Tunable bandgap of graphene/MS₂ (M=W, Mo) heterobilayers for photovoltaic materials

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Keywords: graphene, solar cells, bandgap

Abstract

Solar cells are used widely for generating electricity by absorbing sunlights. Bandgap is one of the effective factors for the efficiency of the solar cells. In this investigation, by means of first-principles calculations, we have studied the electronic structures of graphene/MS₂ (M=Mo, W) heterobilayers. We found that the bandgap of graphene/MS₂ could be tuned by applying vertical and lateral strains. Results show that the bandgap of graphene/MoS₂ can be changed from zero to direct bandgap of 0.65 eV and 0.74 eV by applying the compressive strain vertically and laterally, respectively. The same trend applies to graphene/WS₂ heterobilayers.

1. Introduction

Solar energy, which is transformed from light through solar cells, has played an increasingly important role in our daily life. The photovoltaic effect was first proposed by Alexandre Edmond Becquerel, indicating that certain materials can produce small amounts of electric current when being exposed to light. Since then, how to maximize the efficiency of solar cells has become one of the main challenges. Recently, researchers devised a new type of solar cells with an efficiency as high as 44.5% by using a multi-layered GaSb-based materials to absorb different parts of the light spectrum [1]. Tandem cell strategy for organic photovoltaic cells [2] as well as the window buffer technology [3] were also profoundly studied, which can be used to enhance the performance of CdTe solar cells. A thin CdS buffer layer was inserted to improve the built-in potential by increasing the values of fill factor and open-circuit voltage, which are directly proportional to the performance of solar cells \((\eta)\) as demonstrated in the equation [4], where \(FF, J_{sc}, V_{oc}\), and \(P_{in}\) represent fill factor, short-circuit current density, open-circuit voltage and power density of incident light, respectively: \(\eta = \frac{FF \times J_{sc} \times V_{oc}}{P_{in}} \times 100\%\). It is well-known that the efficiency of the transformation between light and the solar energy is closely related to the bandgap of the material. The energy is generated when an electron receives excess energy to jump over the bandgap. A small bandgap allows more absorbed photons, but also a lower attainable open circuit voltage. On the other aspect, a higher bandgap means a higher attainable open circuit voltage, but fewer photons available at the same time. Therefore, finding an optical bandgap material is one of the primary goals in solar cell development. Silicon has been widely used for producing solar cells because not only because of its commercially viability, but also its ideal bandgap which helps the solar cells reach a high efficiency [5–7]. New 2D materials graphene turns to be a good choice due to its higher mobility. However, graphene is a zero-bandgap semiconductor, which does not fit properly for photovoltaic productions. Therefore, we are looking for a way to open graphene’s bandgap to reach the high-efficiency bandgap of solar cells, aiming a bandgap between 0.75 eV–1.5 eV. Heterobilayer structures could be potentially promising materials since multilayer structures often influence the material’s bandgaps [8]. Considering that most monolayer MS₂ materials have direct bandgaps around 1.5 eV, we combine graphene with monolayer MS₂ (M=W, Mo) to obtain a suitable direct bandgap.

In this research, we analyze possible materials for solar cells by comparing and improving their bandgaps. The effect of biaxial strain modulations and changes in interlayer distance on the electronic properties of graphene/MS₂ structures will be investigated by using first-principle calculations in the framework of density functional theory.
We aim to find a fittable direct bandgap for photovoltaic applications. We first introduce the framework of the calculations in section 2, and give detailed discussions about the bandgap in section 3. In section 4, we give a summary.

Table 1. Converged values of lattice constant $a$, kinetic energy cutoff, $k$-grid, and vacuum of each material.

| Materials      | $a$ (Å) | Kinetic Energy Cutoff (eV) | $k$-grid    | Vacuum (Å) |
|----------------|--------|---------------------------|-------------|------------|
| Graphene       | 2.46   | 462                       | $14 \times 14 \times 1$ | 7          |
| WS$_2$         | 3.19   | 680                       | $7 \times 7 \times 1$   | 14         |
| MoS$_2$        | 3.18   | 734                       | $10 \times 10 \times 1$ | 10         |
| Graphene/WS$_2$| 2.85   | 680                       | $14 \times 14 \times 1$ | 14         |
| Graphene/MoS$_2$| 2.82  | 734                       | $14 \times 14 \times 1$ | 14         |

Table 2. The calculated bandgap for graphene/MoS$_2$ heterobilayer structure when applying a change in interlayer distance $d$ and lattice constant $a$.

| $d$ (Å) | $a$ (Å) | Bandgap (eV) | $d$ (Å) | $a$ (Å) | Bandgap (eV) |
|--------|--------|-------------|--------|--------|-------------|
| 3.18   | 2.82   | 0.00 Direct | 2.27   | 2.79   | 0.65 Direct |
| 2.73   | 2.82   | 0.21 Direct | 2.27   | 2.76   | 0.66 Direct |
| 2.50   | 2.82   | 0.38 Direct | 2.27   | 2.68   | 0.69 Direct |
| 2.27   | 2.82   | 0.64 Direct | 2.27   | 2.57   | 0.72 Direct |
| 2.16   | 2.82   | 0.65        | 2.27   | 2.51   | 0.74 Direct |
| 2.04   | 2.82   | 0.61        | 2.27   | 2.48   | 0.65        |

