Electronic properties of two-dimensional zinc oxide in hexagonal, (4,4)-tetragonal, and (4,8)-tetragonal structures by using Hybrid Functional calculation

C Supatutkul, S Pramchu, A P Jaroenjittichai* and Y Laosiritaworn

Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai, Thailand

*E-mail: atcharapunya@gmail.com

Abstract. This work reports the structures and electronic properties of two-dimensional (2D) ZnO in hexagonal, (4,8)-tetragonal, and (4,4)-tetragonal monolayer using GGA and HSE-hybrid functional. The calculated results show that the band gaps of 2D ZnO sheets are wider than those of the bulk ZnO. The hexagonal and (4,8)-tetragonal phases yield direct band gaps, which are 4.20 eV, and 4.59 eV respectively, while the (4,4)-tetragonal structure has an indirect band gap of 3.02 eV. The shrunken Zn-O bond lengths in the hexagonal and (4,8)-tetragonal indicate that they become more ionic in comparison with the bulk ZnO. In addition, the hexagonal ZnO sheet is the most energetically favourable. The total energy differences of (4,8)-tetragonal and (4,4)-tetragonal sheets from that of hexagonal monolayer (per formula unit) are 197 meV and 318 meV respectively.

1. Introduction

Two-dimensional (2D) materials are a specific type of materials with their thickness being thinned down to a single atomic layer. In many materials, their 2D sheets have been reported to yield very different physical properties from those of their ordinary bulk and other forms of nanostructures. Moreover, band gaps of 2D semiconductor sheets can vary from zero band gap, e.g. graphene, to wide band gap, e.g. BN sheet with about 6 eV band gap [1]. Among many available semiconductors, the monolayer zinc oxide possesses many intriguing properties, such as wide band gap, high charge carrier mobility, flexibility and optical transparency. Therefore, it has become a next generation semiconductor especially for flexible and transparent optoelectronics applications [2]. However, the growth of the 2D structures in typical semiconductors is very difficult to control, where the precise synthesized technique is yet to establish. This is as to form the ultrathin 2D material requires breaking of crystal symmetry and fostering of anisotropies in crystal growth [3]. Up to recent experiments, few were successful but it shows some possibilities. For instance, the epitaxial growth of ZnO monolayer in hexagonal structure on graphene substrate was recently achieved and reported to have band gap up to 4 eV [4]. In addition, sub 100-nm-sized ZnO nanosheet in hexagonal wurtzite was also found to successfully grow in the solution synthesis using surfactant molecules as a facet at the water-air interface [5]. These then illuminate some possibilities in nanostructure-engineering to achieve ultrathin semiconductor with desired properties. However, up to this date, only the synthesis of hexagonal ZnO monolayer is accomplished whereas the other structures of ZnO monolayer have not been synthesized yet, e.g. in tetragonal structures. Note that the (4,8)-tetragonal structure was recently found in the ZnO...
nanorods under high pressure [6], while the (4,4)-tetragonal structure could exist on the atomic plane of rocksalt. Since nano-structuring can introduce some intriguing properties, the 2D ZnO in hexagonal, (4,8)-tetragonal and (4,4)-tetragonal structures were investigated using density functional theory (DFT) to predict their electronic properties and structural stability.

2. Materials and Methods
The electrical properties of the 2D ZnO structure were investigated using DFT with the plane wave pseudopotential method implemented in Quantum Espresso package. The modeled structures were relaxed using Perdew-Burke-Ernzerhof parametrization (PBE) of the generalized gradient approximation (GGA) [7]. Then, the electronic calculation was performed using Heyd-Scuseria-Ernzerhof (HSE) hybrid density functional, which mixes the exact non-local exchange of Hartree-Fork (HF) potential with the exchange and correlation potential from GGA [8]. This is because the HF method lacks of inter-electronic correlation and its exchange interaction is usually overestimated. Consequently, the GGA exchange was considered to partially replace the non-local HF exchange. The percentage of mixing ratio between GGA and HF exchanges were determined from the calibration of electrical properties and the structural parameters with the database of interested compounds. The norm-conserving pseudopotentials including the Zn 3d state in its valence shell and the wavefunctions with energy cutoff of 80 Ry were chosen. Three 2D ZnO structures considered in this work are hexagonal, (4,8)-tetragonal, and (4,4)-tetragonal structures as shown in Figure 1.

![Figure 1](image)

Figure 1. The structures of 2D ZnO monolayer; (a) hexagonal structure, (b) (4-8) tetragonal structures, and (c) (4,4) tetragonal structure. The red spheres represent Zn atoms and the purple spheres represent O atoms. In (b), the longer Zn-O bond length is \( f_1 \) and the shorter one is \( f_2 \).

3. Results and Discussions
In our calculations, we firstly calculated the lattice parameters and band gaps of bulk ZnO in wurtzite and zincblende phases to compare with the experimental measurements. The calculated lattice parameters \( a \) and \( c \) agree well with the experimental values as shown in Table 1. The calculated bond lengths between Zn atom and O atom (Zn-O) are 1.99 Å and 2.00 Å for wurtzite and zincblende ZnO, which are also in agreement with the experiments as shown in Table 1. For the band gap calculations, the GGA underestimates band gaps of both wurtzite and zincblende structures, which are 0.72 eV and 0.65 eV, respectively. The band gap underestimation of GGA in ZnO happens from the shift of \( p \) orbitals of O atom into the gap due to the interaction with \( d \) orbitals of Zn. To overcome this problem, the HSE hybrid functional was considered by mixing the exact non-local exchange from the Hartree-Fork (HF) method with the local GGA exchange. The mixing parameter for the HSE functional in our work was set to 0.4 (40% of HF exchange), resulting from calibration of wurtzite and zincblende ZnO band gaps to match the experimental values [9, 10], i.e. see Table 1.
Figure 2. The band structures of 2D ZnO monolayer in (a) hexagonal, (b) (4,8)-tetragonal and (c) (4,4)-tetragonal structures.

