts. An X-ray diffraction (XRD) pattern from the product is shown in Figure 1f, where all the diffraction peaks can be indexed to wurtzite-type ZnS with lattice constants of a = 0.382 nm and c = 0.626 nm (Joint Committee for Powder Diffraction Studies (JCPDS) Card: 36-1450). By using electron-beam irradiation in SEM, we found that the nanobelts were very sensitive to an electron beam. Figure 1S, Supporting Information, depicts nanobelt SEM images after electron-beam irradiation. Clearly, the nanobelt width increased with an increase in irradiation time.

High-resolution transmission electron microscopy (HRTEM; using a JEM-3000F high-resolution transmission electron microscope) was used to further characterize the beltlike product. By measuring over 100 nanobelts, we confirmed that the typical width of the belts is in the range of 5–30 nm and peaked at 10–20 nm. Figure 2a and b show typical belt TEM images. Very narrow nanostructures were observed, less than 20 nm in width. It can also be seen that a thin amorphous carbon layer coats the side belt surfaces, as marked in Figure 2d and e. Figure 2c is an enlarged image from the area e marked in Figure 2b. All nanobelts are single-crystalline. The smallest width of ZnS nanobelts was measured as 7.5 nm (Fig. 2c). This particular nanobelt is likely to be very thin (ca. 1–2 nm). In fact, we could easily see the lattice fringes for the nanobelt laid behind, as shown in Figure 2c. The nanobelt thickness (Fig. 2d) is likely to be only four atomic layers, as indicated by the arrows in Figure 2c. The nanobelts are easily curled. Figure 2d and e are lattice-resolved HRTEM images taken from individual nanobelts of 9 and 10 nm width, respectively. The marked interplanar d-spacings of 0.31 and 0.33 nm correspond to the (002) and (010) lattice planes of wurtzite ZnS. From Figure 2c–e, it is

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[** This work was supported by the Japan Society for the Promotion of Science (JSPS), in the form of a fellowship tenable at the National Institute for Materials Science, Tsukuba, Japan (X.S.F.). The authors also thank Ms. E. Arisumi, Mr. Y. Uemura, Dr. M. Mitome, Dr. Q. Huang, Dr. R. Z. Ma, and Dr. L. Li for their cooperation and kind help. Supporting Information is available online from Wiley InterScience or from the author.]

DOI: 10.1002/adma.200700078
clear that ZnS nanobelts grew along the [001] direction, and typically had no defects, for example, stacking faults and dislocations. Rarely, stacking faults perpendicular to the growth direction were seen, as shown in Figure S2, Supporting Information. It has been suggested that these stacking faults release the internal stresses.[8,9]

The question arises as to how ultrafine ZnS nanobelts are formed. The key point is a control of the evaporation and agglomeration rates. We used a mixture of commercial ZnS, C, and S powders as precursors instead of the previously adopted pure ZnS powders or nanopowders.[7c,10] The evaporation rate would be very fast if pure ZnS powders or nanopowders are used as precursors within a high-temperature zone. This would result in numerous nucleation centers and fast agglomeration rates in a relatively low temperature zone. So, relatively thick and wide ZnS nanobelts have usually been formed. By contrast, here, we carefully controlled the evaporation and agglomeration rates. First, the ZnS powders and C nanopowders underwent a reaction: $2\text{ZnS} + \text{C} \rightarrow 2\text{Zn} + \text{CS}_2$, to gradually produce a Zn vapor.[2b,11] The Zn vapor reacted with the S vapor to form nanobelts at a relatively moderate temperature (ca. 1000 °C).[12] Superfluous C gas was also transferred to the relatively low-temperature zone and absorbed on the as-grown ZnS nanobelts, blocking the belt width and thickness development more effectively than its length development, because the growth along the [001] direction for ZnS nanobelts is fastest and easiest (according to the growth kinetics). This leads to ultrafine ZnS nanobelt formation.

