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Theoretical Study of Supporting Effect on Vacancies in MoS_2

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Abstract

Supporting effect on the physical properties of charged vacancies are investigated in single-layer molybdenum disulfide. Our analysis shows that both of S and Mo vacancies become less stable by the supporting effect. This means that the vacancies in supported MoS_2 are formed more difficultly than those in freestanding MoS_2. It is suggested that the interaction with substrate suppresses the degradation of devices.

1. Introduction

Two-dimensional materials attract many researchers in recent days. Single-layer molybdenum disulfide (MoS_2) is one of such a two-dimensional material. It is semiconductor with a direct bandgap of 1.8 eV at K point, and is a candidate of future material for electronic and photoelectric devices [1-3]. For these industrial applications, it is necessary to form MoS_2 as defect-free crystal with wafer-scale homogeneity. Chemical vapor deposition (CVD) is one of the promising approach, but a transmission electron microscope (TEM) experiment has reported that the crystal formed by CVD have various vacancies which cause degradation of electronic and optical properties [4]. In our previous study, we studied on the charging effect on such vacancies in freestanding single-layer MoS_2, and theoretically revealed that vacancies are favorably formed when negatively charged [5]. We also compared the results with vacancies in single-layer h-boron nitride (h-BN), and discussed physics behind the similarity and difference between them [6,7].

In this contribution, we focus on vacancies in supported single-layer MoS_2. We consider single-layer MoS_2 and $MoSe_2$ as the supporting substrate. We study the charging effect theoretically, and examine the supporting effect on physical properties of vacancies.

2. Calculation method

We perform the electronic structure calculation using the first principles calculation code, VASP [8]. We employ the density functional of generalized gradient approximation (GGA) [9] and the projector augumented wave (PAW) method. The energy cut off for the plane-wave expansion is 400 eV (about 30 Ry). A 6x6 supercell is adopted for the unit cell (Fig. 1). The unit cell includes 216 atoms for the defect-free pristine case. We use the repeated slab geometry with thick enough vacuum region and 6x6x2 k-points.

The vacancies shown in Fig. 2 are examined in this contribution. The formation energies E_f of various vacancies as the function of the Fermi level energy μ_e are calculated as

$$E_f = E_t - E_p + n_S\mu_S + n_{Mo}\mu_{Mo} + q\,(\mu_e + \varepsilon_v)\,,$$

where n_S and n_{Mo} are the numbers of removed S and Mo atoms in supercell, respectively. E_t and E_p are the total energies of vacancy system and pristine system. ε_v is the energy of valence band maximum. q is the charge state of vacancy. μ_S and μ_{Mo} are the chemical potentials of S and Mo. The upper limits of μ_S and μ_{Mo} are calculated from solid sulfur and bcc-Mo. When μ_S equals to the upper limit and $\mu_{Mo} = E_{MoS2} - 2\mu_S$, we call the condition as S-rich. When μ_{Mo} equals to the upper limit and $\mu_S = (E_{MoS2} - \mu_{Mo})/2$, we call the condition as Mo-rich.

3. Results and discussion

First we optimize the interlayer distance of the supported MoS_2. If we do not consider the van der Waals correction, the total energies do not show minimum as the function of interlayer distance (Fig. 3). Therefore, we employ the Tkachenko-Scheffler type van der Waals correction [10]. The calculated results also suggest the AB stacking is more preferable than the AA stacking.

Next we calculate the formation energies of charged vacancies in supported MoS_2 as the function of Fermi level energy (Fig. 4). The shown figures correspond to the Mo-rich condition. For the comparison, we also calculate the formation energies of charged vacancies in freestanding MoS_2 (Fig. 5). We focus on the conduction band minimum, which is the most stable situation for the Fermi level energy. The formation energy of V_S is 1.08 eV for the MoS_2-supported and 1.49 eV for the $MoSe_2$-supported, while it is 0.64 eV for the freestanding. The formation energy of V_{Mo} is 5.54 eV for the MoS_2-supported and 5.75 eV for the $MoSe_2$-supported, while it is 4.38 eV for the freestanding. These results clearly indicate that supported vacancies are less stable than freestanding ones. In addition, the $MoSe_2$-supported vacancies are the least stable of all. These mean that the vacancy formation is more suppressed for the supported MoS_2 than the freestanding.

To explore the reasons, we analyze the charge redistribution after two freestanding pristine layers are stacked (Fig. 6). We also analyze the electron transfer from the supporting sheet to the supported sheet (Fig. 7). These results suggest that the interlayer interaction stabilizes the pristine MoS_2. Especially for the $MoSe_2$-supported, static electric field induced by the interlayer electron transfer enhances the stability of pristine MoS_2.

