Band gap engineering of FeS$_2$ under biaxial strain: a first principles study

Pin Xiao,$^{ab}$ Xiao-Li Fan,$^{ab}$ Li-Min Liu$^{bc}$ and Woon-Ming Lau$^{bc}$

The promising photovoltaic activity of pyrite (FeS$_2$) is attributed to its excellent optical absorptivity and earth abundance, but its band gap, 0.95 eV, is slightly lower than the optimum value of 1.3 eV. Here we report the first investigation of strained FeS$_2$, whose band gap can be increased by $\sim$0.3 eV. The influence of uniaxial and biaxial strains on the atomic structure as well as the electronic and optical properties of bulk FeS$_2$ is systematically examined by the first principles calculations. We found that the biaxial strain can effectively increase the band gap with respect to uniaxial strain. Our results indicate that the band gap increases with increasing tensile strain to its maximum value at 6% strain, but under the increasing compressive strain, the band gap decreases almost linearly. Moreover, the low intensity states at the bottom of the conduction band disappear and a sharp increase in the intensity appears at the lower energy level under the tensile strain, which causes the red shift of the absorption edge and enhances the overall optical absorption. With the increase of the band gap and enhanced optical absorption, FeS$_2$ will make a better photovoltaic material.

1. Introduction

Pyrite (FeS$_2$) has received a lot of attention as a promising photovoltaic material because of its high abundance, nontoxicity, and strong light absorption ($\sim 10^5$ cm$^{-1}$ for $h\nu > 1.4$ eV).$^{1,2}$ The monocristalline FeS$_2$ photoelectrodes and solid-state Schottky solar cells of FeS$_2$ have shown large short-circuit current densities (30–42 mA cm$^{-2}$) and quantum efficiencies (up to 90%).$^{3,4}$ However, the energy conversion efficiency of pyrite solar cells is still limited by its low open-circuit voltage (OCV) which is less than 0.2 eV.$^3$ Various possible explanations have been proposed for the low OCV, including bulk defects,$^{5-8}$ intrinsic surface states,$^{8-11}$ the low intensity states at the bottom of the conduction band,$^{12}$ and the presence of competing phases (most notably marcasite).$^9$ Most importantly, according to Shockley–Queisser theory,$^{13}$ the optimum band gap of FeS$_2$ is 1.3 eV, which is defined as the band gap value of semiconductor. In this context, alloyed FeS$_2$ with either suitable anions (such as O and As) or cations (such as Ru, Os, and Zn) has been widely studied.$^6,14-19$ Based on the theoretical studies of Sun et al.$^6$ and Hu et al.$^{15}$ the band gap of FeS$_2$ can be increased by alloying an anion with oxygen. However, incorporating oxygen into FeS$_2$ is not easy to control because oxygen may react with the Fe component.$^2$ On the other hand, although density functional theory calculations predicted that Ru or Os alloying increases the band gap of FeS$_2$ by about $\sim$0.1 eV at 50% incorporation concentrations, the incorporation is very limited due to the low solubility of Ru and Os in FeS$_2$, and the elements Ru and Os are not naturally abundant.$^{16}$ Additionally, the earth abundant and low cost Zn alloying makes the band-gap of FeS$_2$ narrowed down significantly at 50% incorporation concentrations,$^{15,16}$ and the application of alloyed FeS$_2$ films with Sn or Mn is very limited due to their high cost although experiment has shown that their band gap has been increased.$^{17-19}$ Thus, an effective approach to increase the band gap of pyrite is still under discussion.

Besides introducing impurities, the band structure of the semiconductor could also be modified by the interatomic distances and relative atomic positions.$^{20-24}$ Hence, external pressure may alter the electronic structure of semiconductors. Previous theoretical studies have predicted that the band gap of bulk FeS$_2$ increases under negative pressure.$^{20,22}$
have demonstrated that the band gap of FeS$_2$ increases by 0.37 eV after moving the sulfur atoms by less than 1% of the lattice constant. They also concluded that the upshift of the conduction band minimum results from the decrease of sulfur–sulfur bonds, which decreases band dispersion at the conduction band minimum. But Muscat et al.\textsuperscript{22} have demonstrated that the increase of sulfur–sulfur bonds make the conduction band minimum move up and the band gap increases by $\sim 0.2$ eV at $-15$ GPa. The decrease of the band gap was also demonstrated by theoretical and experimental studies under positive pressure.\textsuperscript{20–22,25,26} Besides pressure, the strain may also be carried out using $7^2$ meshes, and $11^2$ $k$-meshes were adopted to reproduce the density of states (DOS). A cutoff 400 eV was selected for the plane wave basis set.

