

## Crystal Orientation-Ordered ZnS Nanowire Bundles

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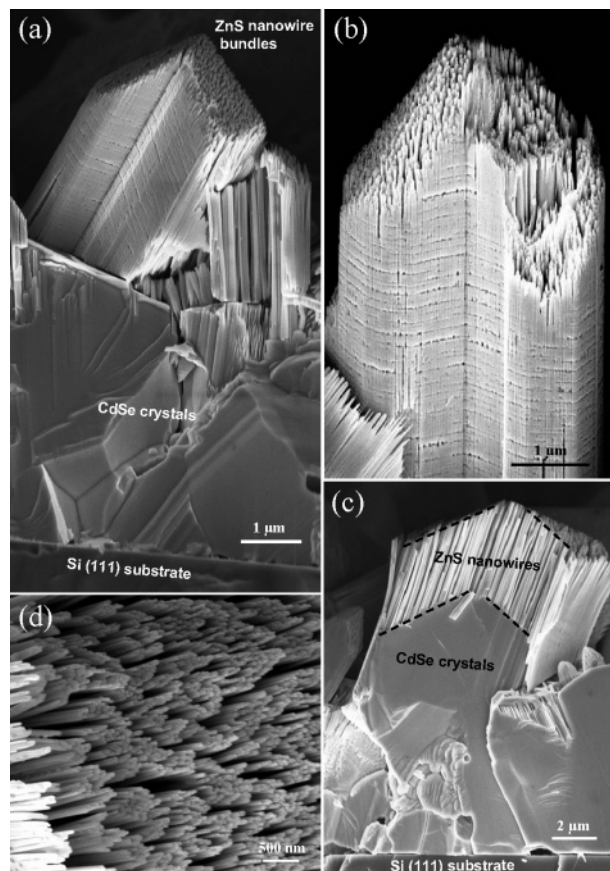
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Due to their potential applications, ranging from nanoscale electronic devices to tools for biomedical applications, one-dimensional semiconductor nanostructures, such as nanowires and nanobelts, offer a high degree of interest for furthering the current state of nanotechnology research and development. Nanorods,<sup>1</sup> nanowires,<sup>2</sup> nanotubes,<sup>3</sup> and nanobelts<sup>4</sup> of various materials have been successfully synthesized, and they demonstrate novel luminescent, electronic, optical, and mechanical properties.

ZnS is a direct wide band gap (3.91 eV) compound semiconductor that has a high index of refraction and a high transmittance in the visible range and is one of the most important materials in photonics research.<sup>5</sup> As a one-dimensional nanostructure, ZnS has been synthesized as nanowires, nanobelts, and nanocombs, but these nanostructures are randomly distributed on the surface of the substrate.<sup>6,7</sup> For applications in photonics, it is needed to create ZnS nanostructures that are highly aligned and ordered, but this type of structure has not been realized experimentally. In this paper, we report a novel approach for growing aligned and *orientation-ordered* ZnS nanowires. Our method relies on a buffer layer of CdSe grown on a Si(111) substrate, on which ZnS nanowires are grown. The growth process of the nanowire bundles is presented. The technique demonstrated could be an effective pathway for growing patterned, aligned, size-controlled, and orientation-ordered ZnS nanowires.

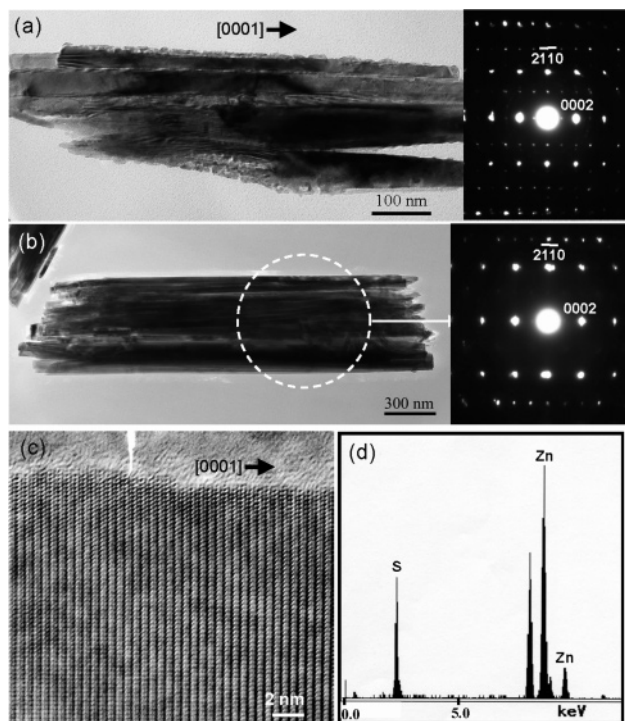
The orientation-ordered ZnS nanowire bundles were synthesized through a two-step thermal evaporation process in a horizontal tube furnace. Commercially available CdSe powder (Alfa Aesar, 99.995% purity, metal basis) was placed in the center of a single-zone tube furnace (Thermolyne 79300). A vacuum was pulled into the tube for several hours to purge oxygen from the chamber. After evacuation to less than  $2 \times 10^{-2}$  Torr, the temperature in the center of the tube was elevated to 750 °C at a rate of 30°/min. A nitrogen (N<sub>2</sub>) gas flow was introduced into the system at a rate of 50 sccm. The gas acted as a carrier for transporting the sublimated vapor to cooler regions within the tube furnace for deposition. The pressure was maintained at 300 mbar. The silicon substrates reached a temperature of about 575 °C. After 1 h, the furnace was allowed to cool. Then, the source material of CdSe powder was replaced by commercially available ZnS powder (Alfa Aesar, 99.99% purity, metal basis). The temperature in the center of the tube was elevated to 1050 °C. Again, a nitrogen gas flow was introduced at 50 sccm, and the pressure was maintained at 300 mbar. The silicon substrates reached a temperature of about 750 °C. The system was held in this condition for a period of 60 min. Single-crystal silicon substrates were used for synthesizing the nanostructures. These substrates were placed downstream from the source material to collect the deposited nanostructures.

