The effects of surface polarity and dangling bonds on the electronic properties of monolayer and bilayer MoS$_2$ on $\alpha$-quartz

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Abstract
We investigate the electronic properties of monolayer and bilayer MoS$_2$ on $\alpha$-quartz substrate through first-principles density functional calculations. Due to the coupling of the MoS$_2$ with the substrate, the valence band edge state at the Brillouin zone center tends to shift upward, reducing the indirect band gap of the MoS$_2$, whereas the direct gap at the $K$ valleys is less sensitive to substrate conditions. By taking into account the van der Waals interactions between the MoS$_2$ and the substrate, we find that monolayer MoS$_2$ exhibits a transition from direct-gap to indirect-gap semiconductor in the presence of surface O-dangling bonds. Moreover, a charge transfer occurs from MoS$_2$ to SiO$_2$, inducing $p$-type doping and lifting the Kramers degeneracy by breaking the time reversal symmetry. In bilayer MoS$_2$, O-dangling bonds break the inversion symmetry by inducing dipole fields across the interface and thereby lower the energy band associated with the one layer relative to the other. Although the time reversal symmetry is also broken, its effect on the spin splitting is extremely small in the $K$ valleys so that a strong coupling between the spin and valley degrees of freedom takes place, similar to that found in free-standing monolayer MoS$_2$.

Keywords: electronic structure, molybdenum disulphide, spin-orbit coupling, local density functional, MoS$_2$
1. Introduction

Following the discovery of graphene, the transition metal dichalcogenides $MX_2$ ($M =$ Mo, W, $X =$ S, Se), which are characterized by their layer structure, have attracted much attention because of their potential applications for low-dimensional electronic and optical devices [1–3]. Whereas graphene has zero band gap, transition metal dichalcogenides are semiconducting, with moderate band gaps. In particular, molybdenum disulphide (MoS$_2$) has emerged as a promising material for field-effect transistors with high current on-off ratios [4, 5]. The electronic properties of MoS$_2$ vary with its layer thickness, exhibiting a transition from an indirect-gap semiconductor ($\sim$1.3 eV) in bulk to a direct-gap semiconductor ($\sim$1.9 eV) in the monolayer limit due to quantum confinement [6, 7]. Because two-dimensional layers are stacked by weak van der Waals forces, single- and few-layer MoS$_2$ can be easily assembled by exploiting the exfoliation technique used for graphene fabrication [8].

Graphene and transition metal dichalcogenides have a hexagonal lattice structure in which the energy states at the $K$ and $K'$ valleys of the Brillouin zone are related to one another by time reversal symmetry. Although spin-orbit coupling is extremely weak in graphene, the $d$ orbitals of metal ions generate much stronger spin-orbit couplings in transition metal dichalcogenides [9]. Moreover, breaking of inversion symmetry allows for an effective coupling between the spin and valley degrees of freedom in the presence of time reversal symmetry [10, 11]. Thus, transition metal dichalcogenides generate more interest in terms of searching for applications of real spin and valley pseudospin. The possibility of valleytronics in graphene systems, based on the control of valley polarization, has been suggested [12, 13]. In contrast with graphene systems, in which staggered sublattice potential raised from substrate, bias voltage, or strain is required to break inversion symmetry [14, 15], inversion symmetry is intrinsically broken in monolayer MoS$_2$. Such valley polarization has been recently observed by optical excitation using circularly polarized light in monolayer MoS$_2$ [16–19]. On the other hand, inversion symmetry is preserved in bilayer MoS$_2$, so the valley-dependent optical selection rule is not allowed. Interestingly, it has been reported that the inversion symmetry in bilayer MoS$_2$ can be controlled by applying an electric field perpendicular to the layer [20]. When bilayer MoS$_2$ is deposited on a SiO$_2$ substrate, it recovers valley polarization even in the absence of an electric field. It was suggested that the existence of valley polarization in bilayer MoS$_2$ is due to breaking of inversion symmetry owing to electron doping induced by substrate [20] or the laser heating effect [17]. In theoretical calculations for monolayer MoS$_2$ on SiO$_2$ [21], the conductivity of MoS$_2$ was shown to depend on the charge polarity of traps at the interface, being $n$-type for Na impurities and $p$-type for O-dangling bonds. However, when MoS$_2$ is deposited on SiO$_2$ substrates, both $p$- and $n$-type conductivities have been observed in ultrathin MoS$_2$ layers [22–24], whereas bulk MoS$_2$ is known to exhibit intrinsic $n$-type conductivity. Moreover, photoluminescence (PL) spectroscopy measurements have shown that PL peaks shift in monolayer and few-layer MoS$_2$ on SiO$_2$ compared with free-standing samples, indicating that the MoS$_2$ layers interact with the substrate [25, 26]. Because the electronic and transport properties of MoS$_2$ vary with substrate and growth conditions, it is important to understand the nature of interlayer interaction between MoS$_2$ and SiO$_2$ and the electronic modification of MoS$_2$ on the substrate.