Biaxial strain was imposed in the (100) plane of FeS$_2$, the term “in-plane” refers to the (100) plane, and “out-of-plane” means the direction perpendicular to the (100) plane, which is the [001] direction. To model FeS$_2$ under certain biaxial strain, the in-plane lattice constant $a$ was fixed at a specific value $a_0$, and the out-of-plane lattice constant $a$ was relaxed during the structural optimization. The in-plane and out-of-plane strains are related to the lattice constant through

$$\eta_\parallel = \eta_{010} = \eta_{001} = (a_0 - a)/a \quad (1)$$

and

$$\eta_\perp = (x - x_0)/a \quad (2)$$

respectively, $\eta_{010}$ and $\eta_{001}$ represent the strain along the [010] and [001] directions in the (100) plane. $a_0$ is the out-of-plane lattice constant after relaxation under the biaxial strain. The uniaxial strain is imposed along the [001] direction fixing the lattice constant along the [001] direction and relaxing those along the other two directions, and the lattice constants are set via formula (1). In the present study, $\eta_\parallel < 0$ stands for the compressive strain, and $\eta_\parallel > 0$ represents the tensile strain.

3. Results and discussion

3.1 Atomic structure of FeS$_2$

As sketched in Fig. 1, pyrite FeS$_2$ adopts NaCl-like cubic structure where Fe ions are located at the face-centered cubic lattice, and S ions are arranged in dimers along the $<100>$ direction occupying the positions of Cl anions. All the Fe ions are octahedrally coordinated by six S ions at equal distances, and each S ion has three Fe neighbors and one S neighbor. The pyrite structure can be specified by two parameters, lattice constant $a$ and Wyckoff parameter $u$, which describe the positions of S atoms. These positions are $\pm(u, u, u)$, $\pm(1/2 + u, u, 1/2 - u)$, $\pm(1/2 - u, 1/2 + u, u)$. Our calculated lattice parameters for strain-free FeS$_2$ are $a = 5.426$ Å and $u = 0.385$, agreeing well with the experimental results of $a = 5.418$ Å and $u = 0.385$,\textsuperscript{20} and

![Fig. 1](https://via.placeholder.com/150)

Fig. 1 The unit cell of FeS$_2$. Violet and yellow spheres represent Fe and S atoms, respectively. $a$ and $u$ are the two parameters denoting the lattice constant and the Wyckoff parameter which describes the position of S atoms.

2. Computational methods

All the calculations in the present study were performed by adopting the spin-polarized density functional theory (DFT), as implemented in the Vienna \textit{ab initio} simulation package (VASP) code.\textsuperscript{32} The ion–electron and electron–electron interactions were calculated by the projector augmented plane-wave (PAW) method,\textsuperscript{33,34} and a plane-wave basis set. The generalized gradient approximation (GGA) of the Perdew–Burke–Ernzerhof formula\textsuperscript{15} plus the Hubbard $U$ approach\textsuperscript{36} (PBE + $U$) was used to calculate the electronic exchange–correlation potential. We used an effective $U$ of 2 eV, which has been shown to give a good description of the bulk properties of FeS$_2$.\textsuperscript{3} Based on the Monkhorst–Pack scheme,\textsuperscript{37} Brillouin zone integration was carried out using $7 \times 7 \times 7$ $k$-meshes, and $11 \times 11 \times 11$ $k$-meshes were used to calculate the density of states (DOS). A cutoff 400 eV was selected for the plane wave basis set. The convergence criterion of energy was set at $1 \times 10^{-5}$ eV. All the atoms were fully relaxed until the force on each atom was smaller than 0.01 eV Å$^{-1}$. The charge populations were calculated using Bader’s atom in molecule (AIM) method based on charge density topological analysis.\textsuperscript{38} The charge density in real space is reconstructed appropriately by the PAW method;\textsuperscript{39} an intensive grid of $72 \times 72 \times 72$ was adopted to reproduce the total core charge accurately.

