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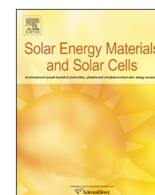

The group VA element non-compensated n–p codoping in $CuGaS_2$ for intermediate band materials

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ABSTRACT

Noncompensated n–p codoping by different element combinations has proven to be an effective approach to create intermediate bands (IBs) in wide band gap semiconductors. Here, we present a new noncompensated n–p codoping case by simultaneously substitute the cation and anion pair with the same element, which is implemented by using group VA element codoped $CuGaS_2$ systems, within first-principles calculations. The results suggest that the M (N, P, As or Sb) element substitutional codoping on Ga and S sites will introduce partially filled and isolated IBs in the band gap, and that the optical absorption is enhanced in all of the M codoped systems compared with the host $CuGaS_2$, due to the additional electron transition though IB. However, the stability analysis suggest that only P, As and Sb can enable stable IB material growth, and N will decompose the compound into more stable binary phase. Hence, M (P, As or Sb) codoped $CuGaS_2$ materials are predicted as promising candidates in photovoltaic applications. Besides, the codoping method may also be used in other functional materials to obtain controllable doping.

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1. Introduction

The intermediate band solar cell (IBSC) was proposed as an appealing concept for developing the third generation solar devices to increase the efficiency of solar cell by extending the solar cell response [1]. Conventionally, the absorption layer of solar cell is a single band gap semiconductor, where only photon whose energy is larger than the band gap can be absorbed. While, an inserted intermediate band (IB) in the band gap can be acted as a stepping stone. Unlike the single band gap semiconductors, electrons can be excited not only from the valence band (VB) to the conduction band (CB) but also from IB to CB and from VB to IB, upon absorption of two extra low energy photons. But that requires IB to be partially filled to have a higher photocurrent benefited from two sub-band gap absorption, and isolated to avoid photo-voltage degradation. Thus, the use of IB materials could promise high conversion efficiencies. The solar cell with the intermediate band can reach an upper efficiency of 63.1% with black body illumination from the detailed balance limit theory calculation [1], which largely exceeds the efficiency of Shockley–Queisser single-junction solar cell (40.7%) [2]. The efficiency will be extended to nearly 80%, by further increasing the number of IBs [3]. Both theoretical ad experimental reports have verified that the IB materials could effectively increase the optical absorption [4–9].

Since the IB concept was proposed, several approaches have been employed to realize intermediate band solar cells, including quantum dots (QDs) [10,11], highly mismatched alloys (HMAs) [12,13] and doped semiconductors. The quantum dot (QD) was first designed as the IB material, in which IB is derived from the confined electron states in CB [14] but lacks of enough density of states. The growth of HMA, on the other hand, is too expensive by using the epitaxy or pulsed laser melted technology [15,16]. Alternatively, IB can be formed through doping appropriate impurities into bulk host semiconductors. Such bulk IB materials are easier to fabricate and present stronger absorption because of the higher density of IB states. There are many kinds of bulk IB host material candidates [9,17–20], among which chalcopyrite material [21–24] has attracted much attention. Particularly, it has been reported that the optimum band gap for photovoltaic energy conversion in Cu-based chalcopyrite solar cells is 2.41 eV with the IB located at 0.92 eV from the CB or VB [25]. Since $CuGaS_2$ [26] has a wide band gap of 2.43 eV, it has been suggested as an ideal IB host material [25]. Up to now, elements of 3*d* transition metal and group IVA, rare earth elements have been used as the substitutes for Ga in $CuGaS_2$ to realize IB materials [24,27–29]. Nevertheless, as to which element can create IB, there is no rule to follow. One

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standing challenge is how to controllably create isolated IBs in the band gap.

Recently, a new concept, termed non-compensated n–p codoping, has been established to generate tunable IBs in the wide band gap semiconductor TiO_2 to enhance its visible-light photo-activity [30]. In the non-compensated n–p codoping, one cation and one anion substituents have been used as a dopant pair, in which cation contributes electrons and anion contributes holes to the host material. Consequently, both thermodynamic and kinetic solubilities are enhanced by the electrostatic attraction within the dopant pair. Particularly, the non-compensated nature ensures the creation of tunable IBs in the band gap. Not only that, but this approach has also been widely used in other functional materials that demand optimal dopant control for property optimization [31–37].

Unlike non-compensated n–p codoping which requires two different dopants, non-compensated n–p codoping can also be achieved in the $CuGaS_2$ using only one kind of atoms. Since Ga is the group IIIA element and S is the group VIA element, logically two VA atoms simultaneously replacing the Ga and S sites of the host $CuGaS_2$ will lead to non-compensated n–p codoping. Besides, non-compensated n–p codoping using one kind of atoms can theoretically reduce the defects in $CuGaS_2$ system for introducing less extrinsic atoms in comparison with two different atoms codoping. As is known, unpleasant defects might be connected with recombination centers, which is detrimental to the efficiency of solar cells, the codoping approach proposed here may have its advantage in respect of defects.