In this work, we study the electronic properties of monolayer and bilayer MoS$_2$ on $\alpha$-quartz through first-principles density functional calculations in which spin-orbit coupling is taken into account. We find that O-dangling bonds at the SiO$_2$ surface lift the Kramers
degeneracy, especially at the center of the Brillouin zone in the single layer of MoS$_2$, whereas they break the inversion symmetry in the bilayer case, allowing for coupling between the spin and valley degrees of freedom. In the next section, we explain the computational method and details of the atomic structures of MoS$_2$ on the Si- and O-polar surfaces of the substrate. Then we discuss the effects of surface polarity, dangling bonds, and van der Waals forces on the interaction with the substrate and the electronic properties of MoS$_2$ and finally present conclusions.

2. Calculation method

Our first-principles calculations were performed mostly by using the exchange-correlation functional of Perdew, Burke, and Ernzerhof (PBE) [27] within the density functional theory (DFT) framework and the projector augmented wave (PAW) potentials [28] as implemented in Vienna Ab-initio Simulation Package (VASP) code [29, 30]. For the Mo potential, the 4s and 4p orbitals were included as semi-core states, with the 4d and 5s orbitals in the valence shell. The wave functions were expanded in plane waves up to a cutoff of 400 eV. We employed a supercell geometry in which monolayer or bilayer MoS$_2$ is placed on $\alpha$-quartz, and we used a $k$-point set generated by the 5 × 5 × 1 Monkhorst-Pack mesh [31] for Brillouin zone integration. Spin-polarized density functional calculations were performed using the scalar relativistic approximation, with the inclusion of intrinsic spin-orbit coupling.

With the PBE functional, the lattice constants were calculated to be $a = 3.184\,\text{Å}$ for monolayer MoS$_2$ and $a = 3.189\,\text{Å}$ and $c/2 = 7.080\,\text{Å}$ for bilayer MoS$_2$. These lattice parameters are overestimated compared with the measured values of $a = 3.16\,\text{Å}$ and $c/2 = 6.147\,\text{Å}$ for bulk MoS$_2$ [32]. In particular, the PBE functional does not properly describe the interlayer coupling. Because the electronic structure is extremely sensitive to the lattice parameters, the lattice parameters of MoS$_2$ were fixed to the measured values in the PBE calculations, whereas the separation of MoS$_2$ from substrate was relaxed. To describe more accurately the interaction between MoS$_2$ and SiO$_2$, we also performed independent DFT calculations with the PBE+D2 functional, which includes van der Waals forces [33]. Due to the lattice mismatch between MoS$_2$ and SiO$_2$, the 3 × 3 and 2 × 2 lateral supercells were taken for MoS$_2$ and SiO$_2$, respectively (figure 1(a)). Although 5% compressive strain was exerted on the SiO$_2$, it did not modify the electronic structure of the MoS$_2$. We considered various (0001) surfaces of $\alpha$-quartz, such as defect-free, Si-polar, and O-polar surfaces, and also investigated the effects of surface Si- and O-dangling bonds on the electronic properties of MoS$_2$. In the slab model with six layers of SiO$_2$, dangling bonds at the back side of SiO$_2$ were fully passivated by hydrogen and a vacuum region of 10 Å was sufficient to prohibit interactions between adjacent supercells. A dipole field correction was included to remove artificial internal electric fields generated across the slabs. The interface structures and the atomic positions were fully optimized until the residual forces were less than 0.02 eV Å$^{-1}$.

