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First principles computational study of wurtzite CdTe nanowires

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Abstract An ab initio computational study was performed for wurtzite [0001] CdTe nanowires enclosed by $(10\bar{1}0)$ surface facets over a range of diameters and cross-sectional topologies. Calculations show that hexagonal nanowires are highly stable, possessing a large electronic band gap and a band structure without dispersionless states in the gap. Passivation of the dangling bonds for the largest hexagonal nanowire was found to have a minimal effect on the electronic structure, resulting in only a 0.05 eV increase in the band gap over the unpassivated nanowire.

Introduction

In recent years, semiconductor nanocrystals (NCs) have aroused considerable interest due to their unique optical and electrical properties, which may differ greatly from the corresponding bulk material. Currently, numerous techniques have been developed for the design and growth of NCs, affording a high degree of control over quantum confinement effects through variations in composition, size, and shape [1, 2]. Among NCs, one-dimensional systems such as nanorods and nanowires are particularly attractive because of their potential as fundamental building blocks in nanoscale electronics [3, 4].

CdTe is regarded as one of the more promising alternatives to crystalline silicon for potential low-cost photovoltaic devices because of its near optimum direct band gap and large absorption coefficient [5]. In the bulk, single-crystal CdTe adopts the zincblende structure, at atmospheric pressure. However, because CdTe in the zincblende and wurtzite phases have similar energies [6], nominally phase-pure zincblende films are often observed to include small amounts of wurtzite [7, 8]. Although the wurtzite phase is metastable in the bulk [9], it can be stabilized in NCs due to quantum confinement. Recently, vertically aligned wurtzite [0001] CdTe nanowires have been fabricated using substrate-based catalytic growth techniques [10]. While these nanowires are expected to exhibit properties similar to those of their zincblende counterparts [10, 11], in certain applications wurtzite nanowires may be more desirable. A particular example would be heterojunction nanowires (e.g., CdSe–CdTe core–shell nanowires), in which CdTe may be either in the core or the shell region and constrained to be in the wurtzite phase [12, 13]. We note that solar cells based on such nanowires offer several advantages over conventional bulk materials. In addition to supporting a larger number of electron-hole pairs (excitons) [14], such one-dimensional structures are expected to exhibit enhanced charge transport [15]. Leveraging these attributes may provide an important starting point to increase the performance solar cells based on CdTe.

The focus of this study is to provide an understanding of the stability and electronic structure of wurtzite CdTe nanowires using ab initio computational methods. The dependence of the total energy, electronic band gap, and tendency for surface atoms to reorient are assessed as a function of the cross-sectional topology and diameter for a series of unpassivated, infinitely long, [0001] CdTe nanowires. Furthermore, the effect of passivating the dangling bonds on the geometric and electronic properties are also

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considered in the context of the largest, most stable nanowire cross-section.

Methods and models

All calculations for this study were performed using the local density approximation (LDA) within SIESTA [16], a local orbital DFT code. Core electrons were described by norm-conserving pseudopotentials, constructed according to the Troullier–Martins scheme [17] with valence state configurations of [*Kr*] $5s^2 4d^{10}$ and [*Kr* $4d^{10}$] $5s^2 5p^4$ for Cd and Te, respectively. Based on prior theoretical work, the pseudopotential of Te was constructed to include scalar relativistic effects [18]. The valence electron wave functions were expanded using a double-ζ plus polarization (DZP) basis set with an orbital confining cutoff radius specified by an energy shift parameter of 0.002 Ry. The equilibrium position of all atoms was determined by requiring the forces experienced by each atom to be smaller than 0.04 eV/Å.