Table 1 The lattice parameters $a$ and $c$, the energy gaps at gamma point, and the bond lengths between Zn and O atom (Zn-O) in bulk and 2D ZnO.

| parameters       | bulk ZnO | 2D ZnO |
|------------------|----------|--------|
|                  | wurtzite | zincblende | hexagonal | 4,8-tetragonal | 4,4-tetragonal |
|                  | Cal.     | Exp.    | Cal.     | Exp. | Cal. | Exp. | Cal. | Exp. |
| $a$ (Å)          | 3.28     | 3.25$^{[11]}$ | 4.62     | 4.47$^{[12]}$ |
| $c$ (Å)          | 5.27     | 5.20$^{[13]}$ | -        | -   |
| band gap (eV)    | GGA      | 0.72    | 0.65     | 1.68 | 2.10 | 0.73 |
|                  | HSE      | 3.34    | 3.37$^{[10]}$ | 3.21 | 3.22$^{[9]}$ | 4.20 | 4.48$^{[14]}$ | 4.59 | 5.54 |
| Zn-O bond(Å)     |         | 1.99    | 1.98$^{[9]}$ | 2.00 | 1.99$^{[1]}$ | 1.89 | 1.82, 1.91$^*$ | 2.01 |

*The shorter bond length is coupled to octagon and square lattices but the longer bond length lies in between the octagon lattices.

Next, the electronic band structures of 2D ZnO sheets were calculated. The band structures show that both hexagonal and (4,8)-tetragonal monolayers have direct band gap at $\Gamma$ but the (4,4)-tetragonal monolayer has indirect band gap at X-$\Gamma$ as shown in Figure 2. The band gaps obtained from using HSE hybrid calculations are 4.20 eV and 4.59 eV for hexagonal and (4,8)-tetragonal sheets respectively, which is wider than that of the bulk ZnO (3.37 eV and 3.22 eV for wurtzite and zincblende). Nevertheless, the (4,4)-tetragonal structure has a direct band gap of 5.00 eV and indirect band gap of 3.06 eV. Note that, only the band gap of the hexagonal monolayer is available measured and has been reported recently at 4.48 eV [12], whereas other 2D structures have not been synthesized yet. These varieties of wide band-gap 2D ZnO then have potentials to be implemented in nanoscale UV optoelectronic via nano-structural engineering. In addition, the relaxed hexagonal (Figure 1 (a)) and (4,4)-tetragonal (Figure 1 (c)) structures shows that the Zn-O bond length is uniform due to their high symmetric geometry. However, the (4,8)-tetragonal structure has two different Zn-O bond
lengths, where the longer Zn-O bond length ($f_i$) locates at line between the two octagon lattices as shown in Figure 1 (b). On the other hand, the shorter Zn-O bond length ($f_s$) lies between the octagon and the square lattices. The calculated Zn-O bond lengths of 2D ZnO structures are also shown in Table 1. The Zn-O bond length is 1.89 Å in the hexagonal ZnO, which is shorter than that of the bulk ZnO whereas the Zn-O bond length in (4,4)-tetragonal structure is 2.01 Å, which is comparable with the bond length in the bulk. As mentioned earlier, the (4,8)-tetragonal ZnO shows two different Zn-O bond lengths, i.e. 1.82 Å for $f_s$ and 1.91 Å for $f_i$, which are shorter than that of the bulk ZnO like in case of the hexagonal sheet. The shrunken of Zn-O bond length means that the interatomic interaction favors more ionic in the 2D structures than that in bulk. For the stability of the structures, we found that the hexagonal ZnO is the most stable structure. The (4,4)- and (4,8)-tetragonal ZnO have total energy per formula of 318 meV and 197 meV higher than that of the hexagonal one, respectively. The small deviations of total energy in (4,8)- and (4,4)-tetragonal structures from the hexagonal structure show the possibilities to be synthesized. With the reported results, these calculated structural parameters and electronic properties could benefit as a database/guideline for future experiments.

4. Conclusion
In this work, the structural and electronic properties of 2D ZnO nanosheets were investigated using DFT with GGA-PBE and HSE hybrid functional. The results reveal that the hexagonal and (4,8)-tetragonal ZnO sheets yield the direct band gaps whereas (4,4)-tetragonal ZnO sheet gives an indirect band gap at X-$\Gamma$. The hexagonal and (4,8)-tetragonal structures have more ionicity compared with that of the bulk ZnO. The calculation also predicts that the hexagonal structure is the most energetically favourable among these three 2D ZnO structures. The small energy differences between these 2D ZnO phases suggest that they may coexist. Moreover, transformation among these three phases is also possible, which can be induced by many factors such as the external hydrostatic pressure, crystallographic defects, stress, and temperature. Consequently, to synthesis 2D ZnO in a particular pure phases require great attention during the preparation.

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