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Theoretical Study on Electronic and Electrical Properties of Nano Structural ZnO

Zhigang Zhu[1], Arunabhiram Chutia[1], Riadh Sahnoun[1], Hideyuki Tsuboi[1], Michihisa Koyama[1], Nozomu Hatakeyama[1], Akira Endou[1], Hiromitsu Takaba[1], Momoji Kubo[1], Carlos A. Del Carpio[1], Akira Miyamoto[1, 2*]

[1]Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, 6-6-11-1302 Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan
[2]New Industry Creation Hatchery Center, Tohoku University, 6-6-10 Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan
Tel.: + 81-22-795-7233; Fax: + 81-22-795-7235; E-Mail: miyamoto@aki.che.tohoku.ac.jp

1. Introduction

Zinc oxide (ZnO) is wide band gap semiconductor, which has many advantage properties such as non-toxicity, good electrical, optical and piezoelectric behavior [1-2]. Recent studies have proven its competence for different potential applications in gas sensors, photocatalyst, transparent conductive oxides, light emitting diodes and laser diodes in the UV-vis range, etc. [3-4] Many morphologies of ZnO with nanoscale characteristics have been fabricated with the aim of expanding its application scope. This is because nano structural ZnO exhibits curious structures and various remarkable physical, chemical, and electrical properties distinctive from those of conventional bulk materials. In fact, ZnO has demonstrated to possess the richest nanostructures of all known materials. So far, In addition to a variety of typical nanostructures including nanowire, nanorod, nanobelt, and nanotube, some other ZnO hierarchical nanostructure, nanowhisker, nanocomb and nanohelices are also been fabricated through different synthesis approaches. In contrast to the larger amount of experimental investigations on ZnO, smaller case theoretical study on the nanostructures ZnO have been reported yet. Very recently, Tu et al. demonstrated the existence of single wall ZnO nanotube by first-principles calculations and proposed that it might be realized by the solid-vapor phase process with carbon nanotubes as templates [5]. In the present work, we then describe our theoretical results for single wall tubular forms ZnO tube by using tight-binding quantum chemical dynamics method. The nanotube are considered here is armchair (10,10) and zigzag (10,0), which are built according to the definition of single wall carbon nanotube. We show electronic and electrical characteristic of these two kinds of nanotube. The effect of intrinsic defect of oxygen vacancy on the physical properties of nanotube is also discussed.

2. Computational Method

First-principles method based on density functional theory (DFT) has been applied to obtain the ground-state structure for given ZnO nano-structures. We employed our original tight-binding quantum chemical molecular dynamics program, "Colors" to calculate the electronic structures for each of the obtained crystal structures. The electronic structure information was utilized to estimate the electrical conductivity for a given system by Monte Carlo simulation [6]. The electrical conductivity for each orbital is estimated with the following formula:

$$\sigma = ne\mu$$

where σ, n, e and μ represents electrical conductivity, number of carriers, elementary charge and mobility, respectively. To determine the carrier mobility, we assumed that a carrier moves along the molecular orbital. The electrical conductivity of a give system is estimated as the summation of the conductivity of each molecular orbital considered.

3. Results and discussion

Before we discuss the property of ZnO nanotube, it is necessary to assess the question on reliability of the method applied. The wurtzite bulk ZnO is the stable crystal structure under the ambient conditions. The partial density of states (PDOS) for bulk ZnO calculated from Colors is shown in Fig. 1(a). The PDOS reveals two primary bands between 0- 10 eV. The valence band with a maximum between –6 to –7 eV is primarily derived solely from Zn 3*d* electrons. The Zn 3*d*-derived bands are split into two groups, leading to a double-peak structure in the DOS. As can be seen in Fig. 1(a), the highest occupied molecular orbital (HOMO) is mainly contributed of oxygen 2*p* with a small amount of Zn 3*d* character, while the lowest unoccupied molecular orbital (LUMO) is prominently contributed from Zn 4*s* orbital along with small mixture of oxygen 2*p* character. The obtained energy band gap as the difference between HOMO and LUMO energies is 3.36 eV. This value is very close to the experimental data of 3.40 eV for bulk ZnO [7]. For the purpose of comparison, the PDOS calculated by DFT method is depicted in Fig. 1(b). The main features of PDOS for bulk ZnO calculated from two methods are well consistent, except the band gap is underestimated to 1.14 eV for DFT method. Systematic underestimation of the band gap is drawback for typical DFT method, which are attributed to an unphysical self-interaction inherent in the common DFT functional. Thus, our tight-binding quantum chemical dynamics molecular method applied here are expected to provide reliable electronic structure results for ZnO systems.