The sample was analyzed on a scanning electron microscope (SEM). The deposited material has an extremely high yield on the substrate and shows high reproducibility. The deposited material in the as-synthesized sample has a dominant morphology consisting of “bundles” of wire-shaped ZnS nanostructures (Figure 1a,b). All



**Figure 1.** (a) SEM image of ZnS nanowire bundles grown on a CdSe substrate that was first deposited on Si(111). The CdSe is a solid film, but the ZnS is a bundle of aligned nanowires. (b) Enlarged SEM image of a ZnS bundle showing traces created due to fluctuation in growth condition, presenting the equal growth rate of all of the nanowires. (c) Fractured surface of the sample showing the direct growth of ZnS nanowires on the CdSe crystals and the preservation in the ZnS nanowire bundles of the surface morphology of the CdSe crystal. (d) Enlarged top view of the aligned ZnS nanowires.

of the nanowires are orientationally aligned, and they grow uniformly along the bundle. Energy dispersive X-ray microanalysis (EDS) found that the ZnS nanowires grow on top of a layer of CdSe film, which is a buffer layer between the Si(111) substrate and the nanowires. Each bundle preserves a fairly good facet structure (Figure 1a,b), as if they are a single entity. SEM examination of a fractured cross-section indicates that the top morphology of the ZnS nanowire bundle preserves the shape of the top of the CdSe crystal (Figure 1c), indicating the equal growth rate of all the nanowires. This result also shows that the ZnS nanowires were initiated at the top surface of CdSe crystal, and that they are spatially distributed following the surface of CdSe. Each individual nanowire is clearly identified. A top view of the



**Figure 2.** (a and b) Low-magnification TEM images of bundles of aligned ZnS nanowires and the corresponding electron diffraction patterns from the bunches showing orientation ordering among the [0001] nanowires. (c) High-resolution TEM image of a nanowire showing uniform lattice structure. (d) EDS of ZnS nanowires showing the chemical composition.

as-grown nanowire bundles clearly shows their vertical alignment as well as a high degree of size uniformity and a high density (Figure 1d).

Transmission electron microscopy shows that the individual nanowires are single-crystal wurtzite ZnS, with trace amounts of CdSe possibly interspersed within the lattice. From the diffraction pattern recorded from a bundle (Figure 2a,b), the single-crystal pattern clearly indicates the orientation alignment among all of the nanowires in the bundle along [0001], and they share the same side surface of (2-1-10) and a top surface of (01-10). The nanowires are aligned not only in length direction but also in crystallography orientation. This is a key characteristic of the sample. High-resolution images of an individual wire confirm that each nanowire is single crystal and that the *c* direction is the fastest growth direction (Figure 2c). There are no dislocations observed in the volume of the nanowire. EDS spectrum taken in the TEM shows that the wires are ZnS (Figure 2d) with negligible signals from CdSe.

The nanowire bundles are formed by a two-step growth process as a result of the two-step synthesis procedure. In the first step, the CdSe thin film grows on the silicon (111) substrate. The [0001]-oriented CdSe has a 6-fold-symmetric *a*-plane, {10-10}, with an interplanar distance of 0.3724 nm, which matches well to the 6-fold-symmetric Si(111) substrate, with an interplanar distance 0.3839 nm, resulting in a *c*-axis-oriented growth of CdSe on Si(111). Due to a larger lattice mismatch, single-crystal thin films are not grown, but rather, multiple nucleation of CdSe results in the growth of a polycrystalline CdSe film. In the second step, the CdSe film serves as a substrate for epitaxial growth of the ZnS nanowires. Because both CdSe and ZnS have wurtzite structure, an epitaxial growth

along the *c*-axis would be preferred to minimize the interface lattice mismatch. All of the nanowires have the same growth rate so that the morphology of the CdSe crystal is preserved (see Figure 1c). All of the aligned nanowires in one bundle are synchronized in response to the growth condition; the topographical shape of the CdSe nanocrystal is maintained as the wire-bundle grows. The bundles also maintain the width and depth profile of the CdSe crystal upon which the wires are originated. The end result is that the nanowire bundles exhibit the same morphology characteristics that larger wurtzite nanocrystals would, including the 6-fold symmetry along the [0001] direction (see the Supporting Information). In the literature, bundles of TiO<sub>2</sub> nanowires that have a morphological structure similar to the ones presented here for ZnS were grown by a chemical etching process of Ti metal.<sup>12</sup> The ZnS nanowire bundles presented here are formed by a very different process.

