First-principles calculations on the surface effects of the ultrathin ZnO nanowire

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INTRODUCTION

Nanostructured ZnO has been intensively studied because of its remarkable performance in optoelectronics, sensors, transducers, and biomedical sciences [1]. Among them, ZnO nanowires are considered as a potential material to the photovoltaic solar cells, the piezoelectric nanogenerators [2], and gas sensors [3]. With the development of nanotechnology, the size of the device decrease rapidly, and surface effects would be more influence on material properties. However, it is obvious that the surface effects become dominant for ultrathin ZnO nanowires compared with the bulk properties, and it would be involved in a relaxation of the surface atoms, and electronic structures. In this work, the surface relaxation and the change of the electronic structure as a function of ZnO nanowire diameter were calculated, and compared the properties of bulk ZnO.

COMPUTATIONAL METHOD

We performed density functional theory calculations on the wurtzite ZnO nanowire using the SIESTA code, as implemented on the EDISON nanophysics web site [5]. The generalized gradient approximation in Perdew-Burke-Ernzerhof marte [6] was included. All calculations were perfomed using a double zeta polarized basis and norm conserving pseudopotentials of the Troullier-Martin's type [7].

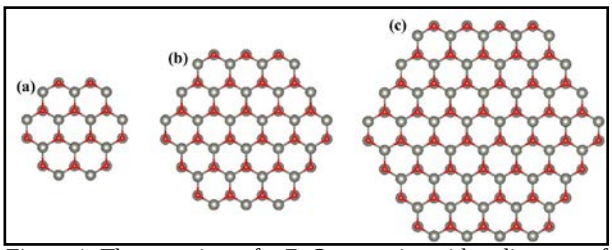

Figure 1. The top wiew of a ZnO nanowire with a diameter of 1nm (a), 1.6 nm (b), and 2.3 nm (c).

The supercell for ZnO nanowire calculations was a rectangle box with a nanowire in the center. A vacuum region of 15Å between the nanowires was considered to avoid the unnecessary interactions. The supercell shape and volume was conserved, and only ionic relaxation was performed. The atomic structures are optimized using the conjugate gradient method until the Hellman-Heynman force was smaller than 0.01 eV/Å.

RESULTS and DISCUSSION

The structure of bulk ZnO is well known that the wurtzite structure is most stable under ambient conditions, and a wide band gap of 3.3 eV. ZnO nanowires grow along the [0001] direction and have same structure as their bulk phase [4, 5]. Thus, the atomic structures of ZnO nanowires were initially constructed from the bulk wurtzite structure.

In our model, ultrathin ZnO nanowires are single crystalline and defect free, and calculated structures of ZnO nanowire have diameter of 1.0 nm, 1.6 nm, and 2.3 nm along the [0001] direction shown in Figure 1.

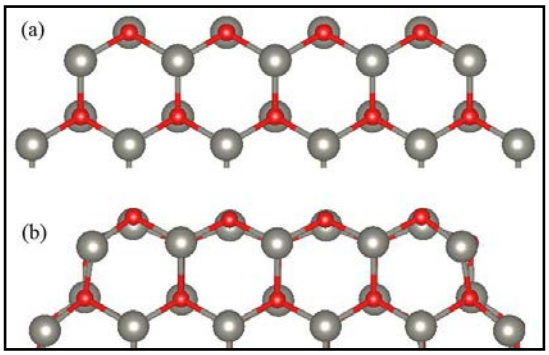

Figure 2. The surface atoms of ZnO nanowires before relaxation (a), and after relaxation (b).

