First principles study in the electronic structures and optical properties of chalcogenide-doped AgInS$_2$

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Abstract
The Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA + U) is adopted to simulate the electronic structures and optical properties of AgInS$_2$ semiconductors with S substitution by chalcogenides. AgIn(S, O)$_2$ semiconductor can be synthesized at the normal conditions due to the formation energy. All chalcogenides doping in AgInS$_2$ remain the semiconductor with the narrow band gaps. In the presence of the impurities, the contributions from p states of chalcogenides are involved, accountable for the reduction of the band gaps. Using the reflectivity and absorption coefficients, the optical properties with extensive absorption range and low reflectivity are attained by incorporating AgInS$_2$ semiconductors with chalcogenides. Finally, this theoretical work launches a broader understanding of the absorber materials and also predicts the natural properties as the alternative for the solar cell applications.

Keywords Electronic structures · Optical properties · AgInS$_2$ · Density functional calculations

1 Introduction
The express development of human economy in present society has led to progressively noticeable environmental pollution and energy shortage problems. The efficient and pollution-free energy resource has become the top significance of human energy advancement in these decades. Ternary chalcogenide materials have been currently received attention from these scientific topics because of their efficient technological applications (Jaffe and Zunger 1984; Delgado et al. 2001; Vaipolin et al. 1988; Krustok et al. 2000; Liu et al. 2014; Sharma et al. 2014; Verma and Bhardwaj 2007; Jayalakshmi et al. 2006 and Nguimdo and Joubert 2015). AgInS$_2$ is one of the I–III–VI$_2$ ternary chalcogenide semiconductors widely used in the active fields of photovoltaic cells, photocatalysis, optoelectronics and nonlinear optics (Kadlag et al. 2013; Torimoto et al. 2012; Deng et al. 2013; Gherouel et al. 2013). In addition, AgInS$_2$ semiconductor is a suitable material to be implemented as visible light
absorber layers because of its optimal band gap, high absorption coefficient and low toxicity (Han et al. 2014; Arredondo et al. 2009). In order to improve the electronic structures and optical properties for the solar cell applications, researchers have adopted numerous routes to improve and manipulate these properties including doping. For instance, chalcopyrite AgInS₂ thin films doped with Sn were synthesized by spray pyrolysis technique (Aguijera et al. 2007, 2009). The n-type to p-type transformation was achieved by incorporating Sn. In addition, the conduction type could be changed from n to p-type by Sb doping in AgInS₂ crystals (Yoshino et al. 2003). AgInS₂ photoelectrode doped with Ga was prepared by a hydrothermal and electrochemical deposition approaches (Cai et al. 2020). Ga doping in AgInS₂ displayed high photocurrent density and improved the absorption range to the visible light. Cu doping in AgInS₂ and AgInS₂/ZnS nanocrystals was achieved via a facile solution technique (Chen et al. 2016). Cu dopant extended the photoluminescence lifetime of these nanocrystals. The synthesis of Zn-doped AgInS₂ nanocrystals was achieved using a facile solution technique (Tang et al. 2012a, b). Using the reaction temperature, Zn doping in these nanocrystals manipulated the optical emissions into the visible light region. The experimental studies (Torimoto et al. 2007; Tang et al. 2012a, b; Hamanaka et al. 2011) underlined that AgInS₂ doped Zn exhibited the multicolour of the visible light waves because of the tunable band gap in the visible region. Using the density functional theory, the electronic structures and optical properties of AgInS₂ in wurtzite phase with vacancy defects and Zn dopant were analyzed (Yin et al. 2016). The reflectivity and absorption coefficients of AgInS₂ were promoted when substituted Ag and In by Zn. But so far, the origin of chalcogenides doping in AgInS₂ semiconductor has not been studied. Herein, it is essential to determine the electronic structures and optical properties of chalcogenide-doped AgInS₂ by simulated calculations to reveal their change mechanism with the purpose to guide the experiments better.

For the demonstration, the state-of-the-art density functional theory technique in the framework of the general gradient approximation (GGA) is commonly implemented by researchers because of the convenient calculation genre and lower demand of computer resource. To fill this gap, the inspiration is to profoundly determine the electronic structures and optical properties of AgInS₂ semiconductors doped with chalcogenides like O, Se and Te by GGA + U method with the Perdew-Burke-Ernzerhof correction (PBE) exchange correlation potential (Perdew et al. 1996). I hope that this work can conduct some praiseworthy theoretical guideline for the solar cell applications based on these studied materials. For the presentation, the manuscript is structured as follows. A brief description of the crystal structure and the theoretical background essential to perform the computations is delivered in Sect. 2. In Sect. 3, the results and analysis of all configurations are reported. Finally, Sect. 4 conveys the conclusions.

