Structure stability, fracture, and tuning mechanism of CdSe nanobelts

Zhongwu Wang[a] and Ken Finkelstein
CHESS, Wilson Laboratory, Cornell University, Ithaca, New York 14853

Chris Ma and Zhong Lin Wang
School of Materials and Engineering Sciences, Georgia Institute of Technology, Atlanta, Georgia 30332

High pressure synchrotron x-ray diffraction studies have been conducted to explore the structural stability, phase transformation, and resulting mechanisms of CdSe nanobelts. 25-nm-thick wurtzite CdSe nanobelts transform to a rocksalt structure with *in situ* fracture at 4.0 GPa; this is greater than the transition pressure of 2.5 GPa in bulk and 25 nm nanoparticle. Decompression results in the formation of wurtzite and sphalerite at 1.2 GPa. Total Gibbs free energy calculations demonstrate that the low surface energy $\pm\{2\bar{1}0\}$ facets are fully responsible for the enhancement of structure stability. A strongest particle size for the rocksalt phase was determined $\sim$12 nm, providing a significant constraint for the fracture of nanobelts and size-tuned enhancement of mechanical properties. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2713172]

CdSe has been extensively investigated as a II-VI semiconductor with a direct 1.8 eV band gap and as a model system to explore chemical processes and applications in electronics, optics, optoelectronics, luminescence as a laser diode, and for nanosensing and biomedical labeling.[1–9] Bulk CdSe has two stable four-coordinated polymorphs, hexagonal wurtzite and cubic sphalerite, that coexist at ambient conditions.[2] Under pressure, they both convert to a denser cubic rocksalt phase at a moderate pressure of 2.5 GPa.[9] Crystal structure as well as particle size, shape, and morphology can affect optical, electrical, and mechanical properties.[1–7] An understanding of how structure is influenced by size, shape, and morphology could provide significant information to design effective paths for synthesis of CdSe nanocrystals with expected properties. Alivisatos and co-workers have conducted a large body of pioneering work, documenting the synthesis, application, and high pressure behaviors of ultrafine CdSe nanocrystals (e.g., <10 nm).[4,6,9–13] In this study, we modify the morphology and size scale of CdSe nanocrystals, combine high pressure synchrotron x-ray diffraction and thermodynamic calculations of the contribution of size- and morphology-tuned surface energy to total Gibbs free energy, and explore the mechanisms of CdSe nanobelt structural stability and phase transformation.

CdSe nanobelts are synthesized by a solid-vapor thermal sublimation technique.[7] Figure 1(a) is a scanning electron microscopy (SEM) image indicating that as-synthesized nanobelts have a uniform cross section along their length and a typical width in the submicron range that extends over several hundred microns; part of nanobelts have a sawlike edge along one side. Electron diffraction [Fig. 1(b)] demonstrates that nanobelts well adopt the hexagonal wurtzite structure. Nanobelt thickness ranges from 20 to 30 nm, and $\pm\{2\bar{1}0\}$ facets dominate the top and bottom surfaces. In Fig. 1(c), high resolution transmission electron microscopy (HRTEM) indicates that nanobelts are defect-free single crystal.

The structural stability, mechanical properties, and phase diagram of CdSe nanobelts were investigated in a diamond anvil cell (DAC) by *in situ* high pressure synchrotron x-ray diffractions at CHESS.[8] The nanobelt sample, along with small ruby chip serving as a pressure marker, is loaded in the DAC in a mixture of methanol, ethanol, and water with ratio of 4:1:1 to maintain a hydrostatic state to a peak pressure of 12 GPa. The key energy dispersive x-ray diffraction patterns are shown in Fig. 2. At ambient conditions, x-ray diffraction agrees with electron diffraction, showing that CdSe nanobelts have a hexagonal symmetry. Upon compression to 4.0 GPa, wurtzite nanobelts rapidly transform to a denser cubic rocksalt structure that remains stable to pressure as high as 12 GPa. Based on the x-ray diffraction peak broadening with compression, CdSe nanobelt appears to maintain a constant shape below the transition pressure of 4.0 GPa, and thus collapses to small pieces upon wurtzite-to-rocksalt phase transformation. These nanobelts are obviously more stable than bulk and 25 nm nanoparticles that remain in wurtzite structure only below 2.5 GPa.[9,10] High pressure
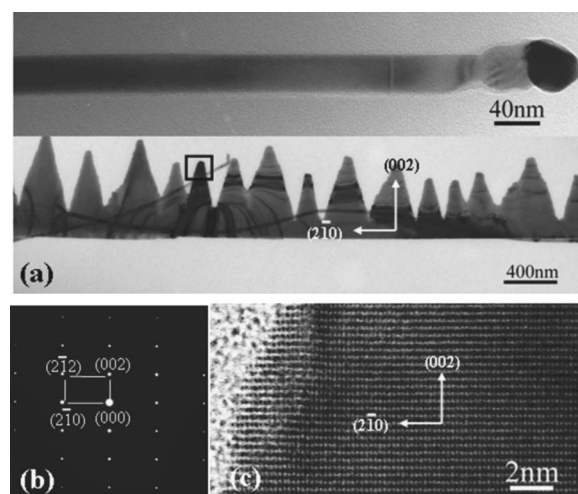

FIG. 1. Morphological and structural characterizations of CdSe nanobelts. (a) SEM images of nanobelt and nanosaw (a saw like edge only along one side), (b) selected area electron diffraction pattern, and (c), HRTEM image showing defect-free and surface facets.

