Band-gap engineering of SnO₂

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Abstract

Using first principles calculations based on density functional theory (DFT), the electronic properties of SnO₂ bulk and thin films are studied. The electronic band structures and total energy over a range of SnO₂-multilayer have been studied using DFT within the local density approximation (LDA). We show that changing the interatomic distances and relative positions of atoms could modify the band-gap energy of SnO₂ semiconductors. Electronic-structure calculations show that band-gap engineering is a powerful technique for the design of new promising candidates with a direct band-gap. Our results present an important advance toward controlling the band structure and optoelectronic properties of few-layer SnO₂ via strain engineering, with important implications for practical device applications.

Key words: Semiconductors, SnO₂, Multilayer, DFT, Band-gap engineering.

Introduction:

Semiconductor nanomaterials as the significant foundations for various nanoscale electronic and optoelectronic devices, such as single-electron transistors, single-molecule sensors, and nanowire lasers, and have attracted a great deal of attention [1-7]. The tin oxide semiconductor nanomaterials are of great industrial interest due to their unique properties, such as the n-type semiconductor character, the high optical transmission in the visible range, the infrared reflection, transparent thermal barrier component, and good chemical stability. They are also used in the design of chemical sensors [8-11]. However, the physicochemical properties of these semiconductors are closely related to the procedures and conditions for their development. Indeed, it will be possible to obtain films having a crystalline or amorphous structure according to the methods of their fabrication; their structural properties are then affected. These play an important role in the optical and electrical properties of the layers. They also influence on their chemical stability in time. Problems related to these deposits can come either from the technology itself or compounds used as precursors or even synthetic conditions. All of these parameters has a major impact on the structural properties (grain size, aggregate size), optical (layer thickness, refractive index, absorption, reflection and transmission in different regions of the electromagnetic spectrum) and electric (electrical conductivity, carrier density, quantum confinement) of the oxide formed [12-14]. Among the transparent conductive oxide (TCO) materials, tin dioxide (SnO_2) has gained extensive attention of researchers over the past decades owing to its excellent electrical, optical, and electro-chemical properties, which is also attractive for potential applications such as solar cells and flat panel displays. However, bulk SnO_2 cannot efficiently emit UV light due to the dipole forbidden nature of its band edge quantum states, which has hindered its potential optoelectronic applications. Most studies reported a dominant broad visible emission band centered at around 540 nm instead of the near band edge (NBE) UV emission for bulk SnO_2 . To recover the optical activity of SnO_2 corresponding to the “forbidden” band gap, and to use it as a UV light emitter, some researchers attempted to utilize SnO_2 nanostructures, including nanowires and quantum dots, to modify SnO_2 electronic structure so that the dipole forbidden rule can be broken. The study of these materials, in thin and ultra thin layers, is motivated by the need to integrate these materials in miniaturized devices as well as the study of new phenomena occurring at the nanoscale. However, to our knowledge, the compressive investigations of these materials in thin and ultra thin layers are still lacking in the experimental and theoretical reports. Therefore, we will study the structural, electronic, and

optical properties of thin layers and ultra thin SnO₂. In this way, the main goal of this work is to study the effect of layer thickness, and the evaluation of the structural and optical properties, as well as their electronic structure properties. The electronic structure and band structure properties of semiconductors have been improved, by the effect of external pressure and internal strain via the interatomic distances and relative positions of atoms.

2. Computational details:

To solve the density functional theory (DFT) one-particle equations, we use a multiple-scattering theory, i.e. the KKR Green's function method combined with the coherent potential approximation (CPA). The relativistic effects have been taken into account by employing the scalar relativistic approximation. The form of the crystal potential has been approximated by a muffin-tin potential, and the wave functions in the respective muffin-tin spheres have been expanded in real harmonics up to " $l=2$ ", where " l " is the angular momentum quantum number defined at each site. In the present KKR-CPA calculations, where the package MACHIKANEYAMA2000 coded by Akai [15] is used, 500 K-points in the whole first Brillouin zone were taken into account. In this study, the KKR method within the Local Density Approximation (LDA) has been used for the parameterization of the exchange energy [16]. The SnO₂ oxide crystallizes in the rutile-type structure (P42/mnm, space group N°136) at ambient conditions. The Wyckoff position of Sn and O are $2a$ (0, 0, 0) and $4f$ (u, u, 0), respectively, where $u=0.3056$ [17]. In order to achieve a good packing, 8 additional "empty" spheres (ES) with ($Z=0$) representing atomic inter-sites are placed in ($\frac{1}{2}, 0, 0.1682$) ($0, \frac{1}{2}, -0.1682$) ($0, \frac{1}{2}, 0.1682$) ($\frac{1}{2}, 0, 0.1682$) ($-0.3125, 0.3125, 0$) ($-0.1875, -0.1875, 0$) ($0.1875, 0.1875, 0$), ($0.3125, -0.3125, 0$). The lattice constants used as input in the calculation are the experimental values [17]. For SnO₂ thin and ultra thin layers are constructed from 3D rutile structure. All structures were treated with periodic boundary conditions in x-, y-direction to simulate an infinite plane, and the supercell was large enough to ensure a vacuum spacing along z-direction to get 2, 4 and 8 layers. The vacuum thickness considered was wide enough to prevent layer-to-layer interactions and we found that a width of 15 °Å was sufficient to ensure that the energy was converged. The optimized (a) unit cell and (b) 1 layer of SnO₂ in the rutile-type structure are displayed in figure 1.

