Research Article

First principles Calculations of Electronic Structure Properties of CdSe$_{0.5}$Te$_{0.5}$ Core and (001)-(1x1) Slab geometry Oxidized Surface

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Abstract

*The electronic structure of (001)-(1×1) oxidized surface and core of II-VI zinc-blende **CdSe$_{0.5}$Te$_{0.5}$** ternary semiconductor alloy Nano -crystals are investigated using Ab- initio Density functional theory (Ab-initio-DFT) at the generalized-gradient approximation (GGA) level with STO-3G basis set coupled with large unit cell method(LUC). Calculations include only 8 core atoms 3D periodic boundary condition (PBC) and using 2D (PBC) with particular regard to the oxygenated (001)-(1x1) slab geometry surface. M any properties included total energy , cohesive energy, energy gap , valence and conduction bands width and density of states for core and surface part have been investigated, as well as the atomic charges of oxygenated (001)-(1x1) surface . The results obtained show that the energy gap and lattice constant of **CdSe$_{0.5}$Te$_{0.5}$** nanocrystal for the surface part are smaller than of core part. Results show the energy gap for alloying composition **CdSe$_{0.5}$Te$_{0.5}$** for 8 core atoms is equal to 2.545 eV, while it is equal to 0.032 eV for **Cd$_8$Se$_4$Te$_4$-O$_4$** .*

*Keywords: Electronic Structure; **CdSeTe** Nano-crystals; Oxidized Surface.*

1. Introduction

Cadmium chalcogenides family is one of the II–VI semiconductor compounds. CdSe and CdTe form a solid solution throughout the entire composition in the compound **CdSeTe**. This ternary is a very important materials for the development of various modern technologies of solid state devices such as solar cells, high efficiency thin film transistors, and light emitting diodes**.** Other areas of successful applications include photo-detectors, light amplifiers, lasers, photo electrochemical cells gas sensors for the detection of oxygen, etc. (S. Ouendadji *et al*, 2011). These materials are characterized by different degrees of covalent, ionic and metallic bonding, and they crystallize in different crystal structures (such as zinc-blende and wurtzite). The main advantage of the **CdSeTe** alloys is its crystal structure and tailoring of band gap by changing the concentration of selenium and tellurium, so that solar energy can be effectively harnessed for maximum conversion to electrical energy.

The study of semiconductor oxides has great technological importance because they appear as native oxides in uncoated semiconductor surfaces, but also can play a key role in semiconductor devices, as SiO2 in microelectronics. Technological developments based on other semiconductors need a proper control

of their oxides, among a family of compatible materials that function as substrates, contacts, coatings, optical windows, etc.(E. Menéndez-Proupin *et al*, 2009).

In the present work the problem is divided into two parts; core part and surface part which is the traditional method used in solid state calculations. Performing the core part, using the LUC method, added to the oxygenated (001)-(1×1) surface case, to obtain a complete electronic structure view of **CdSe$_{0.5}$Te$_{0.5}$** ternary nanocrystals.

2. Theory

The central equation that describes the interaction of the electrons and the nuclei of a many-body system is the time-independent, non-relativistic form of the Schrödinger equation. In the most common formulation of quantum mechanics, solving this problem means solving the N-electron Schrödinger equation:

$$\hat{H}\psi = E\psi \qquad (1)$$

This equation involving the Hamiltonian operator Ĥ, the wave function Ψ , and the eigen value *E*. Here, we will focus on finding the ground state of the system; that is, the eigen function Ψ that gives the lowest energy *E*. Several theories gave approximate solutions to calculate the electronic structure properties for **CdSeTe** nanocrystal for 8 core atoms, one of these

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powerful theories is the density functional theory (DFT) coupled with the large unit cell (LUC). DFT gives a superior accuracy to Hartree-Fock theory, ab-initio and the semi-empirical approaches. The Slater Type Orbitals (STO-3G) basis set is used in the calculation. The central quantity in DFT is the electron density $\rho(\mathbf{r})$. It is defined as the integral over the spin coordinates of all electrons and over all but one of the spatial variables ($\mathbf{x=r}$,s): (R. G. Parr *et al*, 1983).

$$\rho(\mathbf{r}) = N \int \cdots \int |\psi(x_1, x_2, ..., x_N)|^2 \, ds_1 \, dx_2 \, dx_3 \cdots dx_N \quad (2)$$

Where $\rho(\mathbf{r})$ is the probability of finding any of the N electrons within a volume element d$\mathbf{r}$. Because $\rho(\mathbf{r})$ represents the probability, this means that $\rho(\mathbf{r})$ is a non-negative function and vanishes at infinity and integrates to the total number of electrons N. In the large unit cell method, only the lattice constant is optimized for the core part. However, the surface part bond lengths and angles still need to be optimized because of surface reconstruction. The oxidized surface contains the surface oxygen and outer four layers of CdSeTe atoms whereas the core includes the remaining CdSeTe atoms such as previous studied (H.M. Abduljalil *et al*, 2011). Gaussian 03 program is used to perform the core LUC and the oxygenated (001)-(1 × 1) surface that can be added to obtain a complete electronic structure view (M J Frisch *et al*, 2003). We shall use the density functional theory at the generalized gradient approximation (GGA) method level.

