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Novel hetero-bilayered materials for photovoltaics

Jia Zhou [a,b,*]

[a] Department of Chemistry, Harbin Institute of Technology, Harbin 150001, China
[b] Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Bethel Valley Road, Oak Ridge, TN 37831-6493, United States

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ABSTRACT

The recently synthesized GaS and $MoSe_2$ nanosheets have been used as appropriate substrates for other layered materials, e.g. silicene/GaS heterosheets akin to graphene/BN systems. Here, we have performed a comprehensive first-principles study of the electronic and optical properties of two-dimensional (2D) GaS/$MoSe_2$ hetero-bilayers based on density functional theory (DFT). We found almost all proposed GaS/$MoSe_2$ hetero-bilayers in the current study have an indirect band gap from the Γ point to the K point, except for one with a direct band gap at the K point. Tunable band gaps GaS/$MoSe_2$ hetero-bilayers can be controlled by strain modulation. State-of-the-art *GW*-Bethe–Salpeter method, accounting for electron-electron and electron-hole interactions, has been employed to compute accurate absorbance spectra for layered materials. Compared with its composing GaS and $MoSe_2$ monolayers, GaS/$MoSe_2$ hetero-bilayers show superior behavior on optical absorbance, indicating a stronger visible-light absorption and applications in solar energy harvesting. We foresee that the novel GaS/$MoSe_2$ hetero-bilayers would stimulate the fabrication of materials with unprecedented optical and physico-chemical properties that may apply in nanodevices and photovoltaic cells.

1. Introduction

Graphene, a single atomic layer of graphite, has generated tremendous excitement since its discovery decade ago [1,2]. It also triggers a boom for other 2D layered materials. 2D layered materials such as graphene, hexagonal BN (h-BN), and transition metal chalcogenides (e.g. GaSe, GaS, $MoSe_2$, and WS_2) remain planar as separated simply by the mechanical [3] or liquid-phase exfoliation from their bulk layered solids [4]. The exfoliation is facilitated by the weak interlayer van der Waals (vdW) forces. These 2D layered materials have a broad range of applications, such as field-effect transistors, spin- or valley-tronics, thermoelectrics, topological insulators, and energy conversion and storage [5–8].

As a kind of layered semiconducting material, molybdenum dichalcogenides MoX_2 (X = S, Se) have attracted great interest due to a wide range of important properties [9–11]. The monolayer of $MoSe_2$ is composed of three sublayers stacked in the sequence Se–Mo–Se, as shown in Fig. 1c (MoS_2 is similar in structure). MoX_2 (X = S, Se) undergoes a crossover from indirect to direct gap when going from bilayer to monolayer [12], giving rise to enhanced monolayer luminescence [13], thus allowing applications such as transistors, photodetectors and electroluminescent devices [11]. On the other hand, layered gallium monochalcogenides GaX (X = S, Se) have also drawn much research attention for their potential applications in fields such as solar energy conversion [14]. Unlike MoX_2 monolayer, the monolayer of GaX consists of four sublayers stacked in the sequence X–Ga–Ga–X, as shown in Fig. 1a for GaS monolayer. Experimental efforts have since been carried out to fabricate these GaX in monolayer form, and monolayer GaS and GaSe sheets have already successfully been synthesized [15–18]. Soon after, theoretical calculations have also been undertaken to further understand the electronic and photonic properties of GaX monolayers [19,20]. The GaS monolayer applications in the experiments also include transistors and photodetectors [15–18].

Recently, the possibility to combine various 2D materials in vertical stacks creates a new paradigm in materials science: layered hetero-structures [21]. Those hetero-structures are upheld together by vdW interactions, and thus are called vdW hetero-structures. The hetero-structures have been widely used in conventional semi-conductors for achieving tunable electronic properties [12]. Graphene/h-BN vdW hetero-structures are one of the first research targets due to their commensurate structural parameters and distinct electronic properties, and a rich collection of physics and functionalities have been revealed by both experimental and theoretical investigations [22–26]. Moreover, a variety

* Correspondence to: Department of Chemistry, Harbin Institute of Technology, Harbin 150001, China.
E-mail address: jiazhou@hit.edu.cn

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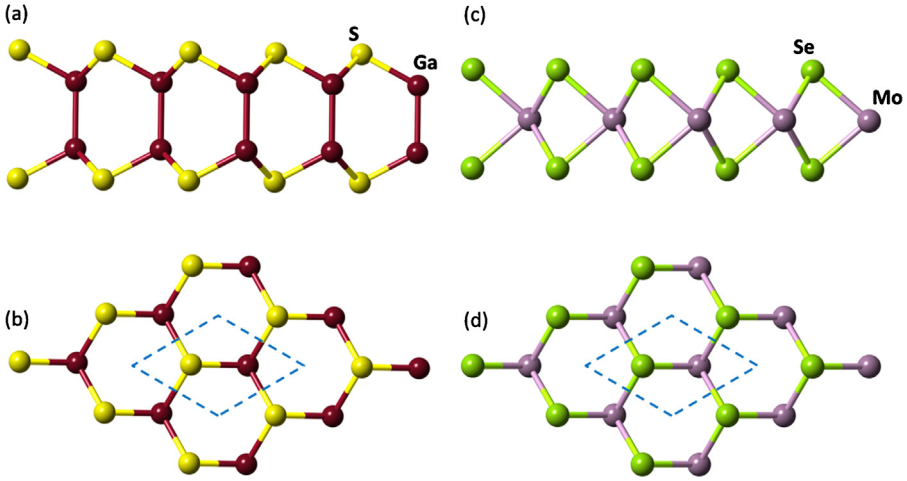

