Journal of Alloys and Compounds 695 (2017) 1392–1396

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Alloy engineering of electronic and optical properties of tetragonal monolayer zinc chalcogenides

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ARTICLE INFO

Article history:
Received 20 September 2016
Received in revised form
24 October 2016
Accepted 27 October 2016
Available online 29 October 2016

Keywords:
Two-dimensional materials
First-principles calculations
Zinc chalcogenides
Alloy
Optical absorption
Water splitting

ABSTRACT

Alloying has been widely applied for band gap engineering of semiconductors, as the band gap of an alloy can be continually tuned as a function of alloy concentration. Recently, the three-atom-thick tetragonal ZnSe and ZnS monolayers demonstrate a strong quantum confinement effect by showing a large enhancement of band gap compared to their zinc blende (ZB) bulk phases. In this study, we are aiming to investigate the electronic and optical properties of various tetragonal alloy ZnS_xSe_{1-x} monolayers based upon first-principles calculations. It is found that these alloy ZnS_xSe_{1-x} monolayers are all direct band gap semiconductors with tunable band gaps, plausible for visible-light-driven water splitting. It is suggested by theoretical optical absorbance calculations that alloy $ZnS_{0.375}Se_{0.625}$ monolayer has a higher absorption performance than pristine ZnSe and ZnS monolayers under certain wavelength within the visible light region. Our results open a new avenue for the future alloy engineering of the tetragonal ZnSe and ZnS monolayers for a wealth of potential optoelectronic applications.

1. Introduction

Two-dimensional (2D) layered materials have drawn great attention since the discovery of graphene [1,2], and they typically have distinct properties from their 3D counterparts. These novel properties make them ideal candidates for nanoelectronic devices, such as field-effect transistors, spin- or valley-tronics, topological insulators, etc. [3–6] In particular, 2D materials zinc chalcogenides ZnX (X = S, Se) have demonstrated an excellent performance in solar-driven water splitting in a recent report. [7] In the report, the freestanding four-atom-thick sheet of ZnSe (and ZnS), with a clean surface and a honeycomb lattice, showed a photocurrent density 4–10 times higher than ligand-coated layers, 8 times higher than quantum dots, and 192 times higher than the 3D bulk. The 2D freestanding honeycomb sheets of ZnSe (and ZnS) were produced by removing the organic ligands from the lamellar inorganic-organic hybrid nanostructures which were synthesized by solvothermal and soft template techniques. [8–14] In addition, a number of research groups studied other freestanding single-to few-layer sheets of ZnX with or without honeycomb lattices as potential synthesis targets by theoretical calculations. [6,15–19] For instance, it was predicted by density functional theory (DFT) methods that a novel tetragonal three-atom-thick ZnSe monolayer is a bit more stable than the honeycomb sheet of ZnSe monolayer, and both of them have a comparable behavior on incident photon-to-current conversion efficiency for solar water splitting. [18,19] Further *ab initio* molecular dynamics simulations demonstrated a couple of routes to synthesize this ultrathin three-atom-thick sheet: structure transition from a four-atom layer in the (100) plane from the X-ray structure of its bulk ZB phase under mild temperature and pressure [19]; structure transition from the experimental honeycomb sheet of ZnSe monolayer under extremely high lateral pressure [20].

It is also well-known that alloying and doping have been mostly applied for band gap engineering of semiconductors, as the band gap of an alloy can be continually tuned as a function of alloy concentration. Selenium and sulfur are very similar in the nature, often co-existing in metal sulfide ores. In our previous study, it is shown by the theoretical calculations that the S-doped ZnSe monolayer exhibits a higher photo absorption performance compared to other doped and undoped tetragonal ZnSe monolayers [21]. Given the excellent behavior of S-doped tetragonal ZnSe monolayer, it becomes attractive if tetragonal alloy ZnS_xSe_{1-x} monolayers with various x values could also be of great use in the