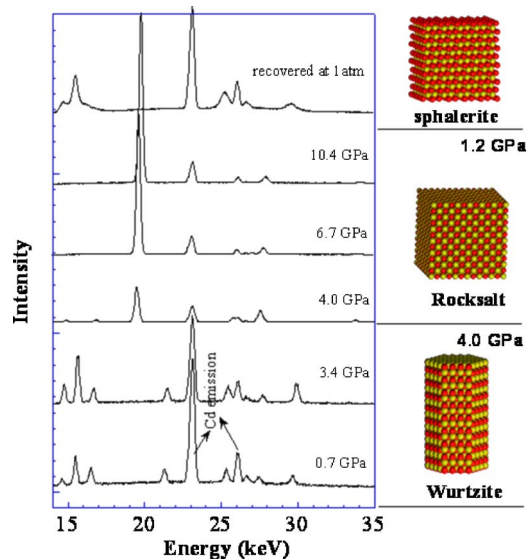a)Author to whom correspondence should be addressed; FAX: 607-225-9001; electronic mail: zw42@cornell.edu

FIG. 2. (Color online) High pressure synchrotron x-ray diffraction patterns of CdSe nanobelts showing the phase transformations and structures.
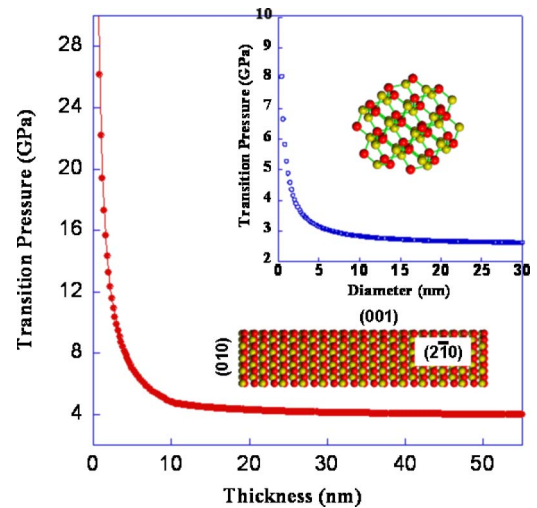

FIG. 3. (Color online) Transition pressure dependence of wurtzite-to-rocksalt phase transformation on thickness (nanobelt) and size (nanoparticle, inset), respectively.

rocksalt phase is not stable during decompression; below 1.2 GPa, it transforms to a mixture of sphalerite and wurtzite. The x-ray diffraction peak width indicates that the recovered phases have an average particle size of ~15 nm, consistent with the observed length scale for the fractured CdSe nanowires.[11] An 18% volumetric shrinkage from sphalerite (or wurtzite) to rocksalt allows one to determine the fractured rocksalt particles as ~12 nm, which is coincidentally consistent with the critical size of 11 nm suggested for ambient rocksalt stability for CdSe.[13]

First-principles calculations indicate that, among all crystallographic facets, the {110} facet has the lowest surface energy of 0.34 J/m^2, consistent with experimental measurements.[9,12,14] In hexagonal structure, the ±{2$\bar{1}$0} facet is symmetrically identical to the {110} facet, so the ±{2$\bar{1}$0}-dominant CdSe nanobelt is likely one of the most stable nanoforms.[8] The average surface energy of three dimension (3D) spherical rocksalt particles can be estimated by considering crystallographic facets; the result is ~0.64 J/m^2.[9,12,14] The Gibbs free energy difference between bulk wurtzite and rocksalt CdSe at one atmosphere and 298 K ($\Delta G_{0,298}$) is calculated to be −15.1 kJ/mol. With decreasing particle size, surface energy should play a significant role, and dramatically change the pressure of wurtzite-to-rocksalt phase transformation. In order to calculate the total energy difference between wurtzite and rocksalt phases for determination of the transition pressure, the development of particle size from the starting wurtzite to fractured rocksalt needs to be considered. Previous studies indicate that a size-induced enhancement of transition pressure appears only for particle size down to 5 nm and that particle size remains consistent before and after compression for these smaller nanoparticles.[9,10] The fractures in CdSe nanobelts and nanowires are found only in the long growth directions, and the resulting particles fall in the range of 10–20 nm.[11] Therefore, it appears that a critical size exists for the fracture of the large scale CdSe forms. When the starting wurtzite CdSe is larger than a critical size of 15 nm, the rocksalt breaks into some small pieces that have a particle size of 12 nm on average; below this size, rocksalt does not break but instead particles reduce in size because of the 18% volu-

metric shrinkage, associated with the structural change.

