Full Length Research Article

INTRODUCING NOVEL INTERMEDIATE BAND MATERIALS FOR HIGH-EFFICIENCY SOLAR CELLS BASED ON ZnSe DOPED WITH TRANSITION METALS

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ARTICLE INFO	ABSTRACT
	Solar cell materials with more than one bandgap offer the possibility to increase the efficiency of the solar cell beyond that of a single bandgap cell. In the present study comprehensive analysis is carried out on ZnSe doped with transition metals. Theoretical studies confirm the formation of suitable mini-bands within ZnSe band gap by doping of transition metals. The mini bands mainly are created by nd orbitals of the transition metals. Absorption coefficient, density of states and band structure are three important features of the proposed materials. Here, we calculated these characteristics for the ZnSe doped with TM=V, Cr, Mn, and Fe as candidates for presenting an isolated partially-filled narrow bands between the valance band and the conduc- tion band. The absorption coefficient in sub-band-gap energy is greatly improved by the induction of the IB compared to the ZnSe host. The simulation shows that ZnSe(V) and ZnSe(Cr) can be create desired IB in in comparison to Mn and Fe.

INTRODUCTION

Intermediate band solar cells (IBSCs) have been the top- ic of interesting researches in recent years due to their promising features and are expected to be a suitable so- lution for high efficiency application. These new solar cells are characterized by a full band (valance band), empty band (conduction band), and a partially filled in- termediate band (IB). In the intermediate band solar cell with metal doping an intermediate narrow metallic band is placed in the traditional forbidden bandgap which ex- tends the absorption spectrum (Tablero *et al*., 2006; Sanchez *et al*., 2009 and Yu *et al*., 2003). This generates extra electron–hole pairs and thus increases the current without decreasing the output voltage and therefore increases the quantum efficiency. Substitution of transition metal (TM) atoms in ZnSe may give rise to a type of high-efficiency photovoltaic materials with intermediate bands to absorb low energy photons.

Numerous ab initio quantum calculations have been per Wahnón and Tablero (Wahnón *et al*., 2002) published Ab initio electronic structure calculations for metallic intermediate band formation in photovoltaic materials in 2002. In 2006 Palacios *et al*. (2006) introduced Energetics of formation of TiGa3As4 and TiGa3P4 intermediate band materials.

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The same authors (Palacios *et al*., 2008) reported Transition metal substituted indium thiospinels as novel intermediate-band materials: Prediction and understanding of their electronic properties in 2008. In 2012 Antonio Luque, Antonio Martí and Colin Stanley (Luque *et al*., 2012) reported a comprehensive article in nature photonics with the topic of intermediate-band solar cells. Conventional materials that have been used in single junction solar cells fabrication have some problems. Low band gap single junction solar cells produce high current density but their voltage is low. This is in contrast for high band gap materials. Shockley and Queisser (1961) showed that the maximum theoretical efficiency of a single junction solar cell is limit to 40.7% for full concentration and However, the maximum power conversion limitation for single-junction solar cells is lower than desired, due to energy loss for solar photons with energy exceeding the bandgap energy and absence of solar cell response to solar photons with energy below the bandgap energy. In the intermediate band solar cells a high band gap material has been used with high open circuit voltage. The IB is designed to be partially filled to permit the absorption of low-energy photons to pass the electrons from the VB to the partially filled IB and from the IB to the CB to support both the high voltage in a large band gap material and high current by absorbing sub-band gap photons without degrading the output voltage of the cell and hence, to yield higher output efficiency. In order to understand of the device performances the band diagram of intermediate band solar cells are shown in Figure 1.
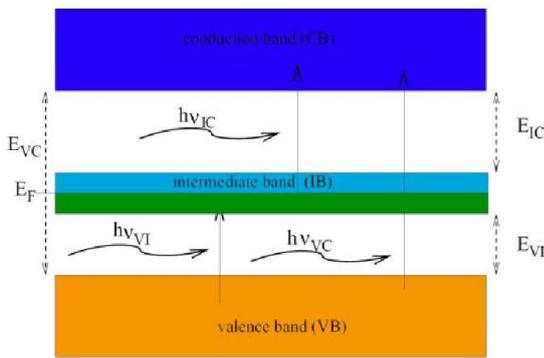
Fig. 1. Band diagram model of the Intermediate band solar cells