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http://dx.doi.org/10.1016/j.jallcom.2016.10.264

area of ultrathin photovoltaics. In this work, we report a theoretical study on the three-atom-thick tetragonal alloy ZnS_xSe_{1-x} monolayers, regarding their electronic and optical properties. As a result, compared to the parent ZnSe and ZnS monolayers, this class of alloy ZnS_xSe_{1-x} monolayers display enhanced absorbance in the visible range of the solar spectrum where the solar spectral intensity is the strongest. Our results suggest that these semiconducting alloy ZnS_xSe_{1-x} monolayers could potentially outperform pristine ZnSe and ZnS monolayers as solar absorbers.

2. Methodology

All the structure optimizations were carried out using the $Dmol^3$ code [22,23]. The Perdew–Burke–Ernzerhof (PBE) [24,25] functional under generalized gradient approximation (GGA) was used to describe the exchange and correlation effects. Double numerical plus polarization (DNP) was employed as the basis set, and the core electrons were treated using DFT semicore pseudopotentials (DSPPs). A 15 × 15 × 1 grid for k-point sampling based on the Monkhorst and Pack scheme [26] was utilized for the unit cell of the tetragonal ZnSe and ZnS monolayers (two zinc atoms and two selenium/sulfur atoms). A 2 × 2 supercell was constructed to simulate the alloy ZnS_xSe_{1-x} monolayers. In the supercell, S/Se atoms were place randomly, and the configuration with the lowest energy was then selected for the following electronic and optical calculations. During the structure relaxation, the lattice vector in the vacuum direction was constrained at ca. 20 Å while the other lattice vectors and the positions of the atoms were fully relaxed. The convergence tolerance of energy was 10^{-5} Hartree, and the maximum allowed force and displacement were 0.002 Hartree/Å and 0.005 Å, respectively. This strategy provides consistent results with our previous calculations [19], which will be shown in the following section. The electronic and optical properties for alloy ZnS_xSe_{1-x} monolayers were calculated by the CASTEP code [27], in which the GGA-PBE functional, the ultrasoft pseudopotentials, and the ultrafine criteria were utilized.

3. Results and discussion

Tetragonal ZnSe and ZnS monolayers, as shown in Fig. 1a, have already been studied by the recent theoretical calculations. [18–20] In the current work, the calculated Zn–Se bond length is 2.53 Å and the Se–Zn–Se angle is 107.9°, both of which are very close to the previous calculated results (2.54 Å and 107.7°, respectively) [19], validating the accuracy of the current model. The calculated lateral lattice constant of ZnS and ZnSe monolayers is 4.00 and 4.09 Å, respectively, in a good agreement with other results as well. [18] Because of the same crystalline structure and the close lattice constants for the end-point constituents, tetragonal ZnS_xSe_{1-x} alloys have negligible variations of the lattice constant (ca. 2.25%) over the entire concentration range, as shown in Fig. 1b. For a given structure of alloy ZnS_xSe_{1-x} monolayers, its stability with respect to segregation into its substituents ZnS and ZnSe is defined by the formation energy (E_f):

$$E_f = E(ZnS_xSe_{1-x}) - xE(ZnS) - (1-x)E(ZnSe) \tag{1}$$

with E(ZnS) and E(ZnSe) being energies of the ground-state structures of the substituents, and all energy terms are normalized per ZnX (X = S, Se) unit. The formation energy of various alloys is shown in Fig. 1c. It is clear that among all the alloys, $ZnS_{0.5}Se_{0.5}$ monolayer is the most stable, followed by $ZnS_{0.625}Se_{0.375}$ and $ZnS_{0.375}Se_{0.625}$ monolayers, and other alloys have positive formation energy relative to their end-point constituents. However, it should be pointed out the alloys near the end-points could also be regarded as the doped systems to some degree, and thus substitution energy could be used to examine their thermo-stability. [21] We also note that the use of 2 × 2 supercells restricts the number of alloy structures explored here. A more comprehensive study of the relative phase stability between different ordering forms requires even larger supercells, and the cluster expansion method to estimate the phase boundaries should be utilized as well [28,29].