Kohn-Sham density theory (W. Kohn and L. J. Sham, 1965) is widely used for self-consistent – field electronic structure calculations of the ground state properties of atoms, molecules, and solids. In this theory, only exchange – correlation energy $E_{XC} = E_X + E_C$ as a functional of the electron spin densities $n_\uparrow(\vec{r})$ and $n_\downarrow(\vec{r})$ must be approximated. The generalized gradient approximation (GGA) (R. M. Dreizler and E. K. U. Gross , 1990; D. C. Langreth and M. J. Mehl , 1983):

$$E_{XC}^{GGA}[n_\uparrow, n_\downarrow] = \int \in_{XC}(n_\uparrow, n_\downarrow, \vec{\nabla} n_\uparrow, \vec{\nabla} n_\downarrow) n(\vec{r}) d^3 r \quad (3)$$

Where $n = n_\uparrow + n_\downarrow$, $\in_{XC}(n_\uparrow, n_\downarrow)$ is the exchange-correlation energy per electron of an electron gas with uniform spin densities $n_\uparrow(\vec{r})$ and $n_\downarrow(\vec{r})$, using the latter (GGA) very good results for molecular geometries and ground-state energies have been achieved (J. P. Perdew *et al*, 1996).

3. Calculations and Results

The nanocrystal core 3D periodic boundary condition (PBC) of **CdSe$_{0.5}$Te$_{0.5}$** nanocrystalls calculations has been studied and using 2D (PBC) with particular

regard to the oxygenated (001)-(1 × 1) surface is added to obtain a complete electronic structure view. Fig. **1(a)** shows the total energy as a function of the lattice constant optimization of 8 atom core part LUC for **CdSe$_{0.5}$Te$_{0.5}$**, (**b**) the optimized geometrical structure of 8 atom core. Fig. **2** (**a**) shows the total energy as a function of the lattice constant optimization of 8 atom surface part LUC for **Cd$_8$Se$_4$Te$_4$-O$_4$** , (**b**) the optimized geometrical structure of 8 atom core.

Stability of the nanocrystal is at equilibrium when lattice constant is equal to 0.620 nm for core part, while it is equal 0.608 nm of the surface part , which the attraction and repulsion forces between atoms are equal such as previous studied (Ibtesam O. Radi *et al*, 2007; M. T. Hussein *et al*, 2013). The optimized bond length Cd-**O** is 1.71 A° while that of Se-**O** is 1.67 A° and of Te-**O** is 2.0 Å. However these values in other studies are 2.0A° for Cd-**O** , 1.53A° for Se-**O** and 2.31 Å of Te-**O** (Mohammed. T. Hussein *et al*, 2013; Mohammed. T. Hussein *et al*, 2013; R. Miotto and F. D. Kiss , 2003) **.** The energy gap of the stoichiometry **Cd$_8$Se$_4$Te$_4$-O$_4$** is 0.032 eV, while in core part is equal to 2.545eV. From comparing the energy gap of LUC of core with the energy gap of oxygenated (001)-(1×1) surface, we can note that the energy gap at the surface is much less than that at the core. Energy gap has been calculated using the following equation:

Eg = | (LUMO) - (HOMO) | (Akram H. Taha *et al*, 2014)

As a consequence, the energy gap is controlled by the surface of nanocrystals.

The results show that the core states larger energy gap and smaller valence and conduction bands. Owing to perfect symmetry of the core, the core states are more density of states. This reflects the broken symmetry and discontinuity at the surface and existence of new kind of atoms (oxygen atoms), and the variation of bond lengths and angles as well as lattice constant (S.M. Sze and K. K.Ng. , 2007; R. Evarestov *et al*, 1975).
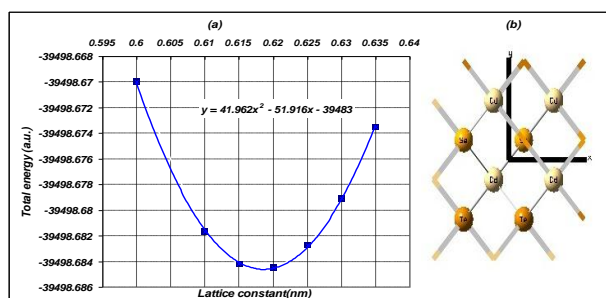

