

SEMICONDUCTOR MORPHOLOGY

Optimizing properties by tuning morphology

The properties of semiconductors are highly dependent on their structural form. The finding that ZnS nanobelts can be tuned to take the wurtzite form therefore adds to the strategies for the control of semiconductor properties by optimization of size and morphology.

LONGWEI YIN AND YOSHIO BANDO*

are at the Advanced Materials Laboratory, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki, 305-0044, Japan.

*e-mail: bando.yoshio@nims.go.jp

Zinc sulphide was one of the first semiconductors discovered, and is considered important for applications such as ultraviolet-light-emitting diodes, flat-panel displays, electroluminescent and triboluminescent devices, infrared windows, sensors and injection lasers^{1,2}. Zinc sulphide is mostly found in one of two structural forms — cubic sphalerite or hexagonal wurtzite, which have wide bandgaps of 3.72 eV and 3.77 eV, respectively³. The wurtzite form is generally considered to be more desirable for its optical properties than the sphalerite form. There is a free-energy difference of $\sim 13 \text{ kJ mol}^{-1}$ between the sphalerite and wurtzite forms at ambient conditions — indeed, sphalerite is more stable than wurtzite up to 1,020 °C. However, on page 922 of this issue, Zhonglin Wang and colleagues demonstrate that ZnS nanobelts with a thickness of $\sim 10 \text{ nm}$ (as shown in Fig. 1) surprisingly take an ultrastable wurtzite structure, even at high pressure⁴. The stabilization mechanism for the metastable phase of wurtzite-ZnS is made possible by size and morphology tuning. This is essential knowledge for preparing ZnS products of the desired structure, and suggests a strategy for manipulating nanostructure properties through their size and morphology, to enable the development of nanosemiconductor devices with easily controlled and superior properties.

Nanobelts, as a representative of quasi-one-dimensional materials, have attracted considerable interest from the fundamental and applied standpoint⁵ because of their proven potential use as both interconnects and functional units in electronic, optoelectronic, electrochemical and electromechanical devices. Nanobelts can be easily synthesized without using any template, have a ribbon shape with a rectangular cross section, a width of between several tens to several hundreds of nanometres and width-to-thickness ratios of ~ 5 to

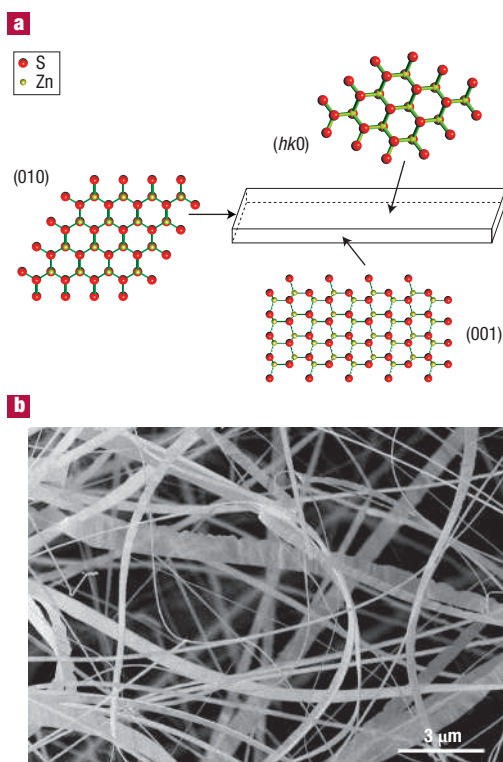


Figure 1 ZnS nanobelts. **a**, The three characteristic surfaces of wurtzite-type nanobelts and the corresponding atomic arrangements. **b**, Scanning electron microscope image of wurtzite-ZnS nanobelts.

10, are free of dislocations and defects, and can be up to several millimetres long.

The local structure of both forms of ZnS is the same⁶, with a tetrahedral coordination for both zinc and sulphur, but a different stacking order of {ZnS} layers: ABCA for sphalerite and ABA for wurtzite. Previous studies⁷ on 25.3-nm-sized wurtzite-ZnS nanoparticles show that the onset pressure for the transformation from the wurtzite into the sphalerite form was 0.5 GPa; on further increasing the pressure, the wurtzite–sphalerite transition was found to be a sluggish process. Wang *et al.* find that ZnS retains its original nanobelt morphology with the wurtzite structure up to pressures as high as 6.8 GPa. Furthermore, the authors observe an explosive

character for the wurtzite-to-sphalerite transformation. These surprising observations are quite different from the standard slow transition kinetics observed in the bulk and ZnS nanoparticles.