3. Results and discussion

3.1. Monolayer MoS$_2$ on SiO$_2$

To understand the electronic properties of MoS$_2$ on SiO$_2$, we first discuss the band folding in the supercell geometry. The $K_{(1\times1)}$ and $K'_{(1\times1)}$ points of the hexagonal Brillouin zone of the
1 × 1 primitive cell are related to one another by time reversal symmetry, and these $K$ valleys are folded to the $\Gamma$ (3×3) point in the 3 × 3 supercell [34], as shown in figure 1(b). The characteristics of the folded $\Gamma_{(1\times1)}$, $K_{(1\times1)}$, and $K'_{(1\times1)}$ states at the $\Gamma_{(3\times3)}$ point are determined by analyzing their charge distributions. Figure 2 shows the PBE band structures of pristine MoS2 in the 1 × 1 and 3 × 3 cells, which are obtained for the measured lattice parameters $a = 3.16 \, \text{Å}$ and $c/2 = 6.147 \, \text{Å}$. In monolayer MoS2, the direct gap at the $K_{(1\times1)}$ point is 1.689 eV, whereas the indirect gap from the $\Gamma_{(1\times1)}$ point to the $K_{(1\times1)}$ point is 1.843 eV (table 1). If the PBE value for the in-plane lattice parameter is used, the planar expansion reduces both the direct and indirect gaps by 110 and 230 meV, respectively. The valence band edge state at the $\Gamma$ point is lower by 154 meV than the valence band maximum in the $K$ valleys without spin splitting due to time-reversal symmetry (figure 2(a)). On the other hand, at the $K_{(1\times1)}$ and $K'_{(1\times1)}$ points, the spin-orbit coupling induces a large spin splitting of $\Delta_K = 148 \, \text{meV}$. However, the valence band edges in the $K$ valleys have opposite spin states due to breaking of inversion symmetry, thus exhibiting valley polarization. In the $K$ valleys, electron-hole pairs can be selectively excited by using circularly polarized light [16, 17]. In a high-quality MoS2 sample, because spin relaxation through inter-valley scattering is suppressed by the large distance between the $K$ valleys in momentum space, the resulting PL emission can be strongly polarized with the same circular polarization as the incident light.

For monolayer MoS2 on SiO2, we consider the Si- and O-polar (0001) surfaces of $\alpha$-quartz and optimize the interatomic distance between the MoS2 and the SiO2 with the in-plane lattice parameter fixed to $a = 3.16 \, \text{Å}$. The PBE results for the interatomic distances and band gaps are
summarized for various substrate conditions in table 1. When surface Si- and O-dangling bonds are fully passivated by hydrogen (figure 3), the MoS2 interacts weakly with the substrate, with binding energies of a few meV per 1 × 1 cell. In the most stable configuration, the separation of the MoS2 from the O-polar surface is $d_{S-O} = 3.38$ Å, which is defined as the distance between the S and O layers. On the Si-polar surface, the larger distance $d_{S-Si} = 4.03$ Å is obtained because of the H atoms lying between the S and Si layers. The electronic structure of MoS2 is similar to that of free-standing MoS2, without any charge transfer between MoS2 and SiO2. On both the defect-free SiO2 surfaces, the monolayer MoS2 exhibits type-I band alignment, with the band edges associated with the MoS2. The valence band and conduction band offsets are calculated to be 2.3 and 2.2 eV, respectively.

It is worth noting that the band alignment may depend on the choice of the exchange-correlation functional. Here we perform additional calculations for the band alignment by using the hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE) for the exchange-correlation potential [35]. It is difficult to use directly the HSE functional for the heterostructure between MoS2 and SiO2 with a vacuum region mainly due to heavy computational demand. Instead, we examine the valence band maximum (VBM) and conduction band minimum (CBM) shifts for

![Figure 2. The PBE band structures of freestanding (a) monolayer and (b) bilayer MoS2 in the 3 × 3 supercell (left panel) and the 1 × 1 primitive cell (right panel). The red and blue lines denote the up- and down-spin states, respectively, at the valence band edges in the K valleys, whereas the green lines represent the valence band edge state at the $\Gamma$ point in the 1 × 1 cell. The valence band maximum is set to zero.](image-url)
individual MoS$_2$ and SiO$_2$ systems by using the HSE functional. In MoS$_2$, the HSE corrections are estimated to be $-0.34$ and $0.13$ eV for the VBM and CBM states, respectively, whereas they are $-1.34$ and $0.49$ eV, respectively, for the VBM and CBM states of SiO$_2$. With the HSE functional, we obtain the valence band and conduction band offsets of $3.30$ and $2.56$ eV, respectively, compared with the corresponding PBE results of $2.3$ and $2.2$ eV. In previous HSE calculations for semiconductor/insulator heterostructures [36], it was shown that the HSE functional changes the difference between the reference potentials of two materials by $\sim 0.1$ eV, which is much smaller than the band offsets. Thus, the type-I band alignment is not altered with the HSE functional, whereas the band offsets increase due to the band gap corrections.