Figure 1. Calculated band structure of (a) graphene, (b) WS$_2$, and (c) MoS$_2$. 

functional theory (DFT). We aim to find a fittable direct bandgap for photovoltaic applications. We first introduce the framework of the calculations in section 2, and give detailed discussions about the bandgap in section 3. In section 4, we give a summary.
2. Method

The underlying structural relaxations and electronic structure calculations are performed in the framework of density functional theory (DFT). The generalized gradient approximation (GGA) [9] expressed by Perdew–Burke–Ernzerhof (PBE) functional as implemented in the ABINIT package [10–13] was adopted. The electron-ion interaction was described by the projector-augmented-wave (PAW) potentials [10], with 2s^22p^2, 3s^23p^4, 5d^66s^2, and 4d^55s^1 configurations treated as valence electrons for C, S, W, and Mo, respectively.

These choices of kinetic energy cutoff, kgrid, and vacuum layer rely on a series of tests on the system we calculated, giving a good converged surface energies (0.1 meV/atom). The converged values are all listed in table 1.

We first calculated the band structures for monolayer graphene, WS2, and MoS2. We considered WS2 and MoS2 as ideal materials for combining with graphene due to their suitable bandgaps, which are around 1.5 eV.
For each heterobilayer material, the original lattice constant is chosen by the average value of two monolayer materials. Moreover, the starting value for interlayer distance is chosen according to the experimental results [14–17].

3. Results and discussions

3.1. Monolayer structure

Before calculating the bilayer structures, we first explored the electronic band structures for isolated graphene, WS$_2$, and MoS$_2$ monolayers. The calculated lattice constants of those monolayers are in good agreement with the published results [18–20]. The band structures of these monolayer materials are shown in figure 1. For MS$_2$ structure, the monolayers are semiconducting materials with direct bandgaps; the electronic band structure are
calculated along with the high symmetry k points \( \Gamma - M - K - \Gamma \) in the first Brillouin zone. The conduction band minimum (CBM) and the valence band maximum (VBM) are located at the K/M point. However, their corresponding heterostructures with graphene become zero-bandgap semiconductors.

Strain modulation has been widely used for adjusting the electronic band structures for low-dimensional systems [8]. For TMD monolayers, several recent calculations [21, 22] have shown the possibility of modifying the bandgaps by changing the distance between two layers. Therefore, changes in interlayer distance are applied to obtain a better bandgap that can be used for photovoltaic applications. Due to various reasons, we have found out that DFT calculations usually underestimate the bandgaps by 40% [15, 23]. Since the optical direct bandgap is 0.75–1.5 eV for producing solar cells, we would like to find materials with direct bandgaps of 0.45–0.9 eV by using density functional theory calculation.

3.2. Graphene/MoS\(_2\) heterobilayer structures

Next, we calculated the band structures for graphene/MoS\(_2\). For the unstrained band structure, it is a zero bandgap, which is a characteristic of graphene’s electronic structure. With a 10%, 15%, and 20% vertical compressive strain, the bandgap is increased to 0.213 5 eV, 0.382 9 eV, and 0.639 5 eV respectively. However, with a 22.5% or 25% vertical compressive strain, the bandgap becomes indirect. The VBM is relocated from K point to the \( \Gamma \) point. The CBM is still located at the K point regardless of the strain. The results have clearly shown that as the interlayer distance decreases, the bandgap will increase, but when the interlayer distance is smaller than 80% of the original distance, an indirect bandgap is formed. Although we have applied vertical tensile strains, there is no obvious changes on the bandgaps. The calculated band structures with different interlayer distance values are listed in figure 3. The computed electronic bandgaps of graphene/MoS\(_2\) as a function of the change in interlayer distance is shown in figure 4(a), indicating that the bandgap will increase when a vertical compressive strain is applied.

We have also applied a lateral compressive strain on the heterobilayer structure to obtain a better bandgap. We started with a 1% lateral compressive strain, which gives us a 0.649 5 eV direct bandgap. Comparing to the previous 0.639 5 eV, we believe that a lateral compressive strain will cause a larger bandgap on the heterobilayer structure. Next, we applied a 2%, 5%, 9%, and 11% lateral compressive strain, which gives a 0.659 2 eV, 0.687 1 eV, 0.723 6 eV, and 0.742 2 eV respectively. As shown in figure 4(b), a decrease in lattice constant will increase the bandgap, however, after the lateral compressive strain is larger or equal than 12%, the bandgap becomes indirect. The calculated electronic band structures with different lattice constants are shown in figure 5, and table 2 shows the corresponding bandgaps with different interlayer distances and lattice constants of graphene/MoS\(_2\). It is wildly accepted that the semiconductors with direct bandgap of 1–1.5 eV give an ideal Shockley–Queisser absorption efficiency. Moreover, monolayer MoS\(_2\) in 1H phase with only \( \sim 0.65 \) nm shows a large absorption coefficient of \( 10^7 \) m\(^{-1}\) which makes it useful for photovoltaic applications. Unfortunately, the major drawback of the MoS\(_2\) thin film is the indirect nature of its bandgap where phonons are required to mediate electron excitations from light. Therefore, graphene/MoS\(_2\) heterostructure with proper interlayer distance and lattice constant will exhibits favorable photovoltaic efficiency.