In conclusion, we have demonstrated a new approach for synthesizing orientation-controlled ZnS nanowire bundles. By growing a thin CdSe film onto a Si(111) substrate, we were able to grow orientation-ordered and aligned ZnO nanowires on Si(111) with CdSe as a buffer layer. This method shows the possibility of growing a large area of orientation-ordered ZnS nanowires with the use of *c*-axis-oriented CdSe film/substrate. It is thus possible to grow patterned and uniformly sized ZnS nanowire arrays for applications in luminescence, electronics, sensors, and other nanotechnologies.

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**Supporting Information Available:** SEM images of ZnS bundles and cross-section of the sample. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) (a) Li, L. S.; Alivisatos, A. P. *Adv. Mater.* **2003**, *15*, 408. (b) Qiao, Z.; Gang, X.; Tao, J.; Nie, Z.; Lin, Y.; Chen, X. *J. Solid State Chem.* **2002**, *166*, 49. (c) Limmer, S. J.; Seraji, S.; Wu, Y.; Chou, T. P.; Nguyen, C.; Cao, G. Z. *Adv. Funct. Mater.* **2002**, *12*, 59.
- (2) (a) Wang, J.; Gudixsen, M.; Duan, X.; Cui, Y.; Lieber, C. *Science* **2001**, *293*, 1455. (b) Cui, Y.; Lieber, C. *Science* **2001**, *291*, 851. (c) Xu, C.; Xue, L.; Yin, C.; Wang, G. *Phys. Status Solidi A* **2003**, *198*, 329. (d) Zhang, Y.; Wang, N.; Gao, S.; He, R.; Miao, S.; Liu, J.; Zhu, J.; Zhang, X. *Chem. Mater.* **2002**, *14*, 3564.
- (3) (a) Fang, Y. P.; Xu, A. W.; You, L. P.; Song, R. Q.; Yu, J. C.; Zhang, H. X.; Li, Q.; Liu, H. Q. *Adv. Funct. Mater.* **2003**, *13*, 955. (b) Wang, J.; Li, Y. *Adv. Mater.* **2003**, *15*, 455. (c) Remskar, M.; Skraba, Z.; Stadelmann, P.; Levy, F. *Adv. Mater.* **2000**, *12*, 814.
- (4) (a) Pan, Z. W.; Dai, Z. R.; Wang, Z. L. *Science* **2001**, *291*, 1947. (b) Seo, H. W.; Bae, S. Y.; Park, J. *Appl. Phys. Lett.* **2004**, *82*, 3752. (c) Wu, Q.; Hu, Z.; Wang, X.; Chen, Y.; Lu, Y. *J. Phys. Chem. B* **2003**, *107*, 9726. (d) Liu, Z.; Peng, S.; Xie, Q.; Hu, Z.; Yang, Y.; Zhang, S.; Qian, Y. *Adv. Mater.* **2003**, *15*, 936.
- (5) (a) Kishimoto, S.; Kato, A.; Naito, A.; Sakamoto, Y.; Iida, S. *Phys. Status Solidi* **2002**, *1*, 391. (b) Falconry, C.; Garcia, M.; Ortiz, A.; Alonso, J. C. *J. Appl. Phys.* **1992**, *72*, 1525.
- (6) Ma, C.; Moore, D.; Ding, Y.; Li, J.; Wang, Z. L. *Int. J. Nanotechnol.* **2004**, in press.
- (7) (a) Wang, Z. L.; Kong, X. Y.; Zuo, J. M. *Phys. Rev. Lett.* **2003**, *91*, 185502. (b) Moore, D.; Ronning, C.; Ma, C.; Wang, Z. L. *Chem. Phys. Lett.* **2004**, *385*, 8-11.
- (8) Brokmann, X.; Giacobino, E.; Dahan, M.; Hermier, J. P. *Appl. Phys. Lett.* **2004**, *85*, 712.
- (9) Hines, M. A.; Guyot-Sionnest, P. *J. Phys. Chem.* **1994**, *98*, 4109.
- (10) Dabbousi, B. O.; Rodriguez-Viejo, J.; Mikulec, F. V.; Heine, J. R.; Mattoussi, H.; Ober, R.; Jensen, K. F.; Bawendi, M. G. *J. Phys. Chem B* **1997**, *101*, 9463.
- (11) Chan, W. C. W.; Nie, S. *Science* **1998**, *281*, 2016.
- (12) Yoo, S.; Akbar, S. A.; Sandhage, K. H. *Adv. Mater.* **2004**, *16*, 260.

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