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Lattice structures and electronic properties of MO/$MoSe_2$ interface from first-principles calculations

Yu Zhang [a], Fu-Ling Tang [a,*], Hong-Tao Xue [a], Wen-Jiang Lu [a], Jiang-Fei Liu [a], Min Huang [b]

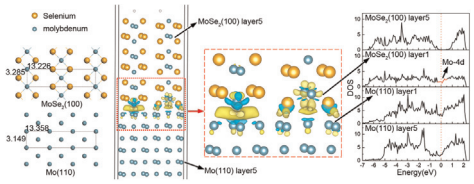
[a] Department of Materials Science and Engineering, Lanzhou University of Technology, Lanzhou 730050, China
[b] State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan 430071, China

HIGHLIGHTS

- The degree of lattice mismatch of Mo (110) / $MoSe_2$ (100) is about 4.2%.
- The interface bonding energy is -1.2 J/m^2, the interface has better stability.
- The atoms near interface have strong charge change.
- The $MoSe_2$ layer on interface has some interface states near the Fermi level.
- A lot of atomic orbital hybridizations appeared on the interface.

GRAPHICAL ABSTRACT

The atomic structure, bonding energy and electronic properties of the perfect Mo(110)/$MoSe_2$(100) interface with a lattice mismatch less than 4.2% are studied using the first principles calculation.



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ABSTRACT

Using first-principles plane-wave calculations within density functional theory, we theoretically studied the atomic structure, bonding energy and electronic properties of the perfect Mo (110)/$MoSe_2$ (100) interface with a lattice mismatch less than 4.2%. Compared with the perfect structure, the interface is somewhat relaxed, and its atomic positions and bond lengths change slightly. The calculated interface bonding energy is about -1.2 J/m^2, indicating that this interface is very stable. The $MoSe_2$ layer on the interface has some interface states near the Fermi level, the interface states are mainly caused by Mo 4d orbitals, while the Se atom almost have no contribution. On the interface, *Mo-5s* and Se-4p orbitals hybridize at about -6.5 to -5.0 eV, and Mo-4d and Se-4p orbitals hybridize at about -5.0 to -1.0 eV. These hybridizations greatly improve the bonding ability of Mo and Se atom in the interface. By Bader charge analysis, we find electron redistribution near the interface which promotes the bonding of the Mo and $MoSe_2$ layer.

1. Introduction

Cu(In,Ga)Se (CIGS) solar cells are the fastest growing thin film solar cells in recent years, have many advantages, such as radiation hardness, long term stability, high efficiency and low cost [1]. The typical structure of the solar cells is Glass/Mo/CIGS/CdS/i:ZnO/ZnO:Al [2,3]. In the laboratory, the photoelectric conversion efficiencies of CIGS solar cells have reached beyond 20% [4].

Mo is widely used as the back contact material, especially in the substrate configuration of CIGS thin film solar cells. Mo back contact layer is contacted with the CIGS absorption layer in CIGS thin film solar cells. Some studies [5–9] found Se diffusion between Mo back contact and CIGS absorption layer during CIGS deposition. During the Se diffusion, part of Mo became $MoSe_2$ compound through selenation, forming an intermediate $MoSe_2$ layer between Mo and CIGS layer. Shafarman et al. [10] studied the

* Corresponding author.
E-mail address: tfl03@mails.tsinghua.edu.cn (F.-L. Tang).

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interface of Mo and CIGS. They found the contact between Mo and CIGS to be ohmic, and mainly because of the formation of an intermediate $MoSe_2$ layer during CIGS physical vapor deposition [11,12]. Besides, some literatures [13,14] also showed that the $MoSe_2$ layer was formed between Mo and CIGS layer during CIGS deposition, owing to Se diffusion from CIGS layer. The formation of a $MoSe_2$ layer is very important to facilitate a quasi ohmic electrical contact across the Mo–CIGS interface in CIGS thin film solar cells. It is helpful to improve the efficiency of the CIGS solar cells. So, study of Mo and $MoSe_2$ films, especially the properties of their interface, is important to further understand CIGS solar cells and to guide the experiments.

On the experiment side, Abou-Ras et al. [13] studied the characteristics of Mo layer, CIGS layer and the interface between it for CIGS thin film solar cells by means of Rutherford backscattering spectrometry (RBS), energy-dispersive X-ray spectroscopy (EDX), electron diffraction (ED) and high-resolution transmission electron microscopy (HR-TEM). They found a homogeneous Mo–Se compound layer on the top of Mo layer, and measured the thickness of the Mo–Se compound layer. By means of EDX, their experimental results showed that the Se signal was twice as large as the Mo signal at the Mo–Se compound layer. They concluded that the Mo–Se compound formed by Se diffusion as $MoSe_2$. Mahatha et al. [15] using Angle-resolved photoemission spectroscopy (ARPES) to study electronic structure of molybdenite $MoSe_2$. Using the X-ray diffraction (XRD), some studies [3,16] found that the Mo layer have a preferential growth orientation in [110], Abou-Ras et al. [13] found that the $MoSe_2$ layer have two prominent peaks, $10\bar{1}0$ and $11\bar{2}0$. Matheis et al. [14] found that the solar cell with a $MoSe_2$ intermediate layer had a better performance than that without the $MoSe_2$ intermediate layer.