As a test of the pseudopotentials and computational method, bulk calculations were performed for wurtzite and zincblende CdTe. Monkhorst–Pack *k*-point meshes [19] of (6 × 6 × 6) for the wurtzite structure and (5 × 5 × 5) for the zincblende structure were found to yield well converged results. From these calculations, it was determined that the equilibrium a and c lattice constants for the wurtzite phase were 4.62 and 7.55 Å and that for the zincblende phase to be 6.52 Å, in good agreement with available theoretical work at the same level of theory [1, 20] and with the corresponding experimental values [9, 10]. Consistent with prior theoretical results [6], the energy difference between the two phases was found to be small, with zincblende being the more stable structure by approximately 8 meV per CdTe pair. Moreover, the calculated band gaps were also quite similar, with values of 1.13 and 1.15 eV for the zincblende and wurtzite phase, respectively. In comparison to the experimental zincblende band gap of 1.48 eV [21], the computed band gap is significantly underestimated, a well known consequence of using LDA. At present, an experimental value for the wurtzite band gap does not exist. However, based on highly accurate quasiparticle calculations [11], it is expected to be similar in magnitude to the zincblende phase.

The wurtzite CdTe nanowires considered for this study were unpassivated, with either hexagonal or triangular cross-sectional topologies. All nanowires are infinitely long, with a periodic length c along the [0001] direction and are enclosed by $(10\bar{1}0)$ surfaces. These surfaces are nonpolar and contain Cd and Te atoms with one dangling bond. This choice was motivated by our previous experience with CdSe [22, 23], where it was determined that nanowires with surface atoms possessing one dangling bond are highly stable, have a large electronic band gap, and exhibit minimal surface reorientation. A vacuum region of 20 Å was used to separate the nanowires from their periodic images. Sampling the Brillouin zone using a (1 × 1 × 10) Monkhorst–Pack *k*-point mesh [19] was employed to achieve well converged results.

In Fig. 1, the largest hexagonal and triangular nanowires studied here are presented. Beginning with a nanowire containing six CdTe pairs, larger hexagonal cross-sections were generated by increasing the number of "shells" of hexagonal units around the central hexagon. The nanowire in Fig. 1a consists of four shells with 96 CdTe pairs. For the nanowires with triangular cross-sections, the smallest structure contained 13 CdTe pairs, with three basic hexagonal units. Larger structures, such as the one shown in Fig. 1b with 78 CdTe pairs, were created by successively adding rows of hexagonal units.

Results

Equilibrium geometry

Once the different nanowires had been constructed, the atomic-level geometries of each were optimized to determine their minimum energy configuration. The total energy

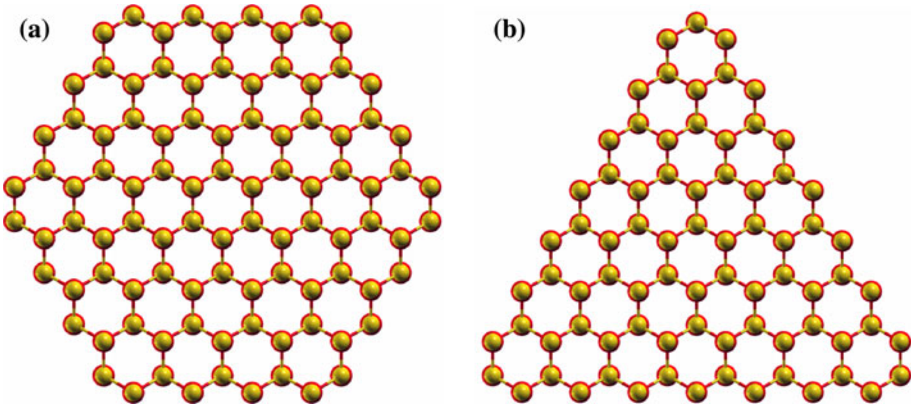

Fig. 1 Cross-sectional topologies of the largest **a** hexagonal and **b** triangular CdTe nanowires, viewed along the [0001] direction. Sidewalls are terminated by $(10\bar{1}0)$ facets. Cd and Te atoms are represented by *red/dark* and *yellow/light*, respectively (Color figure online)