To examine the effect of surface dangling bonds on the electronic structure of MoS$_2$, we generate a single Si- or O-dangling bond by removing one hydrogen atom per 3 × 3 cell from the passivated Si- and O-polar surfaces. Surface dangling bonds are easily created upon thermal annealing of hydrogen passivated surfaces. We find that the MoS$_2$ interacts weakly with the Si-dangling bonds on the Si-polar surface. In the lowest-energy configuration, where the S atom of the bottom S layer is positioned on top of the Si-dangling bond, the binding energy is estimated to be about $6$ meV per 1 × 1 cell. The S–Si distance is reduced slightly to $d_{S-Si} = 3.96$ Å, but MoS$_2$ still weakly interacts with SiO$_2$. The filled spin-up state of the Si-dangling bond is positioned in the band gap, $0.86$ eV above the VBM, whereas the empty spin-down state lies in the conduction band (figure 4(a)). Because the Si-dangling bond is well separated from the MoS$_2$, only the indirect gap is reduced by about $10$ meV, whereas the direct gap is unaffected. It is interesting to note that the time reversal symmetry is weakly broken by the magnetic moment of the Si-dangling bond, lifting the Kramers degeneracy at the $\Gamma$ point. However, the spin splitting ($\Delta \Gamma \sim 4$ meV) at the $\Gamma$ point is extremely small due to the weak interaction with the dangling bond.

On the other hand, the O-dangling bond strongly interacts with the S layer and thus significantly modifies the electronic structure of the MoS$_2$. For the defect density of one O-dangling bond per 3 × 3 cell, the MoS$_2$/SiO$_2$ interface has the lowest energy when the bottom S atom is directly on top of the O-dangling bond, with a binding energy of $69$ meV per 1 × 1 cell. The distance of MoS$_2$ from SiO$_2$ is reduced to $d_{S-O} = 3.02$ Å. The O-dangling bond state is

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**Table 1.** The results of the PBE calculations for the separations of MoS$_2$ from SiO$_2$ ($d_{Si-O}$ or $d_{S-Si}$ in Å), the binding energies ($E_b$ in meV per 1 × 1 cell), the direct gaps ($E_g^{(d)}$ in eV) in the $K$ valleys, and the indirect gaps ($E_g^{(i)}$ in eV) for free-standing monolayer and bilayer MoS$_2$ and those on various SiO$_2$ substrates, such as a bare Si-polar surface, fully H-passivated Si- and O-polar surfaces, and Si- and O-polar surfaces with a single Si- or O-dangling bond (DB) per 3 × 3 cell. The distances ($d_{Si-O}$ and $d_{S-Si}$) are optimized, whereas the lattice parameters are fixed to the measured values of $a = 3.16$ Å and $c/2 = 6.147$ Å.

| Substrate                  | $d_{S-Si}/d_{S-O}$ | $E_b$  | $E_g^{(d)}$ | $E_g^{(i)}$ | $d_{S-Si}/d_{S-O}$ | $E_b$  | $E_g^{(d)}$ | $E_g^{(i)}$ |
|----------------------------|-------------------|-------|------------|------------|-------------------|-------|------------|------------|
| Free-standing              | —                 | —     | 1.689      | 1.843      | —                 | —     | 1.679      | 1.266      |
| H-passivated Si-polar      | 4.03              | 6     | 1.689      | 1.834      | 4.47              | 1     | 1.679      | 1.271      |
| H-passivated O-polar       | 3.38              | 1     | 1.689      | 1.833      | 3.50              | 1     | 1.673      | 1.271      |
| Si-polar with Si DBs       | 3.96              | 6     | 1.689      | 1.830      | 4.13              | 5     | 1.675      | 1.269      |
| O-polar with O DBs         | 3.02              | 69    | 1.663      | 1.698      | 3.13              | 64    | 1.372      | 1.169      |
| Bare Si-polar              | 3.53              | 1     | 1.685      | 1.733      | 3.66              | 1     | 1.673      | 1.260      |
located at about 110 meV below the VBM (Figure 4(b)). Using the Bader charge analysis, we find that about 0.5 electron charge is transferred from the MoS$_2$ to the SiO$_2$. As a consequence, hole doping is induced in the MoS$_2$, with the depletion of more charges in the bottom S layer, thereby breaking the mirror symmetry. The time reversal symmetry is also broken by the magnetic moment of the O-dangling bond. Because the valence band edge states at the $\Gamma$ point, which are composed of the S $p_z$ and Mo $d_{3z^2-r^2}$ orbitals (Figure 4(c)), interact more effectively with the O-dangling bond, a large spin splitting ($\Delta_\Gamma = 22$ meV) takes place at the $\Gamma$ point (Figure 4(d)). On the other hand, because the VBM state in the $K$ valleys is characterized by the in-plane Mo $d_{xy, x'y'}$ orbitals, the effect of the O-dangling bond is very small, resulting in a spin splitting of $\Delta_K = 152$ meV (Figure 4(d)), similar to that of free-standing MoS$_2$. Due to the relatively large spin splitting in the $K$ valleys, hole carriers near the VBM have a longer spin lifetime (a few ns) than that of electron carriers (a few ps) [37]. Thus, $p$-type MoS$_2$ has been suggested to be more promising for spintronics applications than $n$-type MoS$_2$. As the valence band edge state at the $\Gamma$ point shifts upward, the indirect gap is reduced by 123 meV, whereas the direct gap in the $K$ valleys is less affected. Due to the small difference between the direct and indirect gaps, some hole carriers may also be generated in the $\Gamma$ band.

