



## Relative stability of nanosized wurtzite and graphitic ZnO from density functional theory

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### ABSTRACT

First principle calculations are used to determine the relative stability of wurtzite and graphitic phases of ZnO nanostructures. Our results indicate that the relative stability sequence changes with the increasing size of the nanostructure. When the number of ZnO molecules in the ZnO nanostructure is less than a threshold number, we observe the relative stability of the graphitic phase. When the number of ZnO molecules in the ZnO nanostructure exceeds the threshold number, the relative stability of the wurtzite phase is observed. Finally, we discuss the influence of size dependence of these ZnO nanostructures on their electronic properties.

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In recent years, we have witnessed a substantial increase in research in nanostructures, driven largely by their unique properties and a wide range of their current and potential applications, including such areas as mesoscopic physics and fabrication of nanoscale devices [1,2]. As a typical II–VI semiconductor compound, zinc oxide (ZnO) has been receiving considerable attention in this context due to its good optical, electrical, and piezoelectric properties [3]. In recent years, various ZnO nanostructures have been synthesized [4], including nanorings [5], nanohelices [6], nanobelts [7], nanowires [8], as well as nanowire arrays [9]. Stimulated by experimental progress, a number of theoretical efforts have been focused on a better understanding of the properties of ZnO at the nanoscale.

The crystal structures shared by bulk ZnO are WZ (WZ,  $P6_3mc$  space group), zinc blende (ZB,  $F\bar{4}3m$ ), and rocksalt (RS,  $Fm\bar{3}m$ ). WZ is the most stable and commonly observed phase under ambient pressure. ZB can be obtained only on cubic surfaces under specific growth conditions. RS is the result of a transformation from WZ at pressure in the typical range of 8–10 GPa [10]. When the crystal size goes down to nanometers, there have been theoretical arguments that WZ may not be the most stable phase, in particular for two-dimensional (2D) ZnO nanofilms and one-dimensional (1D) nanowires. For example, results by Freeman and his coworkers indicated that 2D ZnO nanofilms can be transformed into a graphitic structure when it is in the form of thin nanoplates (about 10 atomic layers) [11]. Calculations by Zhang and Huang [12,13] further confirmed Freeman's results, indicating that infinitely large ZnO nanoplates and infinitely long ZnO nanowires can be transformed from WZ to a graphitic structure below a critical thickness or diameter. These authors also argued that nanowires of finite

