Pressure-induced structural transformations in cadmium selenide nanorods

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Pressure induced structural transformations in cadmium selenide (CdSe) nanorods are studied using parallel molecular dynamics. Nanorods (4.4 nm in diameter and 4.4 to 53 nm in length) are embedded in a liquid and subjected to pressure. Reversible structural transformations are observed from wurtzite to a single domain rocksalt crystal phase. The simulation results reveal a decrease in transformation pressure with rod length. The transformation mechanism involves atomic shifts within the (0001) plane of the wurtzite structure and is similar to the one observed in electronic structure calculations of pressure-induced structural transformation in bulk CdSe. © 2006 American Institute of Physics. [DOI: 10.1063/1.2338808]

Pressure-induced structural phase transitions in nanoscale systems have been an exciting area of research since the early 1980s. The mechanical and structural properties of nanoparticles have been shown in theory and experiment to determine or influence their optical and electronic properties. Thus, understanding the mechanisms governing structural transformations at the nanoscale can help bring about future developments in nano-materials and devices.

Recent efforts have focused on pressure-driven structural phase transitions from four-fold coordinated zinc blende to six-fold coordinated rocksalt (RS) phase in GaAs and other semiconductors. Electronic structure calculations based on the density-functional theory (DFT) and molecular dynamics simulations have been used to confirm pathways and barriers between pressure-induced zinc blende to rocksalt transformations. Transformation mechanisms from four-fold wurtzite (WZ) to six-fold RS coordinated structures in Cadmium selenide (CdSe), are also of considerable interest. The Alivisatos group has studied CdSe nanorod ensembles under cyclic pressure in experiments and observed reversible transformations between four-coordinated and six-coordinated crystal phases. Single domain formation was observed in shorter rods while multiple domain formation was seen in longer rods. Despite a great deal of interest and activity in this area, the transformation mechanism for wurtzite to rocksalt transformation in CdSe at nanoscale is not well understood.

In this letter, we report the results of molecular dynamics (MD) simulations of CdSe nanorods of varying lengths undergoing forward and reverse structural phase transformation under hydrostatic pressure, infer the pathways for the structural transformation, and report the observation of structural phase transformation pressure dependence on nanorod length.

Four sets of simulations are performed on single nanorods. Each nanorod has a diameter of 44 Å—approximately the diameter of the nanorods in Alivisato’s experiments. The width-to-length ratios of the nanorods are 1:1, 1:2, 1:4, and 1:12. We refer to each simulation by nanorod aspect ratio—\(S_{1:1}, S_{1:2}, S_{1:4}, \text{ and } S_{1:12}\), respectively. The initial configurations of the nanorods are cut from a wurtzite crystal. Cutting planes for nanorods expose \((0001)_{\text{WZ}}\) surfaces and the remaining six side faces are from the \([1210]_{\text{WZ}}\). An example of the nanorod used in the \(S_{1:4}\) simulation is shown embedded in the Lennard-Jones (LJ) pressure medium in Fig. 1.

In MD simulations, a uniform hydrostatic pressure is applied to the nanorods through a liquid medium consisting of atoms interacting via a LJ potential. The LJ potential is parameterized, so that the LJ atoms are in fluid phase at a temperature of \(T=300\) K across a pressure range from \(P=0\) up to \(P\approx 4\) GPa. The CdSe potential consists of two-body and three-body interactions. The fluid-nanorod interaction is modeled by a purely repulsive \(1/r^{12}\) potential.

Simulations are divided into three stages—the initialization stage, where the temperature of the system is raised to 300 K and the pressure correspondingly rise to 180 MPa, the downstroke stage where the pressure is increased to induce the forward transformation, and upstroke at which pressure is decreased and the reverse transformation occurs. The first stage is performed in the microcanonical ensemble (NVE). The second and third stages of the simulation are carried out in the isobaric-isothermal (NPT) ensemble using the Parrinello–Rahman approach.

FIG. 1. (Color online) A CdSe nanorod embedded in a Lennard-Jones fluid, which serves as a hydrostatic pressure medium. Each nanorod has a hexagonal cross section, with a diameter of 44 Å. The MD cell cross section for each nanorod is \(165\) Å \(\times\) \(165\) Å and lengths are \(163, 257, 441, \text{ and } 1171\) Å for \(S_{1:1}, S_{1:2}, S_{1:4}, \text{ and } S_{1:12}\) nanorods, respectively.
Spatially resolved calculations of bond-angle distribution and atomic coordination are performed during each simulation. Atoms in each nanorod are divided spatially along its axis into 11-Å “slices” as well as radially into concentric 10 Å-wide “shells” as shown in Fig. 2.