2 Theory

To request the electronic and optical properties of doped AgInS₂ semiconductors, all calculations are carried out with the density function theory as implemented in Cambridge serial total energy package (CASTEP) (Clark et al. 2005; Segall et al. 2002). The Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA + U) method is utilized to describe the exchange functional. For all calculations, the effective U parameters (12.0 and 7.0 eV (Huang and Persson 2014) for Ag-4d and In-4d, respectively) are selected. The calculations adopt the unit cell of orthorhombic AgInS₂ with Pna2₁ space group.
which consists of 16 atoms as displayed in Fig. 1. Plane waves with kinetic energy up to 520 eV are considered in the calculations. For the sampling of the irreducible Brillouin zone, Monkhorst–Pack k-points meshes with grids of $4 \times 4 \times 4$ are used. The optimization algorithm is selected as the Broyden-Fletcher-Goldfarb-Shanno (BFGS) scheme (Broyden 1970; Fletcher 1970; Goldfarb 1970; Shanno 1970). For the accurate and reliable computations, the convergence criteria is set as follows: the total energy, maximum force, maximum stress and maximum displacement are defined as $2.0 \times 10^{-6}$ eV/atom, $1.0 \times 10^{-5}$ eV/Å, 0.05 GPa and 0.001 Å, respectively. Using this computational technique, AgInS$_2$ lattice constants are $a = 6.6939$ Å, $b = 6.9972$ Å, $c = 8.2733$ Å. These lattice parameters agree well with the previous results {($a = 6.69$ Å, $b = 6.98$ Å, $c = 8.18$ Å) (Nguimdo and Joubert 2015), ($a = 6.69$ Å, $b = 6.99$ Å, $c = 8.27$ Å) (Delgado et al. 2001), ($a = 6.68$ Å, $b = 6.99$ Å, $c = 8.25$ Å) (Krustok et al. 2000), ($a = 6.81$ Å, $b = 7.14$ Å, $c = 8.33$ Å) (Liu et al. 2014)}. In addition, band gap of AgInS$_2$ is 1.402 eV. There is a large discrepancy with the available data {0.40 eV (Nguimdo and Joubert 2015) and 0.65 eV (Liu et al. 2014)}. However, the offset with some literatures {1.98 eV (Huang and Persson 2014), 2.08 eV (Nguimdo and Joubert 2015) and 2.09 eV (Liu et al. 2014)} is demonstrated. Owing to the obtainable comparison, this approach can be a suitable choice to study the electronic and optical properties of AgInS$_2$ semiconductor with S substitution by chalcogenide atoms like O, Se and Te. For the computed demonstration, AgInS$_2$ compounds doped with O, Se and Te are labelled as AgIn(S, O)$_2$, AgIn(S, Se)$_2$, and AgIn(S, Te)$_2$, respectively. To fill this gap, formation energies, band gaps, electronic band structures, density of states, partial density of states, reflectivity and absorption coefficients are utilized to evaluate and analyzed the physical properties.

### 3 Results and discussions

Using GGA + U method with PBE exchange functional, the goal of the following is to understand how the electronic structures and optical properties of AgInS$_2$ change after chalcogenides (O, Se and Te) doping and to predict their abilities for the competent
Table 1 The calculated formation energies and band gaps of AgInS$_2$ materials with S substitution by O, Se and Te

|                  | AgInS$_2$ | AgIn(S, O)$_2$ | AgIn(S, Se)$_2$ | AgIn(S, Te)$_2$ |
|------------------|-----------|----------------|-----------------|-----------------|
| Formation energies (eV) | –         | – 2.259        | 8.474           | 1.491           |
| Band gaps (eV)    | 1.402     | 0.867          | 1.167           | 1.034           |

Fig. 2 Band structures of AgInS$_2$, AgIn(S, O)$_2$, AgIn(S, Se)$_2$ and AgIn(S, Te)$_2$ material