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the theoretical results of $a = 5.422$ Å and $\theta = 0.385^\circ$. Our calculation shows that FeS$_2$ is an indirect band gap semiconductor with a band gap of 0.85 eV; details about the electronic structure will be discussed in the following sections.

We firstly studied the atomic structure of FeS$_2$ under external biaxial and uniaxial strains ranging from $-10\%$ to $12\%$. The structural parameters are summarized in Fig. 2. As shown in Fig. 2(a), the in-plane lattice constants decrease with the increase of compressive strain. Meanwhile, the out-of-plane lattice constants increase slightly. Consequently, the crystal volume decreases and the bond distances of Fe–S along the $x$ axis (denoted as Fe–S($\parallel$)) and S–S also decrease slightly as shown in Fig. 2(b) and (c). A previous study also reported the increase of the S–S bond distance under negative pressure.$^{21,22}$ Additionally, it is shown clearly in Fig. 2(c) that the Fe–S bonds along the $y$ and $z$ axes (denoted as Fe–S($\perp$)) change much faster than Fe–S($\parallel$) and S–S bonds. Under the increasing tensile strain, the out-of-plane lattice constant decreases slightly as shown in Fig. 2(a). But the crystal volume increases gradually due to the increase of the in-plane lattice constant. The Fe–S($\parallel$) bond length increases at the same time. We also note that the lengths of Fe–S($\perp$) and S–S bonds increase slightly and then decrease under the increasing tensile strain, as shown in Fig. 2(c). Moreover, all the above mentioned structural parameters change more obviously under biaxial strain than under uniaxial strain.

### 3.2 Electronic band structure of FeS$_2$ under strain

The above results on the atomic structure of FeS$_2$ revealed that the S–S bond distance increases under increasing tensile strain, which also happened under the negative pressure and induced the increase of the band gap.$^{20}$ Thus, we first characterized the band gap of FeS$_2$ subjected to tensile strain ranging from 0% to 12%. As shown in Fig. 3, there is a knee point positioned at around 6% biaxial and 10% uniaxial tensile strains. At this point, the band gaps reach the maximum values of 1.15 eV and 1.13 eV, respectively. Similar to the phenomena indicated in Fig. 2, biaxial strain changes the band gap more evidently relative to uniaxial strain. Before the knee point, band gap increases, and then decreases after the knee point. Previous experimental and theoretical studies$^{20–22,26}$ demonstrated that FeS$_2$ would turn to metal under 80 GPa positive pressure. We then investigated the electronic structure of FeS$_2$ subjected to compressive strains. Under the unaxial compressive strain from 0% to 10% as shown in Fig. 3, the band gap decreases gradually from 0.85 eV to 0.67 eV. It substantially decreases to 0.37 eV when FeS$_2$ is subjected to uniaxial strain. Therefore, transition from the semiconductor to the metal is expected of FeS$_2$ under certain high uniaxial compressive strain.

For comparison, we recalculated the band gap of FeS$_2$ under biaxial strain using the popular PBE functional. As shown in Fig. 3, the band gaps calculated by the PBE functional are

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**Fig. 2** Calculated structural parameters of FeS$_2$ under biaxial and uniaxial strains. (a) Normalized out-of-plane lattice constant $a/a$, (b) normalized volume $V/V_0$, and (c) bond lengths of Fe–S and S–S. The bonds along the $y$ and $z$ axes (approximately parallel to it) are denoted as ($\parallel$), and the bonds along the $x$ axis (approximately perpendicular to the yz plane) are denoted as ($\perp$).