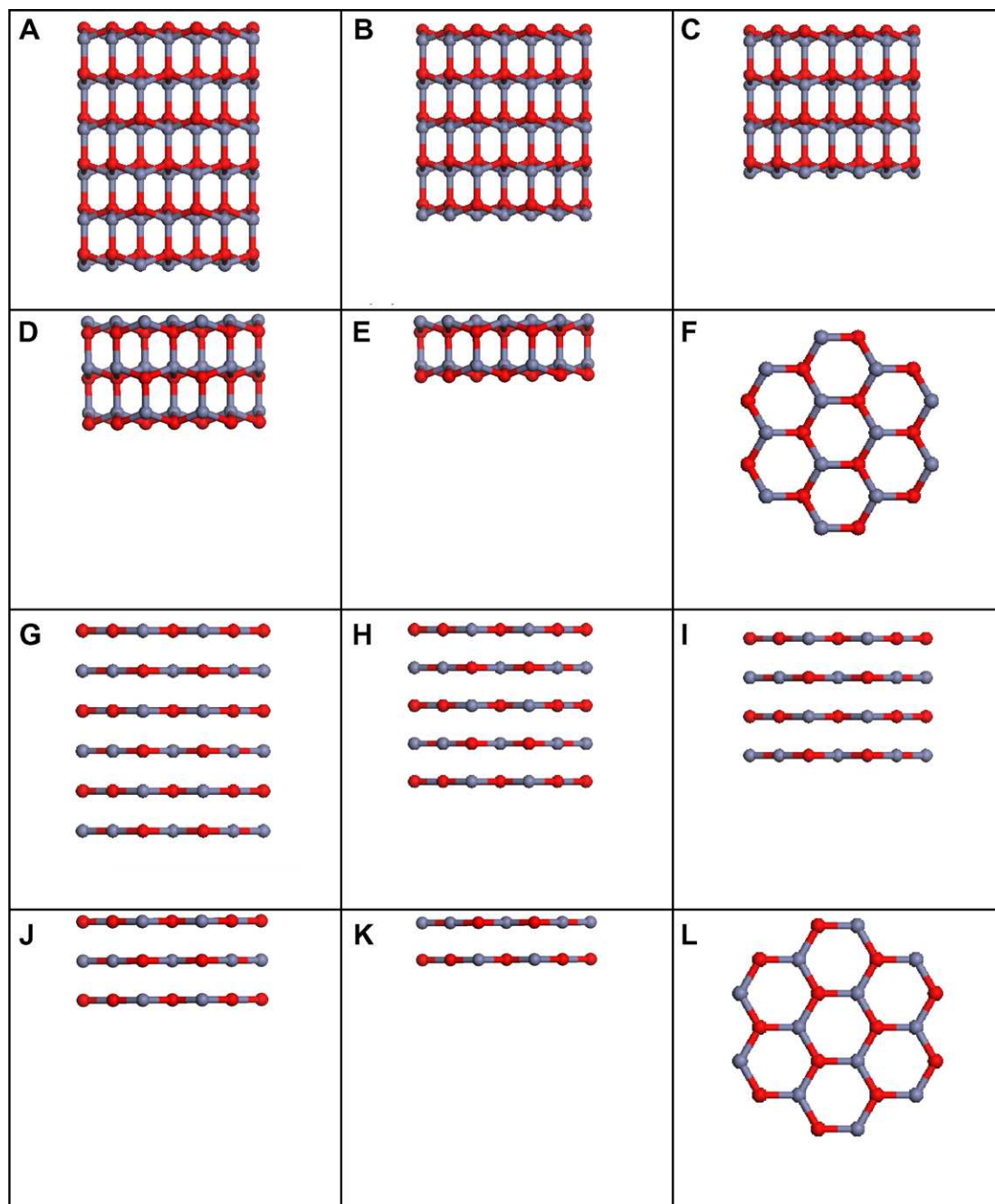
length can go through the same structural transformations at a critical size. Zhou's calculations also indicated that a uniaxial strain of ZnO nanowires along  $[01\bar{1}0]$  can also lead to a transformation from WZ to a graphitic phase [14,15]. While size dependency and electronic properties of zero-dimensional (0-D) ZnO nanostructures have been studied extensively [16–25], until now no results on relative stability of 0-D WZ and graphitic phases of ZnO nanostructures have been reported in the literature.

Studying different phases of materials is a difficult task. At larger scales, this can often be done effectively by using models based on the Landau–Ginzburg theory [26]. Some important physical effects showing the size dependency of nanostructure properties can still be studied successfully with such computational efficient methodologies as finite element [27] and finite difference methodologies [28]. This includes the barrier localization in nanowires [29], coupling effects between electronic states of quantum dots and their wetting layers [30], as well as the aspect ratio effects in finite nanostructures such as rods [31]. However, the problem of relative stability of nanostructure phases requires a more refined analysis. In this work, we address this issue by presenting an accurate description of the relative stability of nanosized WZ and graphitic ZnO structures. State-of-the-art first principle calculations have been carried out using the density functional theory (DFT) in order to determine the total energy for a number of WZ and graphitic ZnO nanostructures. Our results indicate that the WZ phase at less than 1.0 nm (about 38 ZnO molecules) becomes less stable than the graphitic phase.

In this contribution, we analyze in detail a series of WZ and graphitic ZnO nanostructures with hexagonal prism structures. The structure in Fig. 1e is the smallest WZ ZnO nanostructure with hexagonal prism structure in the present work, containing 48 atoms of four layers (two Zn–O double layers). Similar to Ref. [16], we denote it as 2L-48A-WZ. Next, the smallest graphitic

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**Fig. 1.** Side and top views of initial ZnO nanocluster: (A) 6L-144A-WZ, (B) 5L-120A-WZ, (C) 4L-96A-WZ, (D) 3L-72A-WZ, (E) 2L-168A-WZ, (F) top views for (A), (B), (C), (D) and (E); (G) 6L-144A-Gra, (H) 5L-120A-Gra, (I) 4L-96A-Gra, (J) 3L-72A-Gra, (K) 2L-48A-GR, (L) top views for (G), (H), (I), (J) and (K).