On the theoretical research side, Li et al. [17] studied the electronic structure and optical properties of Mo by using the first principles calculations. They calculated and analyzed the energy band of Mo. Tongay et al. [18] used the first principles density functional theory (DFT) to calculated and analyzed the band structures of single layer, 9 layers and bulk $MoSe_2$. Mahatha et al. [15] studied the valence band structure of $MoSe_2$ by using ab initio band structure calculations. Hong et al. [19] studied bond characteristics, interfacial energetic and electronic structure of $Mo/MoSi_2$ (001) interface by the first principles calculation, and emphatically analyzed the interfacial electron redistribution and interfacial density of states.

Although plenty research had studied Mo, $MoSe_2$ and their surface, but the knowledge to understand the lattice structure, electronic properties and the interface states of $Mo/MoSe_2$ interface is still rare. So, in this paper, we used the first-principles calculation to study the local lattice structure and electronic properties of $Mo/MoSe_2$ interface, especially on the interface states. In order to better analyze the lattice structure and electronic properties of interface, we firstly study the bulk Mo and $MoSe_2$, Mo and $MoSe_2$ surface in a certain direction. We also compared our results with previous experimental and calculated results.

2. Methodology

The Vienna *ab initio* simulation package (VASP) [20–23], based on the first principles density functional theory, is utilized, which uses the projector augmented wave (PAW) [24,25] method. The generalized gradient approximations (GGA) functional of Perdew-Burke-Ernzerhof (PBE) [26] was adopted to describe the exchange-correlation energy. In this pseudopotential approach, core electrons that do not participate in the bonding character of the material are frozen and only valence electrons are taken into account. For the pseudopotential that we used, the electronic configurations are [Kr] $4d^5 5s^1$ and [Ar] $3d^{10} 4s^2 4p^4$ for molybdenum and selenium, respectively. Here, Γ-centered *k*-point meshes of $5\times5\times5$, $5\times5\times2$, $8\times2\times1$, $7\times2\times1$ and $7\times3\times1$ were used for calculations for bulk Mo, bulk $MoSe_2$, Mo surface, $MoSe_2$ surface and $Mo/MoSe_2$ interface, respectively. The plane wave energy cutoff of 370 eV and the conjugate gradient (CG) method [27] was applied for the atomic structure optimization. The tetrahedron method with Blöchl corrections [28] was used for the total energy calculations in bulk materials and for the calculation of the band structure and DOS in all models.

3. Results and discussion

3.1. Properties of bulk Mo and $MoSe_2$

Mo is an important contact material of CIGS thin film solar cells. Mo crystal has the A2 type body-centered cubic structure, which has two Mo atoms in each unit cell, with the space groups Oh9 (1m3m). Our calculated lattice parameter *a* of Mo is 3.149 Å. The experimental value *a* is 3.147 Å by X-ray diffraction (XRD) [29]. Other calculated values of *a* are 3.12 Å [17] and 3.152 Å [30]. The calculated band structure of bulk Mo is shown in Fig. 1(a). We can see that Mo has not a band gap, indicating that Mo is a metal with electrical conductivity. Our calculated band structure is very similar with the experimental result [17]. This suggests that our calculation is reliable. Fig. 1(b) is the density of states (DOS) of bulk Mo. Through analysis of partial density of states (PDOS), we can find that different Mo-4d orbital electron contributes to the DOS near Fermi level.

$MoSe_2$ has molybdenite structure with the space groups P63/mmc. Fig. 2(a) shows $MoSe_2$ lattice structure. The optimized lattice parameters *are* $a=b=3.285$ Å, $c=13.226$ Å. Compared with experimental data [13,15] ($a=b=3.28$ Å, $c=12.9$ Å and $a=b=3.299$ Å, $c=12.938$ Å), our calculated lattice parameter *c* is slightly larger than the experimental value, but lattice parameters *a* and *b* only have a small error in the range of 10^{-2} Å. Our results is very similar with other calculated and experimental results [15], proving a good accuracy of our calculation. In Fig. 2(b), we calculated the band structure of the bulk $MoSe_2$. We found that the direct band gap of $MoSe_2$ is about 1.4 eV, showing that $MoSe_2$ is a semiconductor material. The experimental band gap of $MoSe_2$ is 1.48 eV [31]. Other calculated results are 1.41 and 1.34 eV [16,18]. In Fig. 2(c), we calculated DOS of bulk $MoSe_2$. Through analysis of

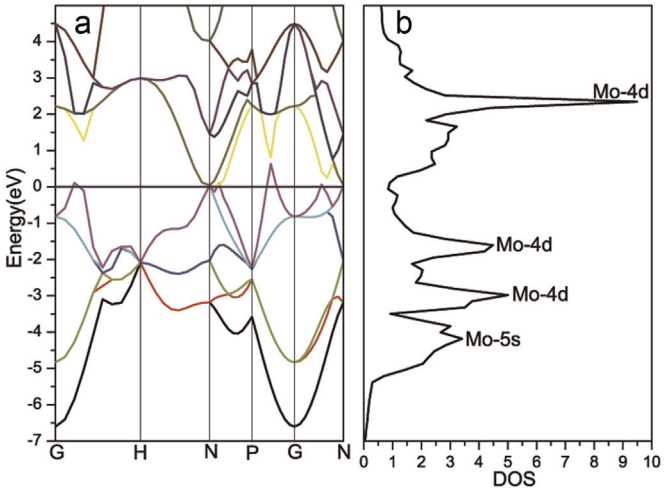

Fig. 1. The band structure and density of states of bulk Mo.