**Fig. 3** Calculated band gap of FeS$_2$ under uniaxial and biaxial strains by PBE and PBE + $U$ functionals.
significantly smaller than those computed by PBE + U. The band gap calculated by PBE + U reach its maximum under 6% tensile strain, while the PBE counterpart reaches its maximum under 11% tensile strain. Note that the PBE method usually underestimates the band gap, but the Hubbard U correction gives more accurate results. Moreover, the nonlinear behavior predicted by the two methods cannot be explained by the deformation potential theory, in which the band gap proportionally varies with the tensile strain. The nonlinear change of the band gap under tension actually results from the shear strain component $\eta_{yz}=\frac{\eta_+ - \eta_0}{2}$. According to the previous studies on the strained Si and Ge shear strain splits the bottom conduction bands and changes their local positions, leading to both degeneracy lifting and band warping. To test the dynamical stability of strained FeS$_2$, we computed the phonon spectrum of FeS$_2$ under 6% tensile strain. As shown in Fig. 5, no imaginary phonon mode is presented, which means FeS$_2$ can bear 6% strain in realistic experiments.

We further studied the band structure of FeS$_2$ under the applied strain to gain insight into the band gap change. As we have mentioned earlier, uniaxial strain changes the atomic structure and the band gap in a similar way as the counterpart of biaxial strain, only less effectively. Thus, Fig. 4 only shows the band structures under biaxial strains of $-6\%$, 0%, 6% and 12%. As shown in Fig. 4(b) for the strain-free FeS$_2$, the valence band maximum (VBM) is near the $X$-point and the conduction band minimum (CBM) locates at the $G$-point. The corresponding indirect band gap is 0.85 eV, which is close to the experimental value of 0.95 eV. The bandgap calculated by methods like DFT is referred to as a quasi-particle or a fundamental bandgap, while that obtained by optical measurements include electron–hole interactions and is referred to as the optical gap. The two values may differ substantially; the optical gap may be larger if the transition associated is indirect. The present calculated bandgap is little smaller than the experimental value, but agrees well with previous calculation results of 0.86 eV.

Furthermore, we found that FeS$_2$ is nonmagnetic at $U$ from 0 to 4 eV, agreeing with previous studies. We also found that the strained system at compressive and tensile strains from 0% to 12% is nonmagnetic. When FeS$_2$ is imposed under 6% biaxial compressive strain, the CBM moves down as shown in Fig. 4(a). Meanwhile, less charge transfers from Fe to S based on the Bader’s charge population analysis listed in Table 1, which makes the VBM move up. Consequently, the band gap decreases from 0.85 eV to 0.62 eV. Fig. 4(c) shows the band structure of FeS$_2$ under 6% tensile strain, which indicates that the CBM at the $\Gamma$-point moves up. But, when the imposed tensile strain is larger than 6%, the CBM starts to move down and its location changes from the $\Gamma$-point to the $R$-point at 12% tension. This change results from the shear strains stated above. At the same time, more charge transfers from Fe to S as summarized in Table 1, which makes the VBM to move down. The CBM moves down farther than the VBM. Consequently, the band gap increases to its maximum of 1.15 eV at 6% biaxial tension and then decreases.

### 3.3 Optical absorption spectra of strained FeS$_2$

To examine the optical absorption spectra of strained FeS$_2$, the absorption coefficient of FeS$_2$ under biaxial strain was further calculated. The calculated results at $-6\%$, 0%, 6% and 12% strains are presented in Fig. 6. The absorption spectra of the strain-free FeS$_2$ start at about 0.6 eV and the first peak locates at 2.7 eV, which agrees well with the corresponding experimental observations of 0.7 eV and 2.5 eV. Fig. 6 obviously shows that, along both $x$ and $y$ axes, the absorption edge blue shifts upon increasing the compressive strain imposed on the $yz$ plane, and

![Fig. 4](image-url) Band structures of FeS$_2$ under biaxial strains of $-6\%$, 0%, 6% and 12%. The Fermi level is set to zero.

![Fig. 5](image-url) Phonon spectrum of FeS$_2$ under 6% tensile strain.

**Table 1** Averaged charge population ($\rho$) on Fe and Fermi level $E_F$ under biaxial strains of $-6\%$, 0%, 6% and 12%.

