First-principles study on domain boundary of MoS2: Origin of band bending

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Abstract

Using first-principles calculations based on density functional theory, electronic structure of domain boundary of MoS_2 in which same polar edges are faced each other are investigated theoretically. We also find that the up-shift of energy bands at the domain boundaries are caused by charge accumulation. For such change in the energy bands, the defect levels at the domain boundaries play a decisive role.

1. Introduction

Atomically thin transition metal di-chalcogenides (TMDs) MX₂ (M=Mo, W, and X=S, Se, Te) have been attracted much interest owing to those electronic and optical properties [1,2]. Unlike graphene which does not have a band gap, TMDs are semiconducting whose band gaps depend on the combination of M and X atoms. Since the TMD base FET shows high on/off ratio with relatively high mobility, TMDs are good candidate for future electronic devices.

For the preparation of TMDs, CVD is widely used [3-5]. The CVD grown TMDs are polycrystalline because nucleation takes place on the substrate everywhere. Therefore, understanding of domain boundary is an important issue for application point of view of TMDs. According to scanning tunneling microscopy/spectroscopy (STM/STS) measurement, up-shifts of energy bands of TMD near the domain boundaries were observed [6-8]. The purpose of this paper is to investigate the origin of change in the energy bands near the domain boundaries of TMDs theoretically.

2. Computational details

First-principles calculations based on density functional gradient approximation is used for the exchange-correlation functional. Ultra-soft pseudo-potential is used for Mo and norm conserving one is used for S. The cutoff energies of plane wave basis sets and charge densities are 25 Ry and 225 Ry, respectively.

Because of ionicity of Mo and S, we consider a model in which two boundaries with polar edge are faced each other in the unit cell. To construct the interface model, zigzag edge (ZZ) MoS₂ nanoribbons and Klein edge (KL) MoS₂ nanoribbons are arranged periodically and alternately. In this model, the S-terminated zigzag edge and Mo-terminated Klein edge are faced vice versa (ZZ|KL). Then, there are four membered rings (4MR) and eight membered rings (8MR) in the interface as shown in Fig. 1. By changing the number of zigzag line in single side of domain, we can Table 1. Obtained domain boundary energy E_{DB} for the ZZ | KL interface. The interface structures can be found in Fig. 1.

Model	Interface structures	$E_{\rm DB}~({\rm eV})$
1	Mo: 8MR, S: 4MR	3.261
2	Mo: 4MR, S: 8MR	5.338
3	Mo: 4MR, S: 4MR	4.157
4	Mo: 8MR, S: 8MR	4.470



Figure 1. (a) Atomic structures of Mo-Mo interface. The purple and yellow balls represent Mo and S atoms, respectively. The characteristic structures are highlighted by colors. (b) Atomic structure of S-S interfaces.

change the combination of the interface structures as summarized in Tables 1. Note that these interfaces consist of purely Mo-S bonds. In our calculations, the length of each domain is more than 40 Å. In the unit cell, there are 96 atoms for the model 1 and 2, and 99 atoms for the model 3 and 4.

3. Results and discussion

Calculated domain boundary energies for the interface models are summarized in Table 1. In this paper, we define the domain boundary energy, E_{DB} , as the relative total en-



Figure 2. Color map plots of LDOS near the Fermi level for the ZZ | KL interfaces of model 1 (a), 2 (b), 3(c) and 4(d). The energies are measured by the Fermi level. Corresponding atomic models are presented top side of figures. The region indicated by white color is bang gap of MoS_2 .

ergy measured from that of the pristine MoS₂. The interface model 1 (Mo: 8MR and S: 4MR) is stable among them. We also consider the interface in which S terminated zigzag edges are faces each other (ZZ|ZZ), where homo-elemental bonds are inevitable for this model. We find that E_{DB} for the ZZ|ZZ models are 5.6~6.2 eV and higher than the ZZ|KL models. This implies that the homo-elemental bonds are not energetically preferable in this system.

Figure 2 shows color map plots of the local density states of the ZZ|KL models. The defect levels can be seen around the domain boundaries. The energy bands around the 4MR at the S-S interface shift downward and adjacent those at the Mo-Mo interface shift upward. It should be noted that electrons are accumulated near the Mo-Mo interface for the models 1 and 3, i.e., the models containing the 4MR at S edge boundaries. For these models, the defect levels just above the valence band maximum at the Mo edge boundaries are occupied, while the defect levels at the S edge boundaries are not occupied. These results indicate that charge accumulation at the defect levels just above the valence band maximum around the domain boundaries induce the band bending. We obtain similar energy band change for the ZZ|ZZ model. Moreover, the band structures can be tuned dramatically by doping of electrons or holes. Since the energy bands are continuously change at the regularly connected interfaces between different TMDs such as MoS₂ and WS₂ [10-13], the defect levels at the domain boundaries are necessary for the appearance of the up-shift of energy bands.

4. Summary

We have investigated the energetics and electronic properties of the domain boundaries of MoS₂ using first-principles calculations. We have found that the up-shift of energy bands widely observed in STM/STS measurements is caused by the charge accumulation at the defect levels of domain boundaries. The defect levels just above the valence band maximum is necessary for the up-shift of the energy bands of TMDs.

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