Figure 3. Side views of the optimized interface structures of monolayer MoS$_2$ on Si-polar (left column) and O-polar (right column) surfaces with surface dangling bonds (a) fully passivated by hydrogen and (b) unpassivated. The blue, purple, red, green, and white balls denote the S, Mo, O, Si, and H atoms, respectively.
Next we examine the effect of surface polarity on the electronic structure of MoS$_2$. The O-polar surface consists of eight O atoms in the 3 × 3 cell, each of which has one dangling bond. Because the active O-dangling bonds interact strongly with the MoS$_2$, the distance between the MoS$_2$ and the SiO$_2$ is reduced to $d_{SO} = 1.49$ Å. The energy of the MoS$_2$/SiO$_2$ interface strongly depends on the relative position of the MoS$_2$. In the most stable configuration (figure 3(b)), the S–O bonds are newly formed at the interface, with bond lengths of 1.55 and 1.60 Å. As a consequence, the MoS$_2$ no longer maintains its two-dimensional characteristics, with severe modification of its electronic structure.

Figure 4. The PBE band structures of monolayer MoS$_2$ on SiO$_2$ surfaces with (a) a single Si- or (b) O-dangling bond per 3 × 3 supercell. The red and blue lines denote the up- and down-spin states, respectively, at the valence band and conduction band edges in the $K$ valleys, whereas the green lines represent the valence band edge state at the $\Gamma$ point in the 1 × 1 cell. The valence band maximum is set to zero, and the black arrows denote the Fermi levels in (a), (b), and (d). For monolayer MoS$_2$ on the O-polar surface with a single O-dangling bond per 3 × 3 supercell, (c) the isosurfaces (yellow clouds) of the up-spin densities are shown for the valence band edge states at the $\Gamma$ and $K$ points and (d) the band structure near the $\Gamma$-band edge is enlarged.
On the Si-polar surface, which has four surface Si atoms per $3 \times 3$ cell, each surface Si atom has two dangling bonds (figure 3(b)). We consider three interface structures of the MoS$_2$ on the Si-polar surface, in which a surface Si atom is positioned just below the hexagon center, the S atom, or the Mo atom of the MoS$_2$. In all cases, the MoS$_2$ is moderately separated from the SiO$_2$, with similar distances of $d_{SSi} \approx 3.53$ Å. Thus, the weak interaction between the MoS$_2$ and the SiO$_2$ results in a small binding energy of about 1 meV per $1 \times 1$ cell. Moreover, the electronic structure of the MoS$_2$ is insensitive to the relative position of the MoS$_2$ with respect to the SiO$_2$. Because the Si-dangling bonds are self-compensated (figure 5(b)), the time reversal symmetry is preserved, with no charge transfer between the MoS$_2$ and the SiO$_2$. Thus, the Kramers degeneracy is maintained at the $\Gamma$ point. Due to the upward shift of the valence band edge at the $\Gamma$ point, the indirect gap is reduced to 1.733 eV (figure 5(a)). However, the VBM still appears in the $K$ valleys.