Figure 3 shows a UV-vis absorption spectrum taken from the present nanobelts. It is known that the relationship between the absorption coefficient ($a$) near the absorption edge and the optical bandgap ($E_g$) for direct interband transitions obeys the following formula[13]

$$(ahv)^2 = A(hv - E_g)$$

(1)

where $A$ is the parameter that relates to the effective masses associated with the valence and conduction bands, and $hv$ is the photon energy. Hence, the optical band gap for the absorption edge can be obtained by extrapolating the linear portion of the plot $(ahv)^2$–$hv$ to $a=0$ from Figure 3. The optical absorption in the edge region can be well-fitted using a relation $(ahv)^2 \sim (hv - E_g)$, as shown in the inset, which indicates that the present nanobelts have a band gap of 4.15 eV, which is blue-shifted (to ca. 0.45 eV) compared to a bulk ZnS material (3.7 eV).[9b] This implies that the belts display a notable quantum-confinement effect. The Bohr diameter of bulk ZnS materials is ca. 5 nm.[9b] The typical thickness of the nanobelts synthesized here is likely to be of several nanometers, which is comparable with the Bohr diameter of bulk ZnS materials.

FE measurements show that the ultrafine ZnS nanobelts are decent field emitters. It is noted that to date, there has only been a single paper devoted to the FE of ZnS nanobelts.[14] The present FE measurements were performed in a vacuum chamber at a pressure of $4.6 \times 10^{-6}$ Pa. A rodlike aluminum probe with a cross section of 1 mm$^2$ was used as an anode and an ultrafine ZnS nanobelt film served as a cathode. A dc voltage sweeping from 100 to 1100 V was applied to the

Figure 1. Structure and morphology of ultrafine ZnS nanobelts. a) Low-magnification SEM image. b) High-magnification SEM image showing a rather uniform belt size. c) High-magnification SEM image verifying a beltlike structure. d,e) High-magnification SEM images of individual nanobelts. f) X-ray diffraction (XRD) spectrum taken from the nanobelts.
The gap between the anode and the cathode was set at 200 \( \mu \)m. Figure 4 shows the FE current density, \( J \), as a function of the applied field, \( E \), for a \( J-E \) plot (Fig. 4a) and a \( \ln(J/E^2)-(1/E) \) plot (Fig. 4b). From Figure 4, a turn-on field is extrapolated as ca. 3.47 V \( \mu \)m\(^{-1} \) at a current density of 10 mA cm\(^{-2} \). The emission current density reached ca. 11.5 mA cm\(^{-2} \) at a macroscopic field of 5.5 V \( \mu \)m\(^{-1} \). The data suggest that the present nanobelts are highly valuable field emitters that rival previously reported ZnO, ZnS, Si, SiC, and AlN nanowires/nanobelts and C nanotubes.\(^{[14,16]} \)

The FE current–voltage characteristics can be expressed by a simplified Fowler–Nordheim equation.\(^{[16b,17]} \)

\[
J = (A\beta^2E^2/\phi)\exp(-B\phi^{3/2}/\beta E)
\]

or

\[
\ln(J/E^2) = \ln(A\beta^2/\phi) - B\phi^{3/2}/\beta E
\]

where \( A = 1.54 \times 10^{-6} \) A eV \(^{-2} \), \( B = 6.83 \times 10^{3} \) eV\(^{-3/2} \) V \( \mu \)m\(^{-1} \), \( \beta \) is the field-enhancement factor, and \( \phi \) is the work function of the emitting materials, which is 7.0 eV for ZnS.\(^{[18]} \)
The field-enhancement factor, $\beta$, is related to emitter geometry, crystal structure, and the spatial distribution of emitting centers. For example, it has been demonstrated that the field-emission performance of ZnO nanowires can be significantly enhanced through decreasing the density of the nanowires, and increasing the aspect ratio (length-to-thickness ratio) of ZnO nanobelts.\[3\] The length of ultrafine ZnS nanobelts is up to several or tens of micrometers, whereas their thickness is likely to be only several nanometers. Therefore, it is logical to several or tens of micrometers, whereas their thickness is calculated from a slope of the fitted straight line in Figure 4b.

In summary, single-crystalline, narrow-size-distribution, ultrafine ZnS nanobelts, revealing a notable quantum-confinement effect, have been synthesized at a high yield by controlling the evaporation and agglomeration rates during the synthesis. A typical width of the belts is in the range of 5–30 nm, being peaked at 10–20 nm. The belt thickness is likely to be only several nanometers. UV-vis absorption spectra were recorded in reflectance mode using a Hitachi U-4100 spectrophotometer. FE measurements were conducted in a vacuum chamber at a pressure of 4.6 × 10^-5 Pa at room temperature.

Received: January 10, 2007
Revised: March 15, 2007
Published online: August 9, 2007