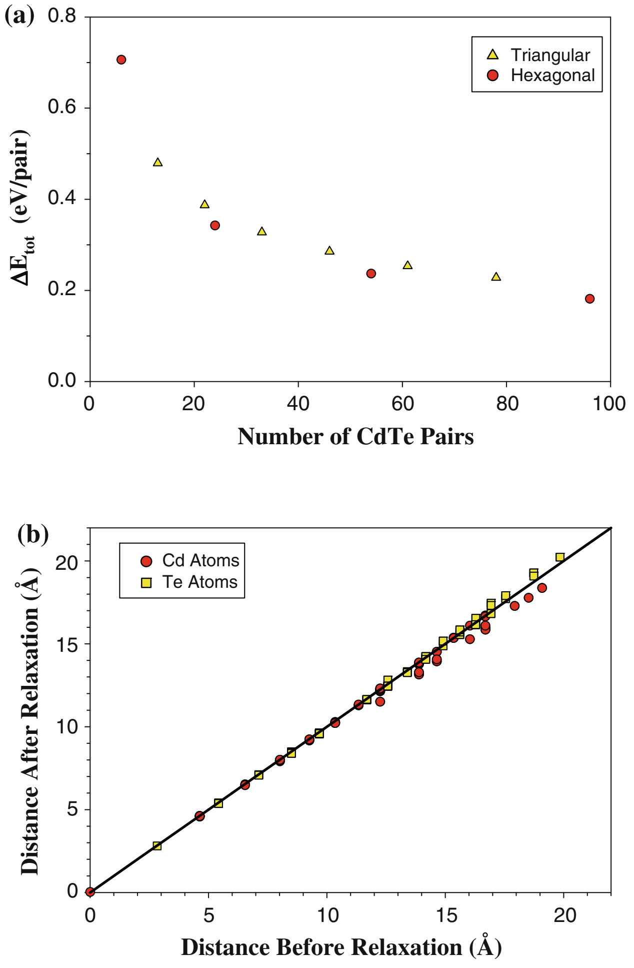

Fig. 2 (Color online) **a** Nanowire energy per CdTe pair relative to bulk CdTe energy (ΔE_{tot}) and **b** atomic coordinate relaxation in the largest hexagonal nanowire containing 96 CdTe pairs

per CdTe pair relative to the bulk energy (ΔE_{tot}), calculated for the various nanowire sizes and cross-sections after relaxation is shown in Fig. 2a. The trends in this diagram agree with those in previous studies focusing on CdSe quantum dots [22] and nanowires [23]. In particular, the total energy per pair decreases with increasing nanowire size, converging to the bulk energy for both nanowire geometries. Among these nanowires, those with hexagonal cross-sections possessed slightly lower energies than those with triangular cross-sections. This is likely due to the gentler, more uniform variations in the angles between adjacent surface facets.

Figure 2b depicts the changes in the atomic positions following geometry optimization for the largest, most stable hexagonal nanowire. For this system, relaxation resulted in a decrease in the total energy of -0.12 eV/pair and an increase in the band gap of 0.62 eV compared to the unrelaxed geometry. It is evident that the atoms within the core of the nanowire, less than $\sim$12 Å from the nanowire axis, undergo a negligible change in position whereas atoms in the outermost $\sim$10 Å relax the most. Consistent with our previous studies on CdSe [23], Cd atoms tend to move inward (below the straight line in Fig. 2b) while Te atoms move outward (above the line) for all nanowire cross-sections. This behavior is also seen when the dangling bonds have been saturated with hydrogen, albeit to a lesser extent. In particular, the Cd and Te atoms in the outermost shells deviate from their initial positions by less than 1%. In comparison to CdSe, the unpassivated CdTe nanowire shows a more pronounced inward relaxation of the Cd atoms with the outward relaxation of Te atoms being roughly similar to that seen for Se. This behavior can be attributed to the larger bond length in CdTe which allows the Cd atoms to relax to a greater extent, especially at the surface.