3.2. Bilayer MoS$_2$ on SiO$_2$

For bilayer MoS$_2$, we consider an $AB$ stacking with inversion symmetry, which is equivalent to the stacking sequence of the 2H structure in bulk MoS$_2$ [32]. Compared with monolayer MoS$_2$, the electronic structure of free-standing bilayer MoS$_2$ is affected by the restored inversion symmetry and the interlayer interaction (figure 2(b)). When the PBE lattice parameters ($a = 3.189$ Å and $c/2 = 7.080$ Å) are used, the valence band edge states at the $\Gamma_{(1\times1)}$ point split into the bonding and anti-bonding states by 220 meV, giving similar direct and indirect gaps. For the measured lattice parameters ($a = 3.16$ Å and $c/2 = 6.147$ Å), we find a much larger splitting of 695 meV at the $\Gamma_{(1\times1)}$ point due to enhanced interlayer interaction [7]. As a consequence, the indirect gap is greatly reduced to 1.266 eV (table 1), with the conduction band minimum (CBM) at the $T$ point along the $\Gamma$–$K$ direction. On the other hand, the interlayer interaction does not affect the valence band edge states in the $K$ valleys, yielding a direct gap of 1.679 eV, similar to that of monolayer MoS$_2$. Although the spin splitting is enhanced to
\( \Delta K = 168 \text{ meV} \) by the combined effect of spin-orbit coupling and interlayer interaction [38], the valley polarization disappears because of the inversion symmetry. The degenerate states with opposite spins at the \( K \) point are distributed in either the top or the bottom \( \text{MoS}_2 \) layer. In contrast with monolayer \( \text{MoS}_2 \), circularly polarized light excites carriers in both \( K \) valleys with equal strength in bilayer \( \text{MoS}_2 \); thus, the degree of PL polarization becomes zero.

When bilayer \( \text{MoS}_2 \) is placed on \( \text{SiO}_2 \), we optimize the interatomic distance between the \( \text{MoS}_2 \) and the \( \text{SiO}_2 \) by keeping the measured lattice parameters of the \( \text{MoS}_2 \). The PBE band gaps for various substrate conditions are listed in table 1. On the Si-polar surface, the S \( p_z \) orbital mainly interacts with the Si-dangling bonds. However, the coupling between the \( \text{MoS}_2 \) and the \( \text{SiO}_2 \) becomes weaker, with a larger distance, \( d_{\text{Si-Si}} = 3.66 \text{ Å} \), than in the monolayer case. The upward shift (6 meV) of the valence band edge at the \( \Gamma \) point is much smaller than the result (110 meV) for monolayer \( \text{MoS}_2 \) on the Si-polar surface. Thus, the influence of substrate on the indirect gap is weakened as the number of \( \text{MoS}_2 \) layers increases. This result is in good agreement with recent photoluminescence spectra measurements for various layers of \( \text{MoS}_2 \) on \( \text{SiO}_2 \) substrate [25], which showed that the indirect gap is reduced by about 80 meV for bilayer \( \text{MoS}_2 \) relative to free-standing bilayer \( \text{MoS}_2 \), whereas its decrease is less than 10 meV for three to five layers.

On the O-polar surface, bilayer \( \text{MoS}_2 \) also strongly interacts with active O-dangling bonds. The inversion symmetry between the two \( \text{MoS}_2 \) layers is broken by the charge transfer from the \( \text{MoS}_2 \) to the \( \text{SiO}_2 \). In the presence of one O-dangling bond per \( 3 \times 3 \) cell, dipole fields induce the potential difference of about 327 meV between the top and bottom layers of \( \text{MoS}_2 \), thereby resulting in band separation, as shown in the local density of states (figure 6(a)). Due to the band separation, the VBM state at the \( \Gamma \) point is mainly associated with the bottom \( \text{MoS}_2 \) layer adjacent to the substrate, whereas the CBM state at the \( K \) point is derived from the top \( \text{MoS}_2 \) layer. The breaking of the inversion symmetry also lifts the degeneracy between the up- and down-spin states in the \( K \) valleys. The band separations (\( \Delta E_K^{(v)} \) and \( \Delta E_K^{(c)} \)) at the \( K \) point are estimated to be 317 and 294 meV for the valence and conduction bands, respectively (figure 6(b)). Due to the interaction of the bilayer \( \text{MoS}_2 \) with the O-dangling bonds, the interlayer interaction between the two \( \text{MoS}_2 \) layers is suppressed. Thus, the spin splitting in the \( K \) valleys is reduced from 168 meV to 146 meV, which is similar to that of free-standing monolayer \( \text{MoS}_2 \). Nevertheless, the valley polarization in the \( K \) valleys, which is absent in free-standing bilayer \( \text{MoS}_2 \), is recovered on the substrate.

Under \( \sigma^+ \) excitation with right-hand polarized light, interband transitions involving the up-spin states occur in both the \( K \) and \( K' \) valleys (figure 7). At the \( K \) point, the band separation \( \Delta E_K^{(v)} \) allows for intra-valley spin relaxation through the interlayer scattering from the bottom to the top layer. On the other hand, at the \( K' \) point, because it requires energy to flip spin from the top to the bottom layer, the PL emission with left-hand polarization \( \sigma^- \) is suppressed. The degree of circular polarization increases as the band separation between the top and bottom layers increases, i.e., as the defect density increases. It was recently shown that the inversion symmetry in bilayer \( \text{MoS}_2 \) can be controlled by varying the gate voltage [20]. At zero gate voltage, non-zero circular polarization was observed for bilayer \( \text{MoS}_2 \) on \( \text{SiO}_2 \), indicating that the inversion symmetry is initially broken in the sample. At a particular negative gate voltage, the valley polarization was shown to disappear because the potential difference between the top and bottom \( \text{MoS}_2 \) layers is eliminated. Because negative gate voltage depletes electrons, the initial electron doping may be caused by charged impurities at the interface or in the substrate.
Our results indicate that valley polarization is also induced in bilayer MoS$_2$ by the $p$-type doping effect of O-dangling bonds. In this case, the valley polarization will vanish by applying a positive gate voltage.