4. Conclusions

We found that vacancies are more difficultly formed in

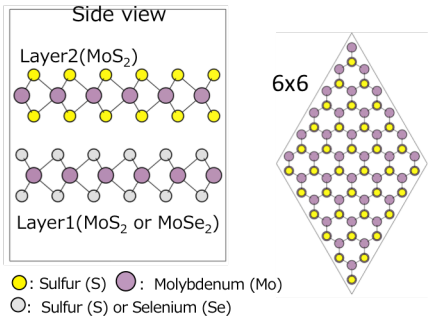

Fig. 1 Atomic structure of calculated model before vacancy formation.

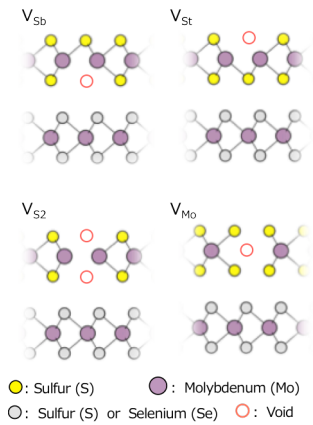

Fig. 2 Atomic structures of vacancies studied in this contribution.

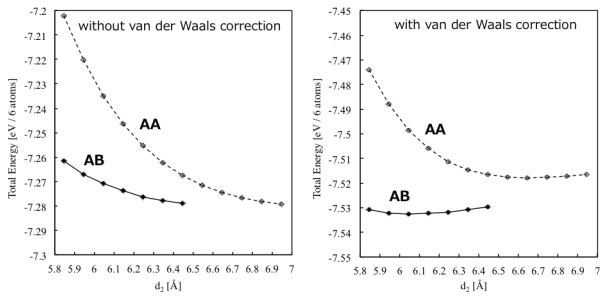

Fig. 3 Total energies of MoS_2-supported pristine MoS_2 as the function of interlayer distance.

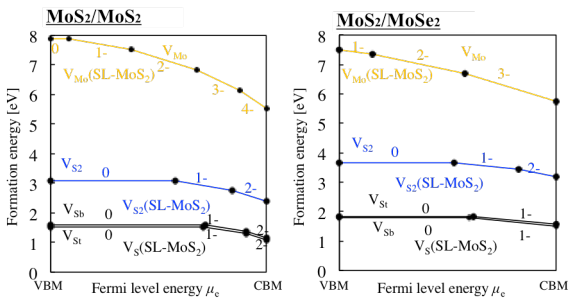

Fig. 4 Formation energies of vacancies in supported MoS_2 as the function of Fermi level energy.

the supported MoS_2 than the freestanding one. This gives hints to control the device properties of MoS_2. It is suggested that the interaction with substrate suppresses the degradation of devices.

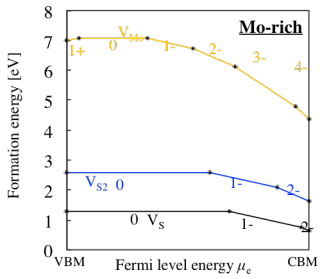

Fig. 5 Formation energies of vacancies in free standing MoS_2 as the function of Fermi level energy.

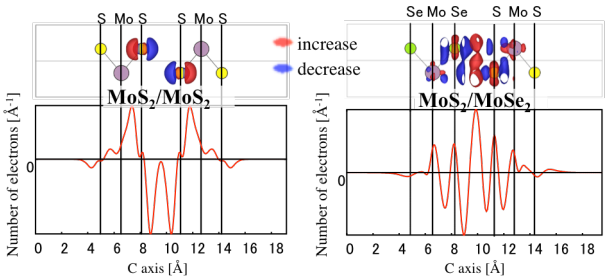

Fig. 6 Charge redistributions after two freestanding pristine layers are stacked.

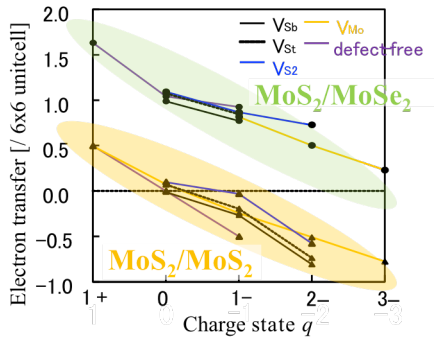

Fig. 7 Electron transfer from the supporting sheet to the supported sheet.

Acknowledgment

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