The limiting efficiency of the IBSC concept for full concentration and at room temperature is 63.2% with optimized absorption energies at 0.7eV up to valance band or below the conduction band, and the main band gap of 1.9 eV, (Luque *et al*., 1997) significantly overcoming the Shockley-Queisser (1961) limit of 40.7% for a conventional single-gap solar cell under the same operating conditions. Zinc selenide (ZnSe), is a wide-band gap semiconductor of the II-VI semiconductor group (zinc and selenium belong to the 12th and 16th groups of the periodic table, respectively). It is an intrinsic semiconductor with a band gap of about 2.70eV at 25 °C (Chadi *et al*., 1994 and Mahalingam *et al*., 2007). The mentioned material can be doped n-type doping with, for instance halogen elements. P-type doping can be achieved by introducing nitrogen. Its band gap is close to optimum band energy. 2.7eV is a band gap that has maximum efficiency of 56% for IB 1.1eV up to valance band or below the conduction band for full concentration condition (Luque *et al*., 1997 and Luque *et al*., 2012). Here we describe a comprehensive study on electronic and optical properties of ZnSe (TM) materials, where TM is the transition metals V, Cr, Mn and Fe, are studied with density functional theory to survey the candidate of intermediate band (IB) material. The result shows that the sub-band formed in the ZnSe some bands are completely isolated from the CB and the VB. The calculation absorption coefficient for proposed materials were performed and it is greatly improved by the induction of the IB compared to the ZnSe host.

Simulation Method

For the past 30 years density functional theory (DFT) has been the dominant method for the quantum mechanical simulation of periodic systems. In recent years it has also been adopted by quantum chemists and is now very widely used for the simulation of energy surfaces in molecules. In our proposed material, for determining the electronic properties of ZnTe (TM) materials, the Schrodinger equation is solved using DFT (Soler *et al*., 2002). The following steps are used the DFT that allows us to map the interacting many-body problem onto a one-body problem using the Kohn–Sham (KS) method (Kohn and Sham, 1965). Materials' properties are dominated by the groundstate. For the groundstate we can use a different form of QM Density functional theory. The groundstate energy E and density $\rho(\mathbf{r})$ of electrons are exactly the same as those of non-interacting particles in a specially modified potential. Non-interacting Schrödinger equations are given as:

$$\left[-\frac{\hbar}{2m}\nabla^2 + V[\rho](r)\right]\Psi_j(r) = \varepsilon_j\Psi_j(r) \qquad (1)$$

V (ρ) is a density functional and given as:

$$\rho(r) = \sum_{j=1}^{N}\left|\Psi_j(r)\right|^2 \qquad (2)$$

There is no exact value for V (ρ), but there are reasonable approximations available. The classical contributions to V (ρ) are given as:

$$E_H[\rho] = \frac{1}{2}\iint\frac{\rho(r)\rho(r')}{|r-r'|} \qquad (3)$$

We must have QM exchange and electron correlation. To introduce the exchange and correlation term we used the Perdew, Burke and Ernzerhof (Perdew and Zunger, 1981) parameterization for Generalised gradient approximations (GGA) and the Ceperley–Alder (1980) parameterization for Local density approximation LDA. Despite its approximations, this theory is one of the few that allows the study of large systems such as crystalline solids and allows us to obtain realistic results for many electron systems. However, LDA and GGA approximations have the problem of un- derestimating the band gaps. Nevertheless, some methods to avoid this inconvenience have been proposed (Ferna´ndez *et al*., 2003 and Wahnón *et al*., 2005). Plane-wave DFT method has been developed, along with a plane-wave quantum mechanics. These methods are very powerful but they require thousands of plane waves to correctly compute the bands. In our case, the KS equations are solved using the CASTEP code. CASTEP is a commercial and academic software package which uses density functional theory with a plane wave basis set to calculate the electronic properties of crystalline solids, surfaces, molecules, liquids and amorphous materials from first principles.