### 3.3. Van der Waals correction to interaction between MoS$_2$ and SiO$_2$

In this section, we examine the effect of van der Waals forces on the atomic and electronic properties of monolayer and bilayer MoS$_2$ on SiO$_2$. As discussed earlier, the PBE functional significantly overestimates the interlayer distance in bilayer MoS$_2$. By including the van der Waals correction to the PBE functional (PBE+D2) [33], we obtain the lattice parameters for free-standing bilayer MoS$_2$, $a = 3.194$ Å and $c/2 = 6.217$ Å, which are close to the experimentally measured and previously calculated values [32, 39]. To maintain consistency in comparison with the PBE results, we fix the in-plane lattice parameter to the measured value.

![Figure 6](image-url)  
Figure 6. (a) The local densities of states in the bottom (red) and top (blue) MoS$_2$ layers and (b) the PBE band structure for bilayer MoS$_2$ on a SiO$_2$ surface with a single O-dangling bond per $3 \times 3$ supercell. In (b), the right panel shows the enlarged band structure near the $\Gamma$-band edge, and the red and blue circles denote the up- and down-spin states, respectively, projected for the Mo $d_{xy/z^2}$ orbitals, whereas the green circles indicate the Mo $d_{3z^2-r^2}$ orbital. The VBM is set to zero, and the black arrows denote the Fermi levels.

[21]. Our results indicate that valley polarization is also induced in bilayer MoS$_2$ by the $p$-type doping effect of O-dangling bonds. In this case, the valley polarization will vanish by applying a positive gate voltage.
a = 3.16 Å and optimize the interlayer lattice parameter. In this case, the PBE+D2 functional yields the interlayer distance of c/2 = 6.225 Å and indirect and direct gaps that are slightly larger than those for c/2 = 6.147 Å (tables 1 and 2). The PBE+D2 functional is also used to optimize the interface structures of monolayer and bilayer MoS2 on SiO2 by keeping the lattice parameter a = 3.16 Å. The PBE+D2 results for the interatomic distances and band gaps are summarized for different substrate conditions in table 2.

For various SiO2 surfaces with and without surface dangling bonds, the interatomic distances between monolayer MoS2 and SiO2 are reduced by 0.06–0.38 Å so that the binding

**Figure 7.** Schematic illustrations of valley polarization in the K valleys for bilayer MoS2 on an O-polar surface with a single O-dangling bond per 3 × 3 supercell. The red and blue arrows indicate the interband transitions with right and left circularly polarized lights, respectively, whereas the green arrows represent the intra-valley spin relaxation process.

**Table 2.** The results of the PBE+D2 calculations for the separations of MoS2 from SiO2 (d_{Si–O} or d_{S–Si} in Å), the binding energies (E_b in meV per 1 × 1 cell), the direct gaps (E_g(d) in eV) in the K valleys, and the indirect gaps (E_g(i) in eV) for free-standing monolayer and bilayer MoS2 and those on various SiO2 substrates, such as a bare Si-polar surface, fully H-passivated Si- and O-polar surfaces, and Si- and O-polar surfaces with a single Si- or O-dangling bond (DB) per 3 × 3 cell. The distances (d_{Si–O} and d_{S–Si}) and the interlayer lattice parameter (c/2) are optimized, whereas the in-plane lattice parameter is fixed to the measured value of a = 3.16 Å.