Like single wall carbon nanotube, ZnO nanotube can be assumed to be a cylinder rolled by graphene-like layer. The relaxed geometries of armchair (10,10) and zigzag (10,0) nanotubes are shown in Figs. 2(a) and (b), respectively. Bond length between zinc and oxygen in the two nanotubes is calculated to be in the range of 1.84-1.85 Å, which is in good agreement with results of recent paper [5]. PDOS for two infinite length ZnO nanotube are shown in Figs. 3(a) and (b). We found that the contributions of

HOMO and LUMO for two nanotubes are similar to that of bulk ZnO. However, the obtained energy band gaps of 3.88 eV for (10,10) nanotube and 3.91 eV for (10,0) nanotube are larger than the bulk value of 3.36 eV. These results differ from that of carbon nanotubes, which is known that armchair (10,10) carbon nanotube has a zero band gap and show metallic property. In contrast, our results are consistent with theoretical work of GaN single wall nanotube. It is reported that band gap of both armchair and zigzag GaN nanotubes are enlarged compared to that of bulk value due to the quantum confinement [7]. One can note that the calculated ZnO nanotube band gaps are very close to each other. This suggests that the diameter and chirality have insignificant effect on the band gap. Prior to discuss the property of nanotube with oxygen defect, we calculated a model of one oxygen atom removed from 64 atoms bulk ZnO, and found a donor level appears at around 0.6 eV below the conduction band minimum (CBM). This is in quite good agreement with the previous DFT+*U* results, which show that oxygen defect level is a deep one and located around 0. 7 eV below CBM [8]. The same with bulk ZnO, it is found that a deep defect level is at 0.8 and 0.9 eV below the CBM for (10, 0) and (10, 10) ZnO nanotubes with oxygen vacancy defect, respectively.

The electrical conductivities of un-defect and oxygen vacancy defect ZnO nanotubes are summarized in Table 1. It is well known that the semiconductor property of ZnO is caused by point defects formed in the bulk structure such as oxygen vacancy and Zn interstitial. The very low conductivity values indicate undefect ZnO nanotubes are insulators because of no defects in their structures. However, if oxygen vacancy defect is introduced in their structure, the insulator properties shift to semiconductor due to the donor level in the forbidden band gap.

4. Conclusion

Tight-binding quantum chemistry method has been applied to investigate electronic and electrical properties of ZnO single wall nanotubes. The consistence between experimental and calculated PDOS for bulk ZnO suggested the validity of our method for ZnO systems. The band gaps of infinite length of (10,0) and (10,10) nanotubes are both calculated to be enlarged compared to the bulk band gap. The estimated conductivities value indicates that un-defect ZnO nanotube exhibit insulator property. Oxygen vacancy defects can shift the insulator to semiconductor property for ZnO nanotube due to a deep donor level below the CBM.

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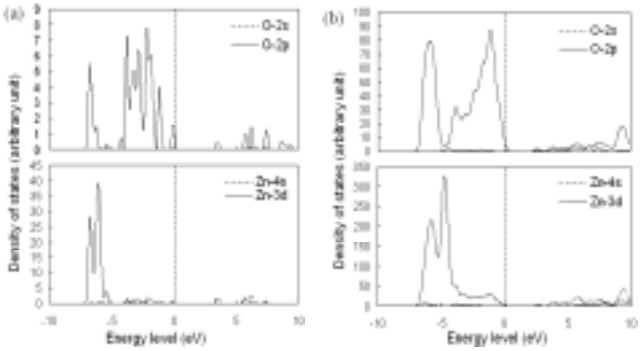

Fig. 1 Calculated partial density of states for bulk ZnO: (a) is from Colors and (b) is from Dmol[3]. Fermi level is set to zero energy.

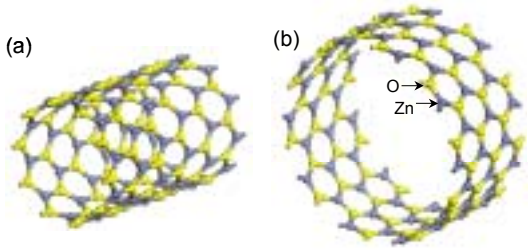

Fig. 2 Relaxed ground-state geometries for (a) zigzag (10,0) and (b) armchair (10,10) nanotube ZnO. Black and white spheres represent zinc and oxygen atom, respectively.

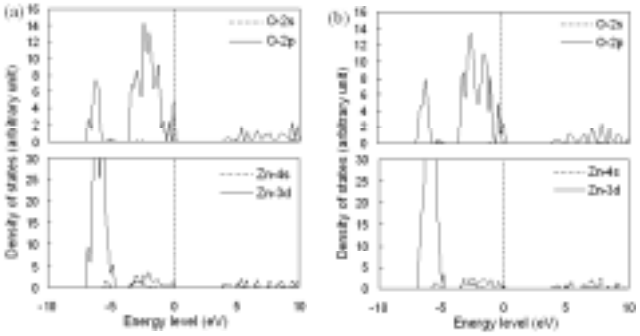

Fig. 3 Calculated partial density of states for (a) armchair (10,10) and (b) zigzag (10,0) infinite length nanotube ZnO from Colors. Fermi level is set to zero energy.

Table 1 Summarized electrical conductivities for un-defect and oxygen-vacancy nanotube ZnO

	(10, 0)		(10,10)	
	Un-defect	Oxygen defect	Un-defect	Oxygen defect
Conductivity (S cm^{-1})	9.35×10^{-30}	1.07×10^{-4}	1.65×10^{-29}	1.27×10^{-5}