Electronic structure

Although LDA poorly predicts the absolute value of the band gap, *changes* in band gap values due to quantum confinement effects are generally well represented with respect to experiment [24]. In Fig. 3, the nanowire band gap relative to the bulk band gap (ΔE_{g}) is presented as a function of diameter and topology. As the size of the nanowire decreases, ΔE_{g} increases, reflecting the impact of quantum confinement. Also shown in Fig. 3 are the results of Li and Wang [25], who calculated the quantum confinement energies (identical in definition to our ΔE_{g}) for zincblende CdTe nanowires in the 2–3 nm range using a corrected empirical pseudopotential ("LDA + C") to account for a major part of the discrepancy between the experimental and LDA band gap. Consistent with our results, their quantum confinement energies decrease with

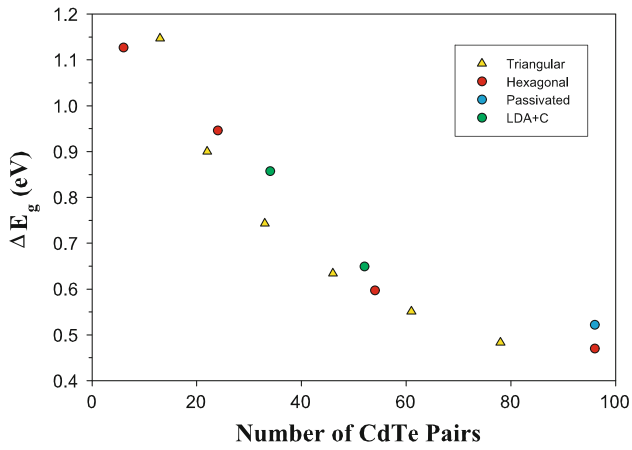

Fig. 3 (Color online) Nanowire band gap relative to bulk band gap (ΔE_{g}) for CdTe nanowires as a function of size. The LDA + C results of Li and Wang [25] for passivated zincblende CdTe nanowires are also shown

increasing diameter. Moreover, these confinement energies are in remarkable agreement with our LDA calculated results, even though they correspond to nanowires with surface atoms whose dangling bonds have been passivated with pseudohydrogen atoms.

The similarity between passivated and unpassivated nanowires of comparable diameters has been addressed before in our prior work on CdSe [23]. There it was determined that nanowires containing surface atoms with one dangling bond rehybridize from sp^3 to sp^2. As a result, nanowires with such surfaces have large band gaps and band structures that are devoid of gap states as though their surfaces were passivated. To further investigate this phenomena, the dangling bonds of the largest hexagonal nanowire (containing 96 pairs, shown in Fig. 1a) were saturated with hydrogen. As shown in Fig. 4, the average bond angle θ for the atoms in each shell of the passivated nanowire is close to the 109.5° that is characteristic of sp^3 hybridization. For the unpassivated nanowire, deviation from tetrahedral bonding occurs only at the surface, where geometric relaxation results in $\theta \approx 120°$, indicative of sp^2 hybridization. Moreover, this rehybridization does not significantly reduce the band gap of the unpassivated nanowire. As seen in Fig. 3, passivation results in only a 0.05 eV increase in ΔE_g compared to the unpassivated nanowire.

The electronic band structure for both the unpassivated and passivated hexagonal nanowire containing 96 CdTe pairs are shown in Fig. 5. As was the case for our earlier work on CdSe, the band structure of the unpassivated CdTe nanowire (Fig. 5a) is free of gap states due to rehybridization (from sp^3 to sp^2) of the dangling bonds upon relaxation. A comparison of this to the band structure of the passivated nanowire finds the two to be nearly identical, with the only noticeable difference being the location of the conduction band minimum (CBM) relative to the valence band maximum (VBM). In the passivated nanowire, the CBM is slightly higher in energy than in the unpassivated nanowire, accounting for the aforementioned increase in ΔE_g.