| Substrate                  | Monolayer |           | Bilayer |           |
|----------------------------|-----------|-----------|---------|-----------|
|                            | d_{S–Si}/d_{Si–O} | E_b | E_g(d)  | E_g(i) | d_{S–Si}/d_{Si–O} | E_b | E_g(d)  | E_g(i) |
| Free-standing               | —         | 1.686    | 1.832   | —       | 1.685    | 1.326   |
| H-passivated Si-polar       | 3.97      | 71       | 1.686   | 1.832   | 3.97     | 73      | 1.679   | 1.378   |
| H-passivated O-polar        | 3.08      | 165      | 1.685   | 1.811   | 3.14     | 88      | 1.675   | 1.380   |
| Si-polar with Si DBs        | 3.58      | 153      | 1.683   | 1.798   | 3.66     | 89      | 1.675   | 1.377   |
| O-polar with O DBs         | 2.70      | 276      | 1.633   | 1.542   | 2.71     | 219     | 1.360   | 1.180   |
| Bare Si-polar              | 3.27      | 146      | 1.683   | 1.652   | 3.30     | 95      | 1.672   | 1.344   |
energies are greatly enhanced, ranging from 71 to 276 meV, compared with the PBE results (table 1). In particular, in the presence of O-dangling bonds on the substrate, the separation of MoS$_2$ from SiO$_2$ is lowest, resulting in the largest increase of the binding energy. As the interatomic distance between MoS$_2$ and SiO$_2$ decreases, the valence band edge state at the $\Gamma$ point is affected more than those in the $K$ valleys. For the defect density of one Si-dangling bond per $3 \times 3$ cell, the valence band edge state at the $\Gamma$ point shifts upward by about 30 meV without altering the direct-gap nature of monolayer MoS$_2$ on the substrate. On the bare Si-polar surface, the upward shift (174 meV) of the valence band edge at the $\Gamma$ point is larger than the PBE result (103 meV). As a consequence, the indirect gap becomes comparable to the direct gap, with a difference of 30 meV. On the other hand, on the O-polar surface with the defect density of one O-dangling bond per $3 \times 3$ cell, a significant upward shift (268 meV) occurs for the valence band edge state at the $\Gamma$ point, making the indirect gap lower by about 90 meV than the direct gap. Moreover, due to the enhanced coupling at the interface, the spin splitting ($\Delta\Gamma$) at the $\Gamma$ point increases from 22 to 45 meV.

When bilayer MoS$_2$ is placed on different substrates, the separations of MoS$_2$ from the substrate are slightly larger than those for monolayer MoS$_2$ except for the H-passivated Si-polar case. Thus, the binding energies are reduced by 51−77 meV (table 2). On the H-passivated Si-polar surface, monolayer and bilayer MoS$_2$ have similar binding energies of about 70 meV due to the weak interaction between the MoS$_2$ and the SiO$_2$. On the other hand, the lattice parameter $c/2$ increases, ranging from 6.216 to 6.308 Å. Thus, the interlayer interaction between the top and bottom MoS$_2$ layers is slightly weakened. Although the PBE+D2 functional induces strong coupling of the MoS$_2$ with the substrate, the splitting of the valence band edge states at the $\Gamma$ point as a consequence of the interaction between the two layers is reduced. Thus, the indirect gaps are generally larger by 10−110 meV than the PBE results obtained for $c/2 = 6.147$ Å, whereas the direct gaps are less affected. On the O-polar surface with the defect density of one O-dangling bond per $3 \times 3$ cell, a greater charge transfer of 0.57 electron takes place. As dipole fields across the interface become stronger, the band separations between the two layers are enhanced to $\Delta E_{K}^{(v)} = 356$ meV and $\Delta E_{K}^{(c)} = 321$ meV, leading to stronger valley polarization.

4. Summary

We have investigated the electronic properties of monolayer and bilayer MoS$_2$ on various surfaces of SiO$_2$ through first-principles density functional calculations. We find that the indirect gap from the $\Gamma$ to $K$ (or $T$) point is sensitive to coupling with the substrate, exhibiting a tendency for the indirect gap to decrease, whereas the direct gap in the $K$ valleys is nearly unaffected. By including van der Waals forces, the coupling of the MoS$_2$ with the substrate becomes stronger, thus decreasing the indirect gap more effectively, especially for monolayer MoS$_2$. In bilayer MoS$_2$, the interaction between the MoS$_2$ layers induces the splitting of the valence band edge states at the $\Gamma$ point and thus affects the indirect gap. We find that MoS$_2$ interacts more strongly with O-dangling bonds than with Si-dangling bonds at the interface. In the presence of surface O-dangling bonds, $p$-type doping is induced in the MoS$_2$ by the charge transfer. In monolayer MoS$_2$, a transition can take place from direct-gap to indirect-gap semiconductor due to the significant upward shift of the valence band edge state at the $\Gamma$ point. On the other hand, in bilayer MoS$_2$, the dipole fields induced across the interface break the inversion symmetry, leading to valley polarization similar to that observed in free-standing...
monolayer MoS2. When Si-dangling bonds exist at the interface, their defect states lie deep in the band gap and do not affect the electronic structure of MoS2 because there is no charge transfer.

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