Figure 4. (a) Computed electronic bandgaps of graphene/MoS\(_2\) as a function of the interlayer distance. (b) Computed electronic bandgaps of graphene/MoS\(_2\) as a function of the lattice constant.
3.3. Graphene/WS$_2$ heterobilayer structures

After that, we calculated the band structures for graphene/WS$_2$, which has similar properties with the graphene/MoS$_2$ heterobilayer structure. First, the results indicate that graphene/WS$_2$ heterojunction is semiconducting with zero bandgap (see figure 2(a)). Therefore, we adjusted different interlayer distance to obtain optical bandgaps. The direct bandgap is increased to 0.156 5 eV with a 10% vertical compressive strain; 0.302 9 eV for 15%, 0.542 8 eV for 20%, and 0.703 4 eV for 22.5%, respectively.

Like the graphene/MoS$_2$ heterobilayer, once the compressive strain is too big, which is 25% for this case, the bandgap will become indirect. The VBM is relocated from M point to the $\Gamma$ point, but the CBM is still located at the M point. Calculated band structures are shown in figure 5. Lateral compressive strains are also applied on the graphene/WS$_2$ heterobilayers. We observed a direct bandgap 0.718 3 eV, 0.732 0 eV, 0.774 8 eV, and 0.805 1 eV for 1%, 2%, 5%, and 7% compressive strain respectively (figure 6). The computed electronic bandgap of graphene/WS$_2$ as a function of interlayer distance and lattice constants are shown in figure 7. As shown in figure 7(b), compressive strains can enlarge the bandgap from 0.703 4 eV to 0.805 1 eV. Similar to the vertical

Figure 5. Electronic band structure for graphene/WS$_2$ heterobilayers with interlayer distance (a) 3.32 Å, (b) 2.84 Å, (c) 2.59 Å, (d) 2.35 Å, (e) 2.22 Å, and (f) 2.10 Å.
Figure 6. Electronic band structure for graphene/WS₂ heterobilayers with lattice constant (a) 2.82 Å, (b) 2.79 Å, (c) 2.71 Å, (d) 2.65 Å, (e) 2.62 Å, and (f) 2.59 Å.

Table 3. The calculated bandgap for graphene/WS₂ structure when applying a change in interlayer distance \(d\) and lattice constant \(a\).

| \(d\) (Å) | \(a\) (Å) | Bandgap \((eV)\) | \(d\) (Å) | \(a\) (Å) | Bandgap \((eV)\) |
|-----------|-----------|-----------------|-----------|-----------|-----------------|
| 3.32      | 2.85      | 0.00 Direct     | 2.22      | 2.82      | 0.72 Direct     |
| 2.84      | 2.85      | 0.16 Direct     | 2.22      | 2.79      | 0.73 Direct     |
| 2.59      | 2.85      | 0.30 Direct     | 2.22      | 2.71      | 0.77 Direct     |
| 2.35      | 2.85      | 0.54 Direct     | 2.22      | 2.65      | 0.81 Direct     |
| 2.22      | 2.85      | 0.70 Direct     | 2.22      | 2.62      | 0.80 Indirect   |
| 2.10      | 2.85      | 0.87 Indirect   | 2.22      | 2.59      | 0.67 Indirect   |
strains, once the compressive strain is too big (8% in this case), the bandgap becomes indirect. Therefore, 0.805 eV will be the largest direct bandgap for graphene/WS2 attainable. Table 3 shows the corresponding bandgaps with different interlayer distances and lattice constants of graphene/WS2. Likely, graphene/WS2 heterostructure with proper interlayer distance and lattice constant will also exhibit good photovoltaic efficiency.

4. Conclusion

In summary, we have systematically studied the influence of strain on electronic band structures of graphene/MS2 (M = Mo, W) using first-principle calculations. Calculated results demonstrate that compressive strains can greatly tune the bandgap of graphene/MS2 so as to convert it into a promising photovoltaic material. Within the experimental accessible strain levels (lateral compressive strains $= 11\%$ and $7\%$), the obtained largest direct bandgaps can reach 0.74 eV for graphene/MoS2 and 0.81 eV for graphene/Ws2, respectively.

Acknowledgments

We acknowledge Dr Gefei Qian for computer technical support.

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