It is difficult to understand these intriguing results from the viewpoint of classical thermodynamics and/or nanosize-confinement effects. However, surface-energy considerations provide a new angle that is useful to explain this behaviour. Their high surface-to-volume ratio, coupled with the fact that each nanobelt is a single crystal, make surface effects very prominent in such materials, and have been shown to greatly modify equilibrium structure and phase stability for nanosized materials. Therefore, when reducing nanocrystal size, surface energy starts to significantly affect the structural stability.

Wang *et al.* attribute the exceptional wurtzite-ZnS structural stability to the particular nanobelt morphology. The wurtzite-ZnS nanobelt represents a structure with a lower surface energy than the sphalerite-ZnS nanoparticles, because the lowest-energy plane in the wurtzite structure corresponds to the largest surfaces (top and bottom) of the nanobelts, in direct contrast to the sphalerite structure. They also find that the nanobelt thickness plays the key role in their structural stability: below a critical thickness of 7.4 nm, a wurtzite nanobelt is found to be more stable than sphalerite. This is easily understood, because as the nanobelt thickness is reduced, the surface-to-volume ratio increases, thereby increasing the relative importance of surface-energy factors. In addition, structural twins and faults may provide further stabilization.

The results provide new insights into the nanobelt-morphology-tuned wurtzite-ZnS stabilization and wurtzite-to-sphalerite phase

transformation mechanisms within a given nanoscale object. It also represents an important step towards harnessing nanoscale semiconductor morphologies for phase and property optimization⁸. It indicates that at ambient conditions, metastable semiconductor structures with superior properties can be achieved by careful control of surface, morphology and size, among which the surface energy is the most important factor to be considered. This observation is important for manipulation of the structure and properties of ZnS nanoscale semiconductors. Moreover, because most important II–VI and III–V group wide-bandgap semiconductor materials have analogous cubic and hexagonal structural forms, which display different properties suitable for different applications, the observations by Wang *et al.* have implications in the synthesis and designs of other semiconductor nanomaterials.

The work by Wang and colleagues gives us an idea of how to optimize phase and properties by selecting suitable morphology. The proposals raised by the authors will stimulate new strategies and experiments with potential technological applications. However, the puzzle of the morphology control of nanoscale semiconductors is very complicated. The influence of the morphology (surface, size, shape, crystallographic characters) on the phase and properties needs to be understood in much greater detail.

REFERENCES

1. Qadri, S. B. *et al. Phys. Rev. B* **60**, 9191–9193 (1999).
2. Huang, F. & Banfield, J. F. *J. Am. Chem. Soc.* **127**, 4523–4529 (2005).
3. Kar, S. & Chaudhuri, S. *Chem. Phys. Lett.* **414**, 40–46 (2005).
4. Wang, Z. W. *et al. Nature Mater.* **4**, 922–927 (2005).
5. Pan, Z. *et al. Science* **291**, 1947–1949 (2001).
6. Gilbert, B. *et al. Phys. Rev. B* **66**, 245205 (2002).
7. Qadri, S. B. *et al. J. Appl. Phys.* **89**, 115–119 (2001).
8. Chen, C. C. *et al. Science* **276**, 398–401 (1997).

ERRATUM

TURBULENCE AHEAD

RUSSELL COWBURN AND DOROTHÉE PETIT
Nature Materials **4**, 721–722 (2005).

In this News and Views piece, Figure 1b was incorrect. It should have appeared as shown here.

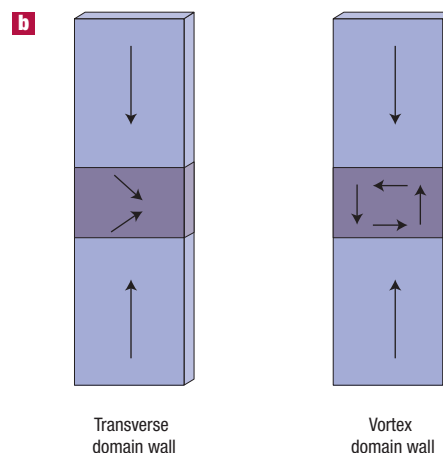


Figure 1 b, Transverse and vortex domain walls in nanowires.