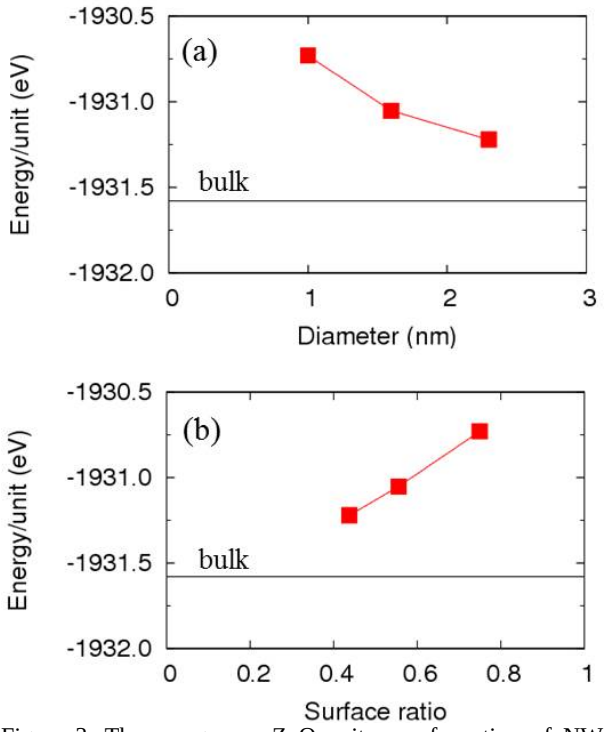

Figure 3. The energy per ZnO unit as a funcation of NW diamter (a), and surface atom ratio (b). The black solid line indicate the ground state energy of bulk wurtzite ZnO.

In Figure 2, it can be seen the after geometry relaxation, the positions of the atoms are displaced to form compact surface layers. Strong surface bonds are presented in the ZnO nanowire.

The atoms in all nanowires were barely relaxed, but the relaxation of surface Zn and O atoms are *small* inward and outward to decrease the average bond lengths of Zn-O, respectively, as shown in Figure 2 (b). As the diameter of the ZnO nanowires decreases, the amount of surface atoms and broken bonds increases, and more surface relaxation and reconstruction occur. And the surface ZnO bonds are compressed when compared to the ZnO bulk equilibrium bond length. The average Zn-O bond length at surfaces is 1.915 Å compared to the 1.962 Å in its bulk phase.

The nanowires with large diameters become energetically more favorable. We can see that the ground state energy per ZnO unit increases as the diameter of the nanowires decreases as shown in Figure 3 (a). This is understandable because the amount of surface atoms and broken bonds increases as the diameter decreases. The smaller the diameter of the nanowires, the larger the surface to bulk atom ratio, and resulting in more

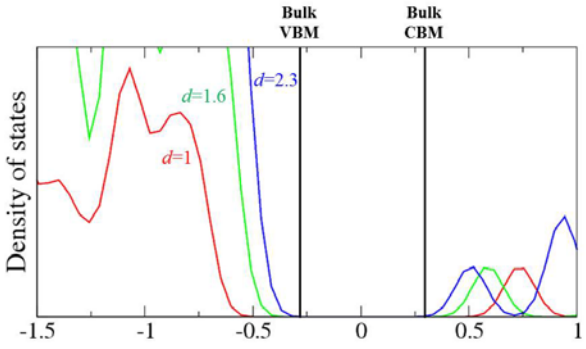

Figure 4. Density of State for ZnO nanowires near the bandgap. The black lines indicate the location of bulk VBM and CBM.

dangling bonds. Figure 3 (b) shows that the ground state energy increases almost linearly as the surface atomic ratio increase.

Our theoretical calculations significantly underestimate the bandgap of ZnO because of LDA band error as well knwon. The experimental bandgap of bulk ZnO is 3.37 eV, but theoretical value in this work is only 0.63 eV.

We found the bandgaps of ZnO nanowires are larger when compared with the calculated bulk ZnO due to the confinement effects, and linearly decrease as the diameter increases as shown in Figure 4. The bandgaps of ZnO nanowires are 1.41, 1.13, and 0.98 for a diameter of 1 nm, 1.6 nm, and 2.3 nm , respectively.

CONCLUSION

The size effects in ultrathin ZnO nanowires have been investigated based on first-principles total energy calculations. We observed that the wurtzite phase is most stable than the hexagonal and rocksalt structures. Thus, we have considered three different diameters of wurtzite ZnO nanowires with [0001] growth direction. We found that most of the atomic relaxations take place on surface atoms, and surface atoms cause change of the electronic structure of ZnO nanowires. The thinner nanowire has more surface atoms and dangling bonds,

The bandgap depend on the diameter of nanowire, while single walled nanotubes nearly independent of tubular structure and diameters. [8]

ACKNOWLEDGEMENT

This work was supported by EDISON nanophysics center.

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