RESULTS AND DISCUSSION

The electronic structure calculations were carried out by using the pervious methodology for evaluation of ZnSe (TM) to find intermediate band materials. The IB principally arise as a consequence of the interaction between the crystalline potential and spin interaction with transitions metal *d* orbitals. We analyzed the electronic properties of a material derived from ZnSe host semiconductor where the transition metals are substituted by its atoms that were shown in Figure 2.
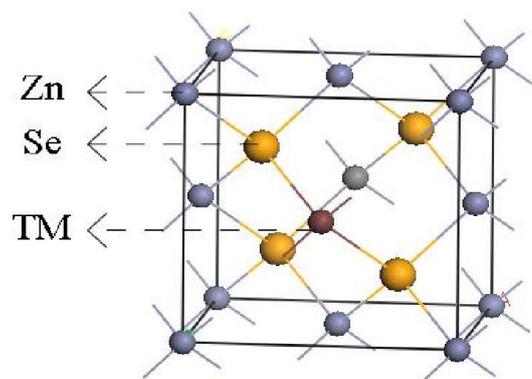
Fig.2. The cubic structure of ZnSe (TM) with TM=V, Cr, Mn, and Fe

The study presented in this work is based on the substitutional doping of TM=V, Cr, Mn and Fe by Zn with atomic concentrations of 2.77%. ZnSe has the space group of F-43m (TD-2) with lattice constant of $a=b=c=5.6676$ angstrom and $\alpha=\beta=\gamma=90$ (a, b, c are lattice constants and α (alpha), β (beta), γ (gamma) are angles).

Band Structure of Proposed Material

Calculating band structures is an important topic in the-oretical solid state physics. In this section we used the above mentioned model to calculate the band structure of proposed materials. At first, we carried out calculations of ZnSe (TM) band structure. The calculated energy-band structures for ZnSe (TM) with TM=V, Cr, Mn, and Fe are given in Figure 3(a)–(d), respectively. The main goal of this calculation is showing the intermediate bands formation in proposed material for high efficiency solar cell application. The obtained curves show it is possible to form intermediate band in ZnSe. All the TM elements have an obvious effect on the band structure of ZnSe, but V and Cr makes IBs in appropriate position ratio to Mn and Fe. However, the components corresponding to the IB present a sub-gap absorption for low energies. This absorption is responsible for the efficiency increase in solar cells based on these materials.

Density of State for Proposed Material

In this section we calculated the DOS of ZnSe (TM) structures, where TM is the transition metals. Figure 4(a) and 4(b) show DOS for "TM =V, Cr "and "TM= Mn, Fe "in ZnSe (TM) (TM were substituted with Zn in the ZnSe host), respectively. The creation of intermediate density of states by mentioned ions are clear in Figure 4.

Fig.3. Energy bands (eV) of ZnSe(TM) in several directions of the Brillouin zone: (a) TM=V, (b) TM=Cr, (c) TM=Mn, and (d) TM=Fe
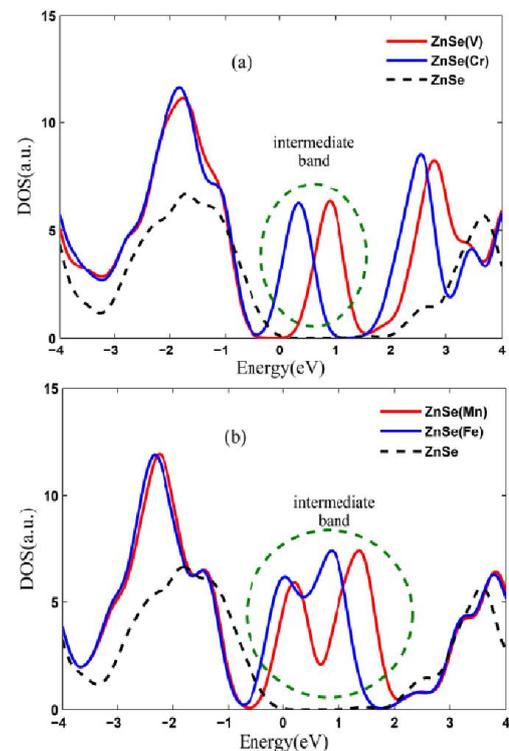
Fig. 4. The calculated DOS for ZnSe(TM): (a) TM=V and Cr, (b) TM=Mn and Fe. DOS for ZnSe showed as a dashed line

In the TM doped system 3d electron orbital mainly form IB and this appears in DOS. Although all the TM elements have an obvious effect on the DOS of ZnSe, IB formation in V and Cr are in more appropriate position.