The calculated band gap of tetragonal ZnS and ZnSe monolayers is 2.82 and 2.27 eV from Γ to Γ at the PBE level (Fig. 2b,d), in accord with the other calculated results (2.86 and 2.22 eV for ZnS and ZnSe monolayers, respectively). [18] We are aware that the PBE functional usually underestimates the band gaps. [30] Unfortunately, the skyrocketing computational cost of more accurate methods, e.g. quasiparticle *GW* and hybrid HSE06 functional, prevents us from utilizing them in large systems (i.e. supercells in our study). In addition, excitonic effect could be very strong in certain 2D materials, so that the increase in the fundamental band gap value (as obtained with *GW* calculations) can be compensated by substantial values of exciton binding energies, which are calculated by Bethe-Salpeter equation. [31–33] However, we believe that basic physics and trend discovered here should not be changed. The alloy ZnS_xSe_{1-x} monolayers still maintain the direct band gap over the entire concentration range, e.g. $ZnS_{0.5}Se_{0.5}$ monolayer in Fig. 2c, a highly desirable property for achieving high efficiency in light absorption among many applications. The band gap of alloy ZnS_xSe_{1-x} monolayers monotonically depend on the S/Se concentrations. As shown in Fig. 2a, the band gap of alloy ZnS_xSe_{1-x} monolayers increases with the increase of the ZnS ratio. It has been reported that tetragonal ZnSe monolayer with different biaxial strains possesses a desirable band edge alignment to straddle the redox potentials of water splitting reaction, making it a potentially effective photocatalyst, e.g., not only as an ultraviolet light-driven but also visible-light-driven photocatalyst for water splitting reaction. [20] We thus calculated the valence band maximum (VBM) and conduction band minimum (CBM), relative to the vacuum level, for various alloy ZnS_xSe_{1-x} monolayers. As also shown in Fig. 2a, VBM of alloy ZnS_xSe_{1-x} monolayers decreases as the ZnS concentration grows, while CBM does not apparently depend on the ZnS concentration, nearly staying put over the entire concentration range. It could be concluded that all alloy ZnS_xSe_{1-x} monolayers have a more desirable band edge alignment for water splitting reaction than tetragonal ZnSe monolayer, by making the VBM energy level further beneath the water oxidation potential (H_2O/O_2 potential) while keeping the CBM energy level above the H^+/H_2 potential.

In order to examine the electron contributions near Fermi level, the total density of states (DOSs) and the partial DOSs of ZnSe and ZnS monolayers, as well as the most stable alloy $ZnS_{0.5}Se_{0.5}$ monolayer, were also computed, as shown in Fig. 3a–c. It is observed for tetragonal ZnSe monolayer that the valence bands from −3 to 0 eV are dominated by Se's 4*p* states, while the conduction bands from 2 to 4 eV mainly consist of the hybridization from Zn's 4*s* and Se's 4*p* states, in good accord with the our previous results. [19] The presence of Zn's 4*s* states in the conduction bands shows the charge transfer from Zn to Se, while the presence of Se's 4*p* states in the conduction bands suggests that the charge transfer is not complete. [19] In the current study, the Hirshfeld charges calculated for the Zn and Se atoms in ZnSe monolayer amount to $q = \pm 0.18$, validating the aforementioned argument. On the other hand, the Hirshfeld charges calculated for the Zn and S atoms in ZnS monolayer amount to $q = \pm 0.22$. Despite the different electronegativity of the Se and S elements, the contributions of Se's and S's electrons on valence and conduction bands of alloy $ZnS_{0.5}Se_{0.5}$ monolayer are nearly equivalent. This is consistent with the phenomenon in the nature that Se is always found in metal sulfide ores, where it partially replaces the sulfur. The similarity of S and Se thus