Fig. 1. Side view (a) and top view (b) of GaS monolayer with unit cell outlined; side view (c) and top view (d) of $MoSe_2$ monolayer with unit cell outlined.

of vdW hetero-structures involving molybdenum dichalcogenides MoX_2 (X = S, Se) [12,27–34] and GaS [35] have also been studied from both experimental and theoretical perspectives, such as silicene/GaS heterosheets and silicene/MoS_2 heterobilayers. It has been shown that MoX_2 and GaX (X = S, Se) are good substrates for other layered materials, such as graphene and silicene, or vise versa. The common ground of these vdW hetero-structures is that the in-plane lattice constants of the composing parts are comparable. From our own survey, GaS monolayer and $MoSe_2$ monolayer meet the above criterion. Given the individual excellent behavior of GaS monolayer and $MoSe_2$ monolayer on photoelectrochemistry, we wonder how the novel GaS/$MoSe_2$ hetero-bilayered materials will perform, in particular for photovoltaics, when GaS and $MoSe_2$ monolayers integrate into vdW hetero-bilayers.

In this work, we perform extensive first-principles calculations to characterize novel GaS/$MoSe_2$ hetero-bilayers, constructed by GaS and $MoSe_2$ monolayers. Electronic and optical properties of GaS/$MoSe_2$ hetero-bilayers are systematically investigated by both DFT and *GW*-Bethe–Salpeter method. Our work is expected to pave the way for a new generation of integrated devices and make hetero-bilayers viable candidates for electronic or photoelectrochemical applications.

2. Computational methods

First-principles calculations were carried out using the Vienna ab initio simulation package (VASP) [36,37]. The Kohn–Sham equations were solved using the projector-augmented wave (PAW) method [38,39]. For the structural relaxations, we employed the Perdew–Burke–Ernzerhof (PBE) functional [40,41] with the long-range dispersion correction implemented by Grimme [42]. The Brillouin-zone integrations were performed on a dense Γ-centered Monkhorst-Pack $16 \times 16 \times 1$ k-point grid [43]. The kinetic energy cutoff for plane waves was set to 500 eV and the "accurate" precision setting was adopted to avoid wrap around errors. The convergence criterion for the electronic self-consistent loop was set to 10^{-5} eV. During the structural relaxations, the vacuum regions were at least 20 Å to ensure the periodic images are well separated while other lattice vectors were fully relaxed. All atoms were also relaxed until the Hellmann–Feynman forces were smaller than 0.01 eV/Å.

The electron-hole interaction plays an important role in the optical response of a material [44]. We calculated the optical spectra of layered materials, including the excitonic interaction, by solving the Bethe–Salpeter equation (BSE), which is implemented in the VASP [45,46]. The BSE spectrum calculations started with the single-shot G_0W_0 quasiparticle energies and the PBE wave functions. For the more expensive G_0W_0 and BSE calculations, a $12 \times 12 \times 1$ k-point grid was applied, which is mostly sufficient for proper description of excitons [47]. The energy cutoff for the response function was set to 150 eV, and the particular pseudopotentials provided in VASP for *GW* calculations (e.g. Mo_sv_GW PAW potential accounting of $4s^2 4p^6 4d^5 5s^1$ valence electrons for Mo) were used for the G_0W_0 and BSE calculations. A total of 96 bands (more than 4 times of the number of occupied bands in almost all cases ensuring the accuracy of the results) and 96 frequency points were included in the G_0W_0 calculations, which were followed by the BSE calculations. The seven highest valence and seven lowest conduction bands were included in the calculation of the excitonic states for monolayers, while fourteen highest valence and fourteen lowest conduction bands were included for bilayers. Spin-orbit effect at the *GW* level was within a few tens of meVs, as indicated in the previous study of similar systems [48], and was omitted here for sake of computational costs. The adopted computational methodology for G_0W_0 and BSE calculations has been validated in our previous work [49] and others [20,29,33,34,48] for similar individual monolayer sheets. This approach balances the accuracy and computational costs of our results, and we expect the general trends predicted in this study to be robust.

3. Results and discussion

For reference, we first study the structures of GaS and $MoSe_2$ monolayers, as shown in Fig. 1. Both of them have a same symmetry as graphene. The calculated lattice constants are 3.58 Å and 3.32 Å for GaS and $MoSe_2$ monolayers, respectively. These values agree well with previous studies of GaS and $MoSe_2$ [9,20,50]. The closely-matched lattice parameters of GaS and $MoSe_2$ monolayers make them possible candidates to form hetero-bilayered structure, as seen in Fig. 2c, without significantly high strain (GaS [19] and $MoSe_2$ [12] monolayers have been studied already with strain up to 10% and 8%, respectively). For comparison, GaS/GaS and $MoSe_2$/$MoSe_2$ bilayers have also been investigated, which are shown in Fig. 2a and b. GaS bulk favors the β structure, which is AB stacking [51]. Previous studies of layered transition-metal dichalcogenides (e.g. MoS_2, $MoSe_2$, and WSe_2) show that only AB stacking, also called C7 stacking [27], gives rise to the lowest energy in most hetero-bilayer systems, and electronic structure is quite insensitive to the stacking [12,27]. Therefore, for all the bilayers in our current work, the two layers are arranged with AB stacking,