The minimal supercells approach for ab-initio calculation in 2D alloying transition metal dichalcogenides with special quasi-random structure

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Abstract
Density functional theory (DFT) is used to investigate MoS2 and WS2 monolayers, which are direct bandgap semiconductors. We study alloying between MoS2 and WS2 by using special quasi-random structure (SQS), through a comparison of the computed pair distribution functions with various sizes of supercells. Our calculations show that a model 3 × 3 × 1 supercell structure of pseudobinary alloy \( \text{Mo}\text{S}1\times x\text{W}x\text{S2} \) can be correctly performed for energy and electronic band structure calculations. DFT is combined with SQS and reveals that alteration of the W concentration supports the band edges and energy gap. The electronic structure of \( \text{Mo}\text{S}1\times x\text{W}x\text{S2} \) clearly supports the results from the experimental observation as well as Monte Carlo simulation. Consequently, our model suggests that the generated alloy \( \text{Mo}\text{W}1\times x\text{S2} \) monolayer with small supercells via SQS can clearly explain the behaviour of this material, using a low computational time but achieving good agreement with the experiment.

1. Introduction

Two-dimensional (2D) materials have attracted great interest from the research community, having manifested several properties such as superconductivity, and as a semiconductor, topological insulator, etc [1–3]. It is worth noting that 2D materials are associated with van der Waals (vdW) interaction, as reported by Novoselov et al [4]. Especially, in the case of transition metal dichalcogenides (TMDCs), investigations of their structural properties [5] found that the layered materials formed by the stacking of layered hexagonal structure exhibited a vdW gap between the layered structure. The vdW interaction included gave an excellent result for electronic properties [6]. For TMDCs it was also reported that the vdW scheme exhibited an interplay between the layered distance. TMDCs are a class of a material with the composition \( \text{MX}\text{X}_2 \), where \( \text{M} \) denotes a transition metal such as molybdenum (Mo), tungsten (W), niobium (Nb), rhenium (Re) or titanium (Ti), and X is a chalcogen such as sulphur (S), selenium (Se), or tellurium (Te). TMDCs have been studied largely by experiments and ab-initio calculations. The TMDC semiconductors have the energy band-gap ranging from below 1 eV to above 2.5 eV [7, 8]. Constructing devices is still opening an opportunity for light generation functions, such as light-emitting diodes (LEDs). Additionally, it is predicted to be suitable for novel applications in optical computing and communications in view of the valley coherence and valley-selective circular dichroism that is observed in diverse monolayer TMDCs.

Molybdenum disulfide (MoS2) is a prototypical TMDC, which is composed of 2D S–Mo–S sheets stacked on top of one another, as shown in figure 1. The inter-layer interaction of MoS2 displays a weak bonding through the role of vdW interaction. On the other hand, the in-plane bonding of MoS2 exhibits strong covalent bonds. Therefore, the bulk of MoS2 can be considered as a monolayer or few-layer nanosheets like graphene. Also, in the multi-layer structure it is found that there is an indirect bandgap, and that it becomes a direct-bandgap
semiconductor in its monolayer structure. The direct bandgap of the MoS₂ monolayer shows that it has efficient light emission. This is similar to tungsten-based dichalcogenides (for example, WS₂) [9, 10], making MoS₂ TDMCs suitable for developing optoelectronic devices. Recently, there have been a few studies on alloying semiconductor in its monolayer structure. The direct bandgap of the MoS₂ monolayer shows that it has efficient light emission. This is similar to tungsten-based dichalcogenides (for example, WS₂) [9, 10], making MoS₂ TDMCs suitable for developing optoelectronic devices. Recently, there have been a few studies on alloying MoS₂ and WS₂. These found that the resultant bandgap can be continuously tuned [11]. Moreover, the role of vdW is important for monolayers of WS₂ as well. In an experimental study WS₂ was observed by angle resolved photoelectron spectroscopy and density functional theory (DFT) calculations were performed, indicating that the solution gave an excellent account of the electronic band structure [12]. It is worth mentioning that both MoS₂ and WS₂ were indicated to us as motivation for finding the electronic structure of Mo₁₋ₓWₓS₂.

In this work, we performed the DFT calculation on a TMDC monolayer of MoS₂ and WS₂ to investigate the bonding distance, cell parameter and band structure. Then we modelled the alloying Mo₁₋ₓWₓS₂ monolayer supercells by using the special quasi-random structure (SQS) method. The development of the band gap and band alignment of Mo₁₋ₓWₓS₂ for each variation as a function of the W concentration will be extensively explored.