<table>
<thead>
<tr>
<th></th>
<th>$-6%$</th>
<th>0%</th>
<th>6%</th>
<th>12%</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho$</td>
<td>0.543</td>
<td>0.617</td>
<td>0.682</td>
<td>0.723</td>
</tr>
<tr>
<td>$E_F$</td>
<td>8.980</td>
<td>7.417</td>
<td>6.123</td>
<td>5.093</td>
</tr>
</tbody>
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red shifts under the increasing tensile strain. This kind of change is not expected actually. As we have mentioned, under compressive strain, the band gap of FeS₂ decreases which normally induces red shift. On the other hand, the blue shift is usually associated with the increasing band gap, which is supposed to occur under 6% tensile strain. The above abnormal phenomena are not new to FeS₂. The associated blue shift and the decrease in the band gap were also reported previously by Schlegel and Wachter based on their personal communication with Batlogg. A theoretical study²⁰,²² also predicted the blue shift associated with the increase of the band gap under positive pressure.

Since the optical adsorption spectra of strained FeS₂ cannot be explained by the band gap, we studied the density of states (DOS) under biaxial strains of -6%, 0%, 6% and 12% as shown in Fig. 7. Fig. 6(a) shows the DOS of strain-free FeS₂. It indicates that the valence band close to the Fermi Level is predominantly composed of Fe-3d states and some S-3p states, and the conduction band near the Fermi level is mainly constituted by S-3p states. Thus the states positioned at the CBM are directly related to the S-S bond. Additionally, the intensity of S-3p states is low in the conduction band below 1.35 eV, and it starts to increase sharply at 1.35 eV.

The calculation results shown in Fig. 7(b) indicate that, under 6% compressive strain, the S-3p low intensity states at the bottom of the conduction band extend and the onset of sharp increase in the intensity moves further away from the Fermi level relative to that of strain-free FeS₂. In the case of tensile strain, the low intensity states at the bottom of the conduction band disappear and the sharp increase in the intensity is observed much closer to the Fermi Level. Based on the report of Lazic´ et al.,¹² the low intensity states extend the length of optical transitions in the pyrite band structure, thus the onset of the absorption edge is not related to the position of the CBM, but is actually decided by the position where the conduction band states start to increase sharply. In this context, the blue and red shifts of the adsorption edge shown in Fig. 6 are actually associated with the onset of the sharp increase in the

![Fig. 6](image_url)

**Fig. 6** Absorption coefficient of FeS₂ along different directions (x and y axes) under biaxial strains of η₁ = -6%, 0%, 6% and 12%.

![Fig. 7](image_url)

**Fig. 7** (a) Total and projected density of states of FeS₂. (b) Projected density of states of FeS₂ under biaxial strains of η₁ = -6%, 0%, 6% and 12%. The Fermi level is set to zero. The inset is a magnified view of density of states at the conduction band minimum (CBM).
When FeS$_2$ is subjected to tensile strain, the low intensity in the blue shift of the absorption edge. More importantly, an increase moves to the high energy level, which results from the conduction band change from S-3p to Fe-3d states. Additionally, the low intensity states at the conduction band extend under the increasing compressive strain and the onset of sharp increase moves to the high energy level, which means that the photon absorption of the strained FeS$_2$ is enhanced. Due to the electronic structure and the band gap of FeS$_2$, tensile strain can effectively improve the electronic and optical properties of FeS$_2$ for photovoltaic applications.

**4. Conclusions**

In summary, the band gap of FeS$_2$ increases with increasing the biaxial tensile strain to its maximum at 6% strain with an increase of 0.30 eV. When FeS$_2$ is subjected to increasing compressive strain, the band gap decreases almost linearly. Uniaxial strain changes the atomic structure and the band gap in a similar way as biaxial strain does, only less effectively.

Density of states shown in Fig. 7 indicates that the states at the bottom of the conduction band change from S-3p to Fe-3d when the strain is larger than 6%, which further explains the transfer of CBM from the $\Gamma$-point to the $R$-point under 12% strain. This change can be observed more clearly from the distribution of the LUMOs shown in Fig. 8. In Fig. 8(a)–(c), LUMOs of FeS$_2$ are contributed by the S-3p states. Whereas LUMOs of FeS$_2$ under 12% tensile strain shown in Fig. 8(d) are comprised of Fe-3d states.

**References**