ZnO nanostructure with hexagonal prism structure is shown in Fig. 1k, containing 48 atoms of two layers. We denote this nanostructure as 2L-48A-Gra. Larger nanostructures are generated by repeating the structures along the [0001] direction. We denote them as 3L-72A-WZ, 4L-96A-WZ, 5L-120A-WZ, 6L-144A-WZ, 3L-72A-Gra, 4L-96A-Gra, 5L-120A-Gra, and 6L-144A-Gra, respectively.

The geometries for these hexagonal prism structures were optimized using the density functional theory with effective core potentials implemented in the Dmol package [32]. We used a double numerical basis including *p*- and *d*-polarization functions (DNP) and adopted the generalized gradient approximation (GGA) with the PW91 parameterization [33] to describe the exchange–correlation interaction. First, we optimized the lattice parameters of the bulk ZnO in the WZ structure. The lattice param-

eters *a* and *c*, obtained for bulk ZnO in the WZ structure, are 3.258 and 5.220, respectively, which agree well with the experimental values already reported in the literature [3].

Since the atom numbers are the same for WZ and graphitic phases of ZnO nanostructures studied in this work, the size-dependent phase stability of WZ and graphitic phases of ZnO nanostructures can be determined by comparing the total energies. In this work, the geometries of these ZnO nanostructures were optimized using the DFT with effective core potentials implemented in the Dmol package, and the total energies for these optimized nanostructures were obtained. The relationship between the total energy and size for various phases of ZnO nanostructures are plotted in Figs. 2 and 3. The total energy per ZnO molecule,  $E_t$ , as a function of the number of ZnO molecules in the nanostructure

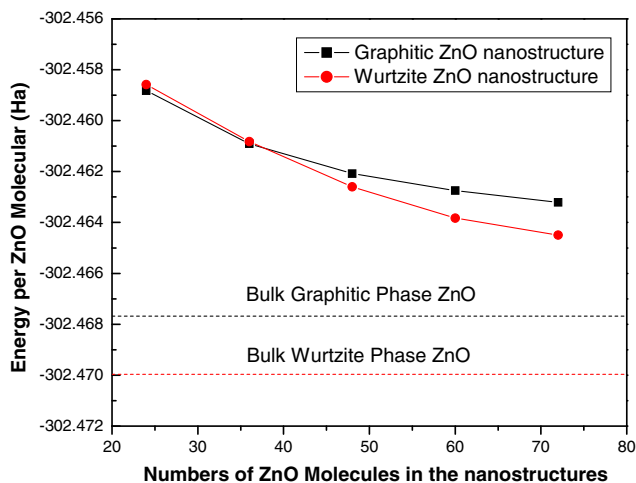


Fig. 2. The total energy per ZnO molecule as a function of the ZnO nanostructure size.

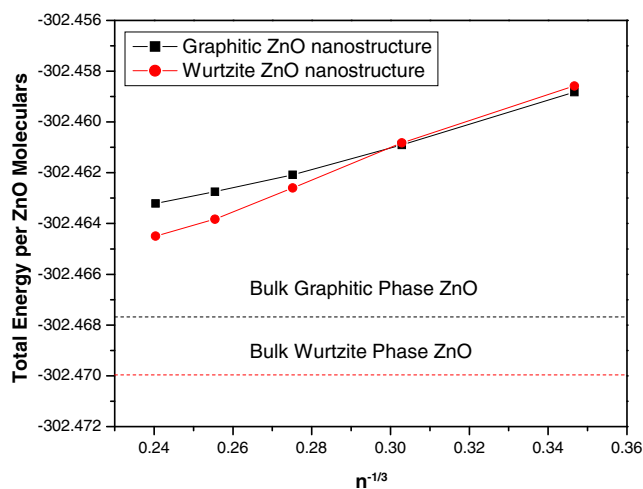


Fig. 3. The total energy per ZnO molecule as a function of the inverse of the cluster size  $n^{-1/3}$  ( $n$  is the number of ZnO molecules in the ZnO nanostructure).