In this work, we employ a screened-exchange hybrid density functional Heyd–Scuseria–Ernzerhof (HSE06) in the density functional calculation of electronic structure and optical properties of M (M=N, P, As or Sb) codoped $CuGaS_2$. The HSE06 calculated band gap of $CuGaS_2$ is 2.25 eV, in good agreement with the experimental measurement 2.43 eV [38]. Our results show that the M codoped $CuGaS_2$ exhibits a good IB concept with half filled IBs appearing in the forbidden gap due to the non-compensated nature. Accordingly, the optical absorption range is largely red-shifted and the optical absorption intensity is enhanced compared with the host $CuGaS_2$. Besides, the formation energy of the M cation-anion codoping is much lowered. Thus, our results explicitly indicate that the same element non-compensated cation-anion codoping approach is workable to generate IBs in the band gap of semiconductors to achieve potential IB materials for photovoltaic fields.

2. Computational details

The ternary semiconductor $CuGaS_2$ has a chalcopyrite structure with the space group of I $\bar{4}$ 2d. Each atom in this structure is tetrahedrally coordinated. Namely, each sulfur ion is coordinated with two gallium and two copper ions, and each cation is coordinated with four sulfur ions. It is worth emphasizing that to form a band rather than defect levels, the doping concentration should be high (larger than 10^{19} cm^3), so that the negative non-radiative recombination would be decreased [39]. Therefore, in order to investigate the doping properties, we used the supercell approach to construct the compound by simultaneously replacing one Ga and a neighboring S atom with two M (M=N, P, As or Sb) atoms in a 64-atom cell (see Fig. 1), which corresponds to 1.65×10^{21} cm^{-3} dopant concentration. The reason to choose this configuration is that the total energy calculations reveal that n-type and p-type dopants exhibit a tendency to form a pair occupying neighboring lattice sites. The energy reduction, compared with the most distant codoping configuration, from the pairing is 2.455 eV, 0.522 eV

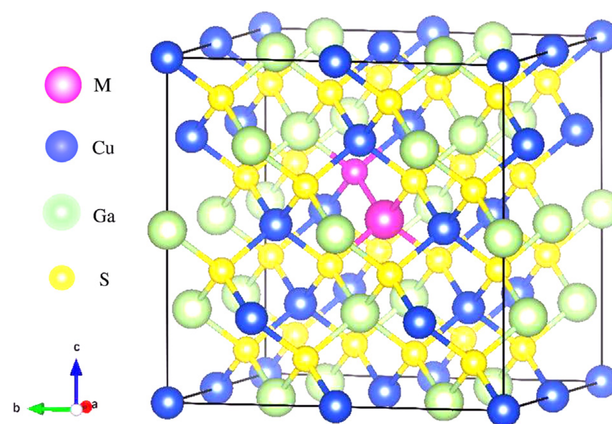

Fig. 1. $2 \times 2 \times 2$ supercell of $CuGaS_2$ with two M dopants.

and 0.48 eV for the P, As and Sb codoping, respectively. While, for the N dopants, the energy is increased from such pairing.

The density functional theory (DFT) [40] calculations are performed using the Vienna ab initio simulation package (VASP) code with the projector augmented wave (PAW) [41] scheme. For the exchange correlation functional part, since relaxation using HSE06 is very time-consuming and has no significant effect on the final properties from our tests, the Perde–Burke–Ernzerhof (PBE) [42] version of the generalized gradient approximation (GGA) is used for the structure full relaxation, and the hybrid nonlocal exchange-correlation functional of Heyd–Scuseria–Ernzerhof (HSE06) is used to calculate the electronic structure and optical properties. The geometry relaxation using PBE is performed until the total energy is changed within 10^{-5} eV/atom and the Hellmann–Feynman force on each atomic site is less than 0.01 eV/Å. In the HSE06 [43,44] functional, 30% of screened Hartree–Fock (HF) exchange is mixed to PBE exchange functional and the screening parameter is set to 0.2 $Å^{-1}$. The cutoff energy for the plane-wave basis is set to 300 eV, and a $2 \times 2 \times 2$ Γ-centered Monkhorst–Pack [45] k-point mesh is used in both PBE and HSE calculations.

To obtain a better prediction in both intensities and peak positions in the optical absorption spectrum, a complex dielectric function is performed using HSE06 with the consideration of interband and direct transitions, but not the local field effects. The optical calculations count the contribution from 800 electronic bands.

3. Results and discussion

3.1. Structural and electronic properties

The optimized structure of the host $CuGaS_2$ compound presents the average bond lengths of Ga–S and Cu-S to be 2.32 Å and 2.31 Å, which are consistent with previous theoretical and experimental results [46]. The codoping of M into the host $CuGaS_2$ leads to changes in both the lattice parameter and bond lengths. The changes are particularly obvious in the bonds nearby the M dopants (Ga–M, Cu–M, M–M), as shown in Table 1, due to the size mismatch (M vs Ga, and M vs S) in atomic radii and electronegativities. The average bond lengths of Ga–S increase to 2.36 Å , 2.35 Å, 2.34 Å and 2.37 Å in M-codoped (M=N, P, As and Sb) $CuGaS_2$, respectively. Therefore, the Sb or N induces the largest lattice distortion. The characteristics of structure change in M-codoped $CuGaS_2$ indicate that the M dopants mainly alter the local geometry around the M ions.

The HSE06 calculated band structure of host $CuGaS_2$ shows a direct band gap of 2.25 eV at the Γ point, which is larger than that

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