Columns (a) and (b) in Fig. 3 of bond-angle distribution and atomic coordination, respectively. Quantities in rows 1–3 were computed for the nanorods at three different pressures, which we will refer to as the initial, intermediate and final stages of structural transformation. All graphs are color-coded red, blue, and green to correspond to calculations performed in the innermost, middle, and outer shells, respectively. Structural quantities in row 1 show the 1:1 initial configuration at 180 MPa and 300 K. Here, the bond-angle peak centered about 109.4° in Fig. 3(a1) indicates the nanorod’s initial tetrahedral wurtzite crystal structure. Atomic coordination plots in Fig. 3(b1) show that atoms inside the nanorod have four-coordinate, with three-fold and four-fold coordinated atoms at the surface. Shell-resolved bond angle and atomic-coordination distributions for simulations $S_{1:2}$, $S_{1:4}$, $S_{1:12}$, at 180 MPa and 300 K are the same as shown for $S_{1:1}$ in row 1. Row 2 shows structural quantities for the intermediate phase at 2.5 GPa, where the atomic bi-layers in the (0001)$_{WZ}$ plane of the $S_{1:1}$ nanorod have flattened under compression along the [0001]$_{WZ}$ direction into stacked honeycomb lattices, which we refer to as the honeycomb-stacked (HS) structural state. Row 3 shows the structural quantities of the $S_{1:1}$ system at the final pressure where the crystal structure of the nanorod has transformed to RS. The RS crystal phase is indicated in the bond angle distribution in Fig. 3(a3) by peaks at 90 and 180 deg and by six-coordinated atoms dominating in all three shells in Fig. 3(b3). The structural transformation mechanism we observe is one of several atomic mechanisms described by Shimojo et al. in their studies on structural transformations in bulk CdSe using the DFT. They report the WZ-RS-II transition as most favorable, having the lowest energy transition barrier. Final pressures for the nanorods in simulations $S_{1:1}$, $S_{1:2}$, $S_{1:4}$, and $S_{1:12}$, were ~4.0, ~3.0, ~3.0, and ~2.5 GPa, respectively.

The final RS phases of the nanorods are highly crystalline. This is apparent in the side and top view images of the $S_{1:1}$ nanorod in Fig. 4. The structural transition results in a single domain, columns of atoms form periodic arrays from end to end in each nanorod. The cross section of the nanorod has changed shape from its original hexagonal shape, as shown in Fig. 4(a1), to a multidiametered shape shown in Fig. 4(a3). All nanorods also contract during transformation along the $z$ axis by ~25%, which is in good agreement with 18% volume contraction observed in experiment on CdSe nanocrystals as well as in the work done in the DFT calculations on CdSe bulk by Shimojo et al., where the lattice constant ratios for the HS and RS phases are 0.813 and 0.707, respectively. By comparing bonding geometries between the different domains, we can infer that the changes in atomic coordination are due to changes in bond angles and bond lengths.
transformation compared to atoms closer to the axis of the nanorods. Thus longer rods, having lower surface-to-volume ratios approaching properties of bulk CdSe, undergo structural transformations more readily compared to shorter nanorods. Surface effects prevail in mitigating crystal phase transformation to a greater extent shorter nanorods as they have higher surface-to-volume ratios.

In conclusion, we have observed a considerable degree of reversibility between structural phases of CdSe nanorods under pressure, with nanorod length shown to be a factor in both forward and reverse structural transformations. Our simulations have shown forward transformation pressure to decrease with increasing nanorod length, which is consistent with experimental observations. Smaller nanoparticles have been reported in experiments to undergo reversible structural transformations with less hysteresis than high-aspect ratio nanorods. In our simulations we see forward and reverse transformation occur more readily in larger nanorods. It should be pointed out that nanorods in experiments are passivated with organic ligands. Nanorod surfaces are not passivated in our simulations. Because surfaces have a strong and direct influence over reverse transformation, surface passivation is an important consideration for future work.

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