is shown in Fig. 2. Note that with an increase in the number of ZnO molecules, the total energy per ZnO molecule,  $E_t$ , for both WZ and graphitic phases, decreases monotonously. Fig. 3 shows the total energy per ZnO molecule,  $E_t$ , as a function of  $n^{-1/3}$  (the inverse of the cluster size), where  $n$  is the number of ZnO molecules in the ZnO nanostructure. As can be seen from Fig. 3, the total energy per ZnO molecule,  $E_t$ , increases almost linearly with the inverse of the cluster size,  $n^{-1/3}$ , for all nanostructures studied in this work. For the WZ ZnO nanostructure, with the increasing inverse of the cluster size  $n^{-1/3}$ , the total energy per ZnO molecule,  $E_t$ , increases approximately according to the following linear relationship:  $E_t^{\text{WZ}} = -302.47337 + 0.0416n^{-1/3}$ . For the graphitic ZnO nanostructure, with the increasing inverse of the cluster size  $n^{-1/3}$ , the total energy per ZnO molecule,  $E_t$ , increases approximately according to this linear relationship:  $E_t^{\text{Gra}} = -302.47823 + 0.0569n^{-1/3}$ . Note, however, that the total energy per ZnO molecule,  $E_t$ , for both WZ and graphitic ZnO nanostructures is larger than that of bulk ZnO. Our results also indicated that with the increasing size of ZnO nanostructures, their stability increases. From Figs. 2 and 3, it can be seen that the total energy curves intersect, which indicates that the relative stability sequence changes with the increasing size of nanostructures. When the number of

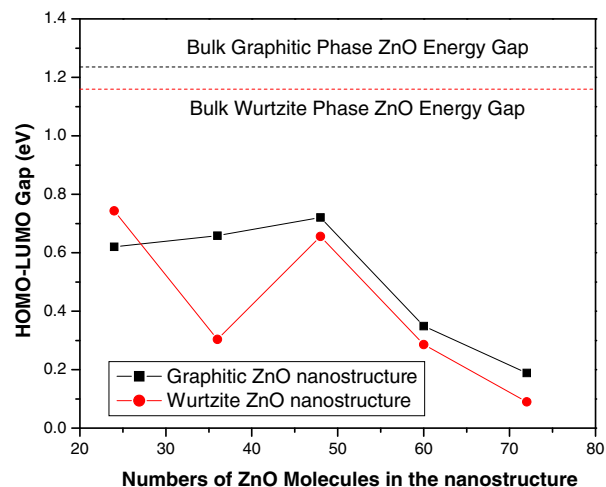


Fig. 4. The HOMO–LUMO gap as a function of the ZnO nanostructure size.

ZnO molecules in the ZnO nanostructure is smaller than  $\sim 38$ , we observe the relative stability of the graphitic phase. Likewise, when the number of ZnO molecules in the ZnO nanostructure is larger than  $\sim 38$ , we observe the relative stability of the WZ phase.

In order to understand the electronic properties of these ZnO nanostructures, size-dependent HOMO–LUMO energy gaps have been calculated and plotted in Fig. 4. It is known that the GGA approaches to the DFT often fail to describe systems with localized (strongly correlated)  $d$  and  $f$  electrons as a result of neglecting electron correlation. This is especially true for ZnO structures, where the experimental energy gap of ZnO (B4) is 3.44 eV [3], whereas our calculated band gap is only 1.16 eV for the WZ ZnO structure. The value obtained here is quite close to the results of local-density approximation (LDA) and GGA band gap calculations presented in [34–36]. For all ZnO nanostructures considered in this work, the calculated HOMO–LUMO energy gap was also estimated from below and it was found that all HOMO–LUMO energy gaps are lower than that of bulk ZnO. For ZnO nanostructures larger than around 48 molecules, with the increasing cluster size, the HOMO–LUMO energy gap decreases, and the HOMO–LUMO energy gap for the WZ phase is lower than that of the graphitic phase. However, for the graphitic ZnO nanostructures smaller than about 48 molecules, with the increasing cluster size, the HOMO–LUMO energy gap increases. For WZ ZnO nanostructures smaller than about 48 molecules, with the increasing cluster size, the HOMO–LUMO energy gap decreases. The results also indicate that, with the increasing cluster size, the stability of ZnO nanostructures increases.

In summary, in this letter we have determined the relative stability between graphitic and WZ phases of ZnO nanostructures by using first principle calculations. We have also obtained the size dependence HOMO–LUMO energy gaps. Our results indicate that the relative stability sequence changes with the increasing size of nanostructures. When the number of ZnO molecules in the ZnO nanostructure is smaller than  $\sim 38$ , the relative stability of the graphitic phase is sustained. When the number of ZnO molecules in the ZnO nanostructure is larger than  $\sim 38$ , the relative stability of the WZ phase is sustained. Such a change in the relative stability sequence is due to the energy difference for different phase structures being a function of the increasing cluster size.

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