3. Results and discussion:

3.1. Optimized structures calculations:

The structures optimizations for bulk and SnO₂ layers have been done according to three different methods: according “*a*” (where “*c/a*” is fixed, **Fig.2.a**), according “*c/a*” (**Fig.2.c**), and according to “*c*” where the “*a*” parameter is fixed see **Fig.2.b**. The equilibrium parameters correspond to the minimal energies calculated for each cases cited above. The **Fig.2** shows that optimized parameters “*a*, *c*” and “*c/a*” of the layers are lower than those of SnO₂ bulk and increase by increasing the numbers of layers from 2 to 8 layers of SnO₂.

3.2 Electronic structure calculations:

Before studying the multilayer SnO₂ materials, it is necessarily to understand the electronic properties of bulk SnO₂. For this purpose, the total (DOS) and the partial (PDOS) densities of the electronic states of SnO₂ have been calculated, see **Fig. 3**. The electronic structure of the rutile SnO₂ exhibits a nonmetallic character with a band gap equal to 2.30 eV calculated by the LDA approximation (**Fig. 3**), which is smaller than the experimental value 3.40 eV [18]. The difference between the experimental result and our calculation is due to the principles calculations based on the density functional theory which usually suffers from the errors in the estimation of the band-gap [19,20]. From the PDOS (**Fig. 3**), we found that the valence band of SnO₂ consists mainly of *O-2p* states and a few *5p* states of Sn, whereas the conduction band originated mainly from *O-2p* and *Sn-5p* states. The study of the effect of external pressure and the internal strain on the electronic structure has been done by means of the variation of the inter-atomic distances and the relative positions of atoms. According to the 3 methods of relaxation (see section 3.1), the structural parameters change (“*a*”, “*c*” parameters, the ratio “*c/a*” and the positions of atoms) and therefore the electronic properties of SnO₂ change also. This changing can be seen by the decrease or the increase of the band gap in the band structure (see **Fig. 4** and **Fig. 4**). The band structure of nanofilms (2, 4, 8 layers) and bulk SnO₂ when the “*c*” parameter is fixed and “*a*” relaxed is plotted in **Fig.4**. It follows that the SnO₂ films exhibit a semiconductor character like the bulk system (**Fig. 3**) and have a direct band gaps at the *Γ* point. The band gaps of SnO₂ films (2, 4 and 8 layers) are larger than the gap of the bulk with a rutile-structure and decreases with increasing the film thickness. This should probably be attributed to the fact that with increasing of the film thickness, the electrons in the film are less confined. As a result, the confinement effects in the film become weaker, leading to the decrease of the band gap. The same results was

observed in the case of (b , a) fixed and c/a relaxed. However, when we relax the “ c ” parameter where “ a ” is kept fixed (**Fig. 5**), one can see that the band gap increases when the film thickness increases, and it converges to the value of the band gap energy of the SnO₂ bulk layer when the number of layers increases above 8 layers. The values of the band gap as function of the numbers of layers are summarized in **Fig. 6**. Electronic-structure calculations show that band-gap engineering is a powerful technique for the design of new semiconductor materials and devices. We show that the effect of external pressure and internal strain can be studied via the interatomic distances and relative positions of atoms and also a good way to understand the effects of dimensionality in quantum confinement systems. **We found that the band structure of SnO₂ semiconductors could be modified by the interatomic distances and relative positions of atom, and the epitaxial along “c-axes” is more efficient than the epitaxial along “a-“ or “b-axes” for tuning the band gap of SnO₂.**

Conclusion:

In this work, using the DFT within LDA, we studied the effect of external pressure and internal strain via the interatomic distances and relative positions of SnO₂. The density of states and band structure of semiconductors have been discussed to improve the properties of this material. We show that the band structure of semiconductors could be modified by the interatomic distances and relative positions of atoms. The electronic-structure calculations showed that band-gap engineering is a powerful technique for the design of new semiconductor materials and devices.

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Figure Caption:

Figure 1: Optimized stable (a) unit cell and (b) 1 layer of SnO₂.

Figure 2: First-principles calculation of total energy versus lattice parameter of SnO₂ multilayer compared to the bulk system.

Figure 3: The total and projected DOS for the bulk rutile SnO₂.

Figure 4: Band structure of film and bulk SnO₂ with the equilibrium (relaxation method along *a*): a) 2 layers; b) 4 layers; c) 8 layers ; d) bulk

Figure 5: Band structure of film and bulk SnO₂ in the equilibrium structure for layers (2, 4 ,8 layers and bulk (relaxation method along *c*): a) 2 layers; b) 4 layers; c) 8 layers ; d) bulk

Figure 6: Variation in the band gap of SnO₂ film as function as number of layers (2, 4 and 8 layers): relaxation method along *c/a* (*black line*); relaxation method along *c/a* (*red line*); relaxation method along *c/a* (*blue line*)

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6