absorber materials in the photovoltaic devices. The theoretical recommendation before the actual manufacture is imperative. The chalcogenides doping in AgInS$_2$ material lead to the changes in the physical properties due to the alteration in crystal symmetry. First, Table 1 itemizes the formation energies and their band gaps at equilibrium. Due to the formation energies, AgIn(S, O)$_2$ semiconductor can be synthesized at the normal conditions. All chalcogenides doping in AgInS$_2$ remain the semiconductor with the reduced band gaps. To scrutinize the electronic properties, the electronic band structures of AgInS$_2$ semiconductors doped with different chalcogenides are schemed in Fig. 2 along the several high symmetry lines in the irreducible Brillouin zone. As can be seen in AgIn(S, O)$_2$, AgIn(S, Se)$_2$ and AgIn(S, Te)$_2$ semiconductors, the conduction band minimum and the valence band maximum are both located at the Γ point, subsequently displaying the direct band gaps. The decreased band gaps of these semiconductors can be described by the fact that the
Conduction bands shift towards the Fermi level ($E_F$). Combining this downshift of the conduction band minimum by dopants, these materials can provide an approach to optimize the band edge positions and band gaps for the solar cell applications. Through the electronic properties, these explorations are supportive for the absorption of spectra with special frequencies corresponding to their band gaps. The composition of the calculated band structures under various doped chalcogenides is analyzed via the total and partial density of states as shown in Fig. 3. The valence bands of AgInS$_2$ are mostly formed by S-p states and marginally from In-p states. Above the Fermi level, the conduction bands are mainly from the hybridization of In-p and S-p orbitals. In the energies greater than 4.0 eV, In-p states are mostly promoted in the upper conduction bands. In the presence of the impurities, the contributions of p states from chalcogenides are additionally included into both lower conduction and upper valence bands. These p states from the dopants mainly play an important role in decreasing the conduction band edge, thus yielding the reduction of the band gaps.

In addition, AgInS$_2$ is a gorgeous semiconductor for optoelectronic and photovoltaic applications owing to its relatively great absorption coefficient and suitable energy band gap. Therefore, the optical properties of AgInS$_2$ semiconductors incorporated with different chalcogenides are imperative to be determined. The reflectivity coefficients of AgInS$_2$ semiconductors under various dopants are plotted in Fig. 4. The static reflectivities ($R(0)$) are improved in AgIn(S, O)$_2$ and AgIn(S, Te)$_2$, while these values are reduced in AgIn(S, Se)$_2$. The highest value is probed in AgIn(S, Te)$_2$. The chalcogenides doping in AgInS$_2$
reduce the first peaks of the reflectivity curves. The maximum peaks of all compounds are positioned in the ultraviolet region. The results highlight that the reflectivity coefficients of all doped AgInS$_2$ are reduced in the ultraviolet section compared with pure AgInS$_2$. To obtain more detailed optical properties, the computed absorption coefficients of AgInS$_2$ semiconductors doped with various chalcogenides are plotted in Fig. 5. The first peaks of the absorption coefficients are located in the energy range from 0.0 to 2.0 eV because of the direct inter-band transitions from the highest valence band to the lowest conduction band. In the presence of the dopants, the red shift in the first peaks of the absorption spectra is obtained, leading to the extension of the absorption assortment. The absorption coefficients of these peaks are reduced when doping with chalcogenides. The main peaks are located in the ultraviolet area with the energy ranging from 5.0 eV to 10.0 eV. There are manifold peaks around the main peak, representing a high absorption region in the extensive energy range nearby the main peak. In addition, the absorption coefficients at these peaks have continually decreasing tendency when doping. The lowest optical property is perceived in AgIn(S, Se)$_2$ compound. Therefore, the optical properties with extensive absorption range and low reflectivity are carried out by doping AgInS$_2$ semiconductors
with chalcogenides. Finally, the theoretical prediction recommends that these studied materials are of prime importance for the absorber of solar cells based on chalcogenide-doped AgInS$_2$ semiconductors.

4 Conclusions

I successfully determine the electronic structures and optical properties of chalcogenide-doped AgInS$_2$ semiconductors by the GGA + U method with PBE exchange functional. To sum up, the remarkable results are presented as follows:

1. Electronic properties: According to the formation energy, AgIn(S, O)$_2$ semiconductor can be synthesized at the regular conditions. All chalcogenides doping in AgInS$_2$ display the semiconductor with the reduced band gaps. The decreased band gaps can be explained by the fact that the conduction bands shift towards the Fermi level ($E_F$).

2. Density of state: The valence bands of AgInS$_2$ are mostly formed by S-p states and slightly from In-p states. The conduction bands are mainly from the contribution of In-p and S-p orbitals. In the presence of the dopants, the contributions of p states from chalcogenides are included into both lower conduction and upper valence bands. The p states of the dopants principally play an important role in decreasing the conduction band edge, thus leading to the reduced band gaps.

3. Optical properties: The reflectivity coefficients are condensed by the impurities. In the presence of the dopants, the red shift of the absorption coefficients is attained, thus leading to the expansion of the absorption range. The optical properties with wide absorption variety and low reflectivity are achieved by doping AgInS$_2$ semiconductors with the impurities.

Finally, it is expected that these theoretical investigations deliver a detailed understanding to enlighten the enhancement of the photovoltaic performance in the solar cell applications based on doped AgInS$_2$ semiconductors.

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