2. Methods

All structures were investigated by DFT calculations. The generalised gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) [13] for the exchange–correlation energy was used, as implemented in the Quantum ESPRESSO code [14]. The atomic cores of the TMDC were represented by using ultrasoft pseudopotentials [15]. The electronic wavefunctions were described by the plane-wave basis sets, with a kinetic energy cutoff of 60 Ry, and the energy cutoff for the charge density was set to 540 Ry. The first Brillouin zone is sampled with an 8 × 8 × 1 Monkhorst–Pack grid for the monolayer system. Band structures were calculated along the high symmetry points following the K—Γ—M—K path. For the calculation of Mo₁₋ₓWₓS₂ we used a 3 × 3 × 1 supercell from a primitive cell representation, and the band structure of the system is simulated from this supercell. In order to compare the result with those from a high-symmetry unit cell, the unfolding bands are performed as described in the previous works [16, 17]. The hexagonal structure of the MoS₂ and WS₂ monolayers [18, 19] was relaxed by calculating the total force acting on each atom until the total forces over the whole cell were less than 10⁻⁶ eV Å⁻¹. We used the special quasi-random structure (SQS) [20–24] to generate the supercell structure and combined this with DFT calculation in order to examine the electronic properties.

3. Results and discussion

We used DFT calculations to relax the MoS₂ and WS₂ structures. The results of the lattice parameters, bond angle and energy gap are shown in table 1. We obtained a remarkable result, as shown in figure 2. The computed energy band gaps (Eg) of the MoS₂ and WS₂ monolayers (1.80 eV and 2.00 eV) were in good agreement with the experimental results [25, 26].

The solution of the structural parameters indicated that MoS₂ and WS₂ are suitable to consider for the substitution of W into Mo. In this case, we propose a model structure of Mo₁₋ₓWₓS₂, which is generated by the SQS structure, using pair correlation functions with a spanning distance up to the twentieth atomic neighbour shells.

First, we investigate the suitable size of supercells by comparing the pair correlation functions and total correlation error between various sizes of supercells (2 × 2 × 1, 3 × 3 × 1 and 4 × 4 × 1). In figure 3 it is
obviously noticeable that the $2 \times 2 \times 1$ supercell has a better order of atomic arrangement than the $3 \times 3 \times 1$ and $4 \times 4 \times 1$ supercells (for the values of the pair correlation function, a value equal to 1 implies that every atom among the atomic neighbours is the same). As shown in figure 4, we found that the $3 \times 3 \times 1$ supercell is a suitable size, because the total correlation error values are not very different from the $4 \times 4 \times 1$ supercell, and the difference of the energy for each SQS is small. It can be concluded that the $3 \times 3 \times 1$ SQS is suitable for calculation of the energy and band structure respectively, with the lowest computational cost. Thus we chose a $3 \times 3 \times 1$ supercell with 27 atoms per supercell. By comparing the ensemble average of the pair correlation functions $\langle P_{Sm}^2 \rangle$ for each arrangement of atoms in the model structure with $\langle P_{Sm}^2 \rangle$, we can choose any structure that gives the best match. Some $\langle P_{Sm}^2 \rangle$ of the chosen configurations are shown in table 2. The crystal structures of $Mo_{1-x}W_{x}S_{2}$ at $x = 0.11$ of the $3 \times 3 \times 1$ supercell have all possible $\frac{9!}{1!3!3!} = 9$ configurations. The SQS shows that every configuration has the same value for the pair correlation functions up to the ninth atomic

Table 1. Calculated structural parameters (atom distances $d_{Mo-S}$, $d_{W-S}$; separation of the M and X layers $d_{Mo-S}$; bond angle, $\theta_{Mo-S-Mo}$, $\theta_{W-S-W}$) and energy band gap, $E_g$ of the MoS$_2$ and WS$_2$ monolayers; comparison with other work (in brackets) and experiments [25–28].