By including the above-mentioned factors in a practical calculation, the correlation between transition pressure and nanobelt thickness is obtained and it shows the relative importance of surface energy when compared to internal energy (Fig. 3). The calculated transition pressure at a belt thickness of 25 nm is close to 4.0 GPa, in excellent agreement with our experimental observation. The calculated transition pressure dependence on particle size in 3D CdSe nanocrystals is given (inset, Fig. 3). This is also in agreement with experiments.[9] Our results suggest that the low energy surface structure and the size-tuned effect are fully responsible for the enhanced structure stability.

The fracture of materials normally involves the two factors: stress distribution and yield strength (or fracture toughness). The yield strength and fracture toughness prove to be closely related to the particle size, and reducing particle size to a critical value can permit a material to reach theoretical values (maximum values). This critical particle size (D) can be calculated by[15]

$$D = \frac{\pi\gamma G}{h^2} \tag{1}$$

where D, γ, G, and h denote critical size (nm), surface energy (J/m^2), Young's modulus (GPa), and Vickers hardness (GPa), respectively. Using experimental values of these parameters in Eq. (1), the critical particle size of rocksalt CdSe phase is found to be ~12 nm. Nanomechanics simulations of heterogeneous materials under pressure indicate that stress concentration does not exist when particle is below 12 nm. Such materials should display theoretical yield strength.[15] However, above the critical size, structural heterogeneities behave similar to that in bulk. In defect-free nanobelt under hydrostatic pressure, reduction in strength can occur at the interfaces between starting and high pressure phases, which can only be produced through phase transformation. Therefore, in materials above a critical size and under conditions close to a phase transformation, the appearance of *in situ* fracture of nanobelt and the formation of 12 nm rocksalt particles at the transition pressure of 4.0 GPa are expected. Moreover, the enhanced properties of CdSe with particle size

below 12 nm may explain the observed critical size of 11 nm, suggested for ambient stability for CdSe.[13]

In summary, the high pressure behaviors and associated mechanisms of large scale CdSe nanobelts have been clarified by using synchrotron x-ray diffraction and thermodynamic calculation along with the size-related surface energy effect. The low surface energy of $\pm\{2\bar{1}0\}$ facets fully responds to the increased transition pressure of wurtzite CdSe nanobelts. The size-dependent variations of stress field, yield strength, and interface-induced stress concentration cast critical constraints for the fracture of nanobelts and formation of rocksalt particles with an average size of 12 nm. These results provide significant information for improving our abilities to control the uniformity of size, shape, structure, and surface properties of nanocrystals with tunable optical and mechanical properties for technological applications.

[1] G. Hodes, A. Albuyaron, F. Decker, and P. Motisuke, Phys. Rev. B **36**, 4215 (1987).

[2] M. G. Bawendi, A. R. Kortan, M. L. Steigerwald, and L. E. Brus, J. Chem. Phys. **91**, 7282 (1989).

[3] C. B. Murray and M. G. Bawendi, Science **270**, 1335 (1995).

[4] V. L. Colvin, M. C. Schlamp, and A. P. Alivisatos, Nature (London) **370**, 354 (1994).

[5] W. C. Chan and S. M. Nie, Science **281**, 2016 (1998).

[6] M. Bruchez, M. Moronne, P. Gin, S. Weiss, and A. P. Alivisatos, Science **281**, 2013 (1998).

[7] C. Ma, Y. Ding, D. Moore, X. Wang, and Z. L. Wang, J. Am. Chem. Soc. **126**, 708 (2004).

[8] Z. W. Wang, L. L. Daemen, Y. S. Zhao, C. S. Zha, R. T. Downs, X. Wang, Z. L. Wang, and R. J. Hemley, Nat. Mater. **4**, 912 (2005).

[9] S. H. Tolbert and A. P. Alivisatos, J. Chem. Phys. **102**, 4642 (1995).

[10] J. N. Wickham, A. B. Herhold, and A. P. Alivisatos, Phys. Rev. Lett. **84**, 923 (2000).

[11] D. Zaziski, S. Prilliman, E. C. Scher, M. Casula, J. Wickham, S. M. Clark, and A. P. Alivisatos, Nano Lett. **4**, 943 (2004).

[12] L. Manna, L. W. Wang, R. Cingolani, and A. P. Alivisatos, J. Phys. Chem. B **109**, 6183 (2005).

[13] K. Jacobs, J. Wickham, and A. P. Alivisatos, J. Phys. Chem. B **106**, 3759 (2002).

[14] J. Y. Rempel, B. L. Trout, M. G. Bawendi, and K. F. Jensen, J. Phys. Chem. B **109**, 19320 (2005).

[15] H. Gao, B. Ji, I. J. Jager, E. Arzt, and P. Fratzle, Proc. Natl. Acad. Sci. U.S.A. **110**, 5597 (2003).