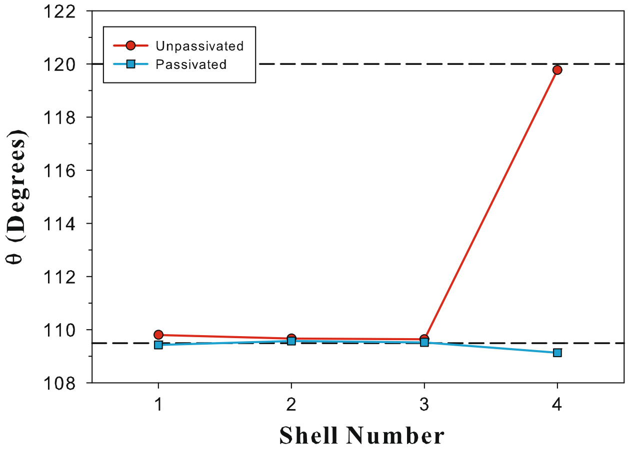

Fig. 4 (Color online) Average bond angle (θ) for the atoms in each shell of an unpassivated hexagonal nanowire containing 96 CdTe pairs. Also shown is the θ for the same nanowire passivated with hydrogen. The dashed lines at 109.5° and 120° indicate the bond angles associated with sp^3 and sp^2 hybridization, respectively

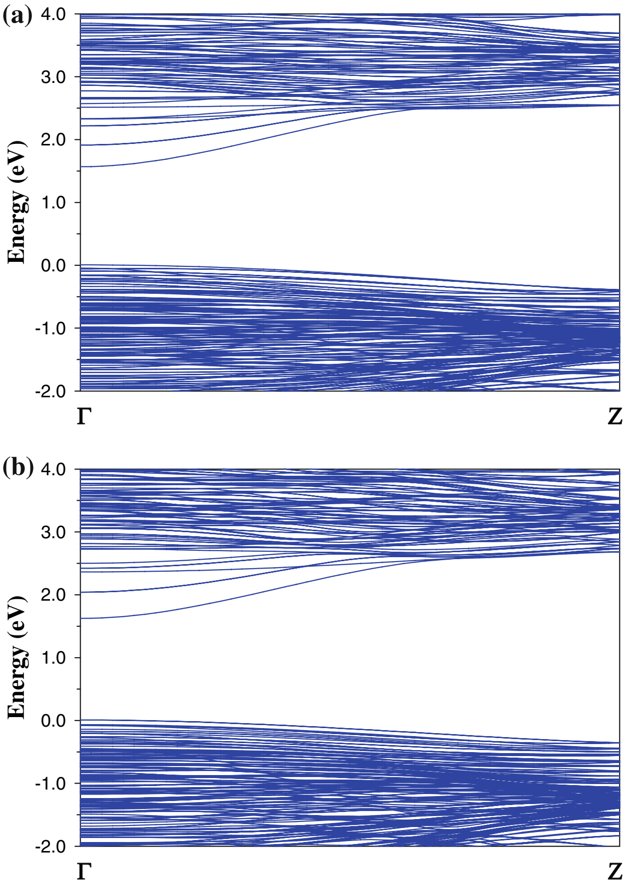

Fig. 5 (Color online) **a** Band structure of an unpassivated hexagonal nanowire containing 96 CdTe pairs. **b** Band structure of the same nanowire passivated with hydrogen. In both, the zero of energy is chosen to correspond to the valence band maximum

Conclusion

In conclusion, ab initio first principles computational techniques have been performed to examine the electronic and geometric properties of wurtzite CdTe nanowires in the [0001] growth direction containing surface atoms with one dangling bond over a range of cross-sectional topologies and diameters. Consistent with our prior work on CdSe nanowires, we find that CdTe nanowires with hexagonal cross-sections are more stable and possess a larger band gap than those with triangular cross-sections. Owing to the sp^3 to sp^2 rehybridization of the dangling bonds upon relaxation, the unpassivated nanowires have large band gaps with their band structures devoid of gap states. Comparing the band structures of the largest hexagonal nanowire when the dangling bonds are passivated and unpassivated, we find the difference between the two to be negligible, indicating that upon relaxation, unpassivated nanowires with surface atoms displaying one dangling bond are equivalent to passivated nanowires.

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