|          | Calculation | Experiment |
|----------|-------------|------------|
|          | $a$ (Å)     | $d_{Mo-S}$/$d_{W-S}$ (Å) | $d_{Mo-S}$ (Å) | $\theta_{Mo-S-Mo}/\theta_{W-S-W}$ | $E_g$ (eV) | $a$ (Å) | $E_g$ (eV) |
| MoS$_2$  | 3.19, (3.19) | 2.42, (2.43) | 1.56, (1.56) | 80.67, (80.68) | 1.80, (1.72) | 3.17 | 1.90 |
| WS$_2$  | 3.19, (3.19) | 2.42 | 1.56, (1.56) | 80.95 | 2.00, (2.10) | 3.162 | 2.07 |
neighbor shells, so we chose one of them, denoted by SQS-1. In the same way as for correlation functions, denoted by SQS-2 and SQS-3. For all possible random correlation. For the 3 correlation function of the groups. The result shows that most of the pair correlation functions are close to random, except for the pair -band edges of the complex. Hence, the bands need to be unfolded electronic band structure of the supercell. We found that the electronic band structure of the supercell is quite complex. Hence, the bands need to be unfolded [16, 17]. Then we investigate the results of the band gaps and band edges of the Mo\(_{1-x}\)W\(_x\)S\(_2\) alloys. The results show that the band gap decreases moderately from \(x = 0\) to 0.33 and increases moderately from \(x = 0.33\) to 0.67, but then rises more rapidly from \(x = 0.67\) to 1 (see figure 6(a)). The results resemble a parabolic characteristic or a bowing effect of the band gap. Modification of
the band gap by varying the W concentration can be expanded into nanoelectronics and optoelectronics applications. For the band edges of the conduction band and the valence band from $x = 0$ to 0.44, the conduction band minimum shifts only a little, whereas the valence band shifts significantly. In contrast, from $x = 0.56$ to 1, the results show that the conduction band shifts more significantly than the valence band (see figure 6(b)). From the results of the band edges, it can be concluded that if the W concentration is dominating the Mo concentration in the $\text{MoW}_x\text{S}_{12}$ alloys, then the conduction band is swung by WS$_2$, and by contrast, if MoS$_2$ dominates, then the valence band is swung. Since the valence band maxima of MoS$_2$ and WS$_2$ originate from the $d_{xy}$ and $d_{x^2-y^2}$ orbitals of the metal, doping a W atom in MoS$_2$ instantly shifts them up in energy. In contrast, the conduction band minimum is dominated by the $d_z^2$ of the metal in the case of MoS$_2$ but by the $d_{xy}$, $d_{x^2-y^2}$, and $d_{z^2}$ states in the case of WS$_2$, which is described by the density of states for the valence and conduction bands in these works [29, 30]. For $x = 0$ to 0.33, W contributes slightly to the conduction band minimum, resulting in small energetic upshifts. For $x = 0.33$ to 1, the W contribution becomes dominant and thus the upshifts are enhanced. This feature can be explained by the different positions of the band edges in MoS$_2$ and WS$_2$.

4. Conclusion

In summary, the atomic distributions in the monolayer semiconducting transition metal dichalcogenide $\text{Mo}_1-x\text{W}_x\text{S}_2$ alloys have been investigated by using the density functional theory and modelling with the special quasi-random structure customised for the 2D material. We showed that this model can describe the nature of the 2D band structure and is in good agreement with the result from the first-principle calculation by Monte Carlo simulations [31], a large supercell calculation [29], and experimental results [32, 33]. It is notable that the result obtained by using a small periodic cell ($3 \times 3 \times 1$ with 27 atoms in the model structure) generated by the SQS can be used very well for calculation of further properties, although this model only exists at low temperature according to the SQS and the DFT simulation. The $\text{Mo}_1-x\text{W}_x\text{S}_2$ alloys displayed a good miscibility as the negative of formation energy. The band gaps and band edges are demonstrated in the $\text{Mo}_1-x\text{W}_x\text{S}_2$ monolayer alloys. Our result reveals that the minimum gap appeared at around $x = 0.33$. This shows that the tunable band gap can be greatly broadened, leading to the applications of transition metal dichalcogenide monolayers. As mentioned above, the 2D SQS $\text{Mo}_1-x\text{W}_x\text{S}_2$ is an interesting finding that can be used for studies.
of other physical and electronic properties. In this remarkable approach, the calculation utilised a small periodic cell that is suitable for DFT calculations and better capable of explaining physical properties than other methods like Monte Carlo simulations. In addition, by decreasing the number of atoms in the supercell, the calculation consumes fewer computing resources, which allows the simulation to be done in a smaller computing laboratory.

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