Fig.1 (a) Total energy as a function of lattice constant of **CdSe$_{0.5}$Te$_{0.5}$** for 8 core atoms per LUC, (b) The optimized geometrical structure of 8 atom core
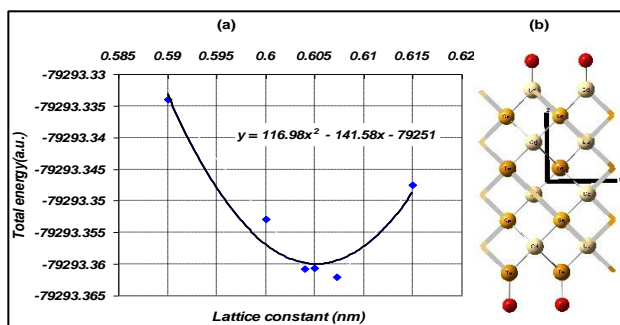
Fig.2 (a) Total energy for 8 core atoms oxygenated (001)-(1×1) $Cd_8Se_4Te_4$-O_4 surface as a function of lattice constant, (b) The optimized geometrical structure of 8 atom core

Fig.(**3-a,b**) shows the density of states of $CdSe_{0.5}Te_{0.5}$ for 8 core atoms and surface respectively , which exhibits a lower density of states and higher degenerate state of surface part compared with core part. This lower density of states in surface part is caused by the existing of oxygen atoms. The discontinuity of surface imposes level splitting on the higher degenerate state. The splitting of energy level does not affect the number of degenerate state only but also the conduction and valence bands width (Mohammed. T. Hussein *et al*, 2013; Mudar A. Abdulsattar *et al*, 2012). Also, the splitting of states and additional states has an effect on the band gap.
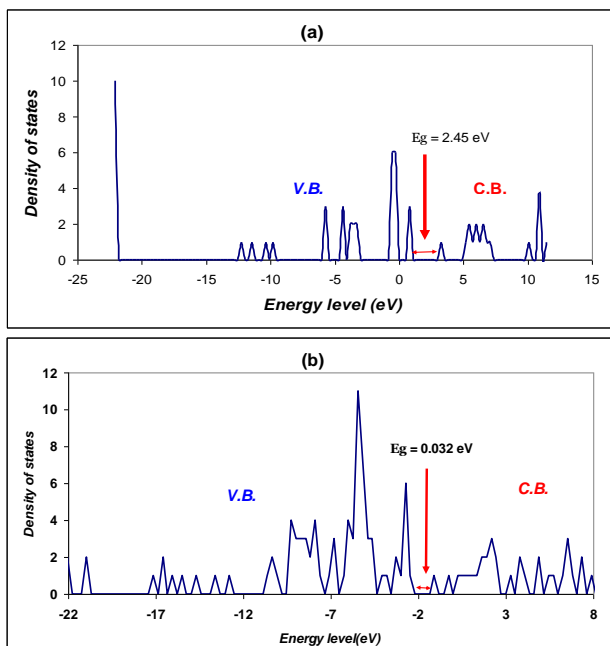

Fig. 3 Density of states as a function of energy levels of (a) $Cd Se_{0.5}Te_{0.5}$ for 8 core atoms per LUC . (b) for $Cd_8Se_4Te_4$-O_4 for surface oxygenated (001)-(1×1) slab having a^2 area.

The properties of the $CdSe_{0.5}Te_{0.5}$ nanocrystal (001)-(1×1) oxidized surface is also investigated using slab geometry of the stoichiometry $Cd_8Se_4Te_4$-O_4 LUC. This

stoichiometry is repeated periodically (in 2D surface) and restricted to the actual surface size of the nanocrystal. Surface calculations are more demandable in computer time than core because of lack of symmetry which is the reason for restricting our calculations for the upper mentioned surface only.

In Fig.**4** shows the atomic charges of oxygenated (001)-(1x1) surface calculated for stoichiometry $Cd_8Se_4Te_4$-O_4 atoms as a function of layer depth using the slab geometry method, which appear the negative and positive charges are assigned to Te and Cd atoms, the Te and Cd atoms take the charges **-0.002** and **+0.359** arbitrary unit (a.u), respectively.
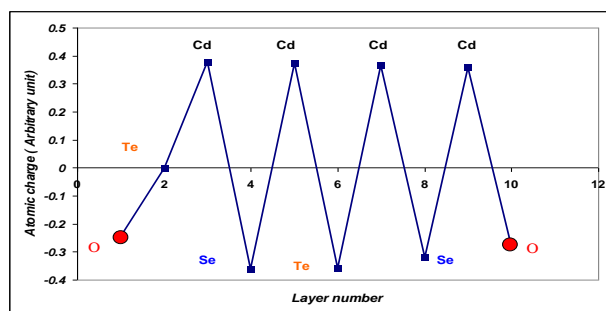

Fig.4 Atomic charges as a function of layers depth of oxygenated (001)-(1x1) surface for $Cd_8Se_4Te_4$-O_4 nanocrystal surface using slab geometry.

Conclusions

Nanocrystal oxidized surfaces shows smaller energy gaps and lattice constant of *CdSeTe* alloy composition , while the surface exhibits higher degenerate state as compared with core part. This reflects the broken symmetry and discontinuity at the surface with existence of new kind of atoms (oxygen atoms), and the variation of bond lengths and angles.

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