Effects of surface sulfur structure on the band gap of Pyrite: DFT Calculations

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Clean Pyrite Surfaces

Fe_{14}S_{24} (S_{-1})
Fe_{14}S_{28} (S_{0})
Fe_{14}S_{30} (S_{0.5})
Fe_{14}S_{32} (S_{1})

- Surface sulfur density
- Surface sulfur structure
- S defects
- Band gap of Pyrite surface

Band gap
Spin up/down
~0.54/1.01 eV
~0.75/0.92 eV
~0.66/0.87 eV
Metallic
DFT calculation details

- DFT calculations with the plane-wave-based Vienna Ab initio Simulation Package (VASP)
- Potential: PAW-GGA(PBE)
- Energy cutoff: 300 eV
- Kpoints: 8×8×1 MK
- Atomic model: a seven-layer slab with a vacuum of ~15 Å thick
Fe56S114
($S_{0.125}$)

$E_{\text{tot}} = -897.719 \text{ eV}$
The image contains a graph showing the relationship between sulfur chemical potential and surface energy, with the band gap labeled as approximately 0.54/1.01 eV. Additionally, there are density of states (DOS) plots for Fe56S114, Fe(S), and Fe(B) showing metallic characteristics and band gaps of approximately 0.75/0.92 eV and 0.66/0.87 eV. The graph also includes the density of states for S(S) and S(B) with a band gap of ~0.54/1.01 eV.
\[ E_{\text{tot}} = -906.061 \text{ eV} \]

(1)

\[ E_{\text{tot}} = -904.427 \text{ eV} \]

(2)
Sulfur chemical potential (eV)

Surface energy (J/m²)

Band gap

~0.54/1.01 eV

~0.75/0.92 eV

(1) ~0.67/0.88 eV (2) ~0.60/0.79 eV

~0.66/0.87 eV

Metallic

Fe56S116

Fe56S116 (2)
Fe56S126
(S0.875)

$E_{\text{tot}} = -947.471 \text{ eV}$
SO$_2$  

**Surface energy (J/m$^2$)**

- $S_{-1}$
- $S_0$
- $S_{0.5}$
- $S_1$

**S atom**

- $S_8$

**Band gap**

\[ \sim 0.54/1.01 \text{ eV} \]

\[ \sim 0.75/0.92 \text{ eV} \]

\[ \sim 0.66/0.87 \text{ eV} \]

\[ \sim 0.27/0.36 \text{ eV} \]

**Metallic**

**Fe56S126**

**Density of States**

- Fe(S)
- Fe(B)

**Energy (eV)**

- $\Gamma$
- $X$
- $M$
- $\Gamma$
$E_{\text{tot}} = -237.560 \text{ eV}$

$E_{\text{tot}} = -239.172 \text{ eV}$

Surface sulfur structure
The band gap is approximately 0.54/1.01 eV, 0.75/0.92 eV, and 0.66/0.87 eV for different sulfur chemical potentials. The system is metallic.
The image shows a graph plotting the surface energy (J/m²) against the sulfur chemical potential (eV). The graph includes various curves representing different sulfur concentrations.

Key points:
- The x-axis represents the sulfur chemical potential (eV).
- The y-axis represents the surface energy (J/m²).
- The graph includes curves for different sulfur concentrations:
  - $S_{-1}$: ~0.54/1.01 eV
  - $S_0$: ~0.75/0.92 eV
  - $S_{0.5}$: ~0.66/0.87 eV
  - $S_{0.125}$: ~0.67/0.88 eV
  - $S_{0.25}$: ~0.67/0.87 eV
  - $S_{0.875}$: ~0.27/0.36 eV
  - $S_1$: metallic

The graph also indicates the band gap for majority/minority at $S_{-1}$: ~0.54/1.01 eV.
single sulfur vacancy

\[ E_{\text{tot}} = -949.771 \text{ eV} \]

the effect of vacancy and impurities on the band gap of Pyrite surface;

dynamic features of vacancy filling process;

the control of Pyrite defects;

\[ E_{\text{tot}} = -956.688 \text{ eV} \]

vs.

\[ E_{\text{tot}} = -956.688 \text{ eV} \]
Summary

- Using density functional calculations, we studied the band gap and electronic properties of S-rich surfaces as a dependence of surface Sulfur density.

- The increase of S on pyrite surface reduce the band gap; the surface shows the metallic feature when it is covered by the S network.

- The formation of S-S dimers on the S-rich Pyrite surfaces are energetically preferred; S-\(p_x,p_y\) states appear near the Fermi level.

- Various surface sulfur structures without/with defects will be extensively studied by DFT calculations through close collaborations with experiments.