Optical Absorption Coefficient

We present with first-principles calculations, optical properties of new TM-substituted In ZnSe compounds presenting a narrow half-filled intermediate band isolated from the VB and the CB of the host semiconductor. Figure 5 depict the optical absorption coefficient for pro- posed materials. The computed optical absorption of these compounds compared to the corresponding undoped semiconductor predicts a significant absorption below the band gap of the parent semiconductor and an enhancement of the optical absorption in the whole energy range of the visible region. Moreover, introducing these systems can be developed more efficient novel optoelectronic devices. From the comparison between ZnSe (TM) for TM= V, Cr, Mn and Fe, it can be found that the absorption coefficient of ZnSe (TM=V, Cr) is higher than that of ZnSe (TM=Mn, Fe) from 0 to 5 eV. The reason may be that V and Cr ions 3d electrons have good interaction with host semiconductor atoms and gives a better possibility for the transition from the IB to the CB. As a result, ZnSe(V) and ZnSe(Cr) have more ideal absorption coefficients in the energy range of solar radiation.
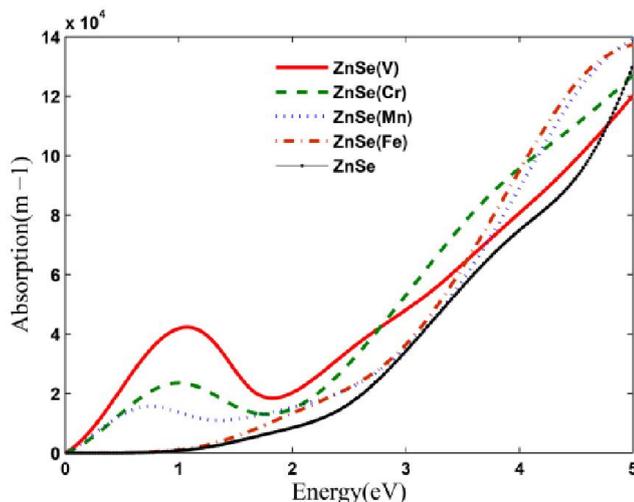
Fig. 5. The calculated optical absorption coefficient for undoped ZnSe and doped ZnSe with (TM=V, Cr, Mn, and Fe) (46050 suns) according to the model described in. (11)

Efficiency Potential of Proposed Materials

The energetic position of the intermediate band will strongly influence the power conversion efficiency of the solar cell. In this work we calculated the limiting efficiency of the ZnSe(TM) as a function of IB position. Calculations were carried out at maximum solar concentration assuming that the sun is a black body at 6000K and the cell operates at 300K. Calculations of the efficiency versus energetic position of intermediate band for ZnSe with band gap of 2.7eV are shown in Figure 6. The maximum efficiency of 56% is obtained and this is15.3 points higher than the limiting efficiency of single gap solar cells calculated under the same conditions (40.7%). The total efficiency of 56% comprises of

transitions from the VB to the CB, transitions from the IB to the CB and transitions from the VB to the IB. The efficiency has two maximum values at 1.1eV up to valance band and 1.1eV below the conduction band for full concentration condition.
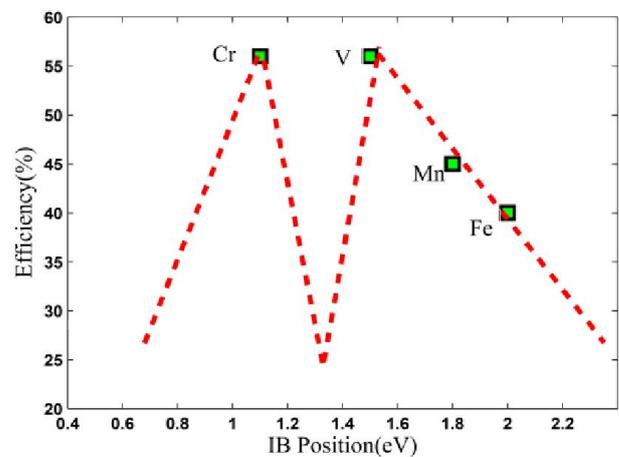
Fig. 6. Efficiency versus intermediate band energy level for ZnSe

Conclusion

The new intermediate band materials based on ZnSe (TM) (where TM is V, Cr, Mn, and Fe) for high efficiency solar cell application were introduced in this article. We have carried out a comparative study of these compounds in order to identify the basic features of the isolated intermediate band formation in the semiconductor band-gap. We use an abinitio fully self-consistent density functional theory method in the local density approximation (LDA), with norm-conserving, non-local pseudopotentials for core electrons. Evaluation of band structure, DOS, and optical properties were performed for proposed materials. Development of new intermediate band materials doped with the transition metals opens new promising horizons in high efficiency solar cells. The simulation also shows ZnSe(V) and ZnSe(Cr) are interesting candidates for intermediate band solar with efficiency higher than 56%.

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