


Cite this: *RSC Adv.*, 2020, 10, 28725

First-principles study of vacancy defects at interfaces between monolayer MoS₂ and Au

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The performance of MoS₂ based devices is closely related to the quality and defect morphology of the monolayer MoS₂ deposited on metal. First-principles calculations were performed to investigate the vacancy effects of Au–mMoS₂ contact. Four possible S-vacancy and a Mo-vacancy were considered in our calculations. Energetic studies show that S-vacancies are easier to form than Mo-vacancy in Au–mMoS₂ contact, while S-vacancy (hollow site at interface, V_{S4}) has the lowest formation energy under Mo-rich environments. Electron and charge redistribution analysis of defective Au–mMoS₂ contact indicate that the lower contact resistance and higher electron injection efficiency of defective Au–MoS₂ contact than perfect ones. Notably, the S-vacancy at top layer showed better electronic performance than that at bottom layer of monolayer MoS₂ in the contact. High quality n-type Au–mMoS₂ contact can therefore be expected through defect engineering.

Received 1st June 2020

Accepted 27th July 2020

DOI: 10.1039/d0ra04833j

rsc.li/rsc-advances

Introduction

The discovery of graphene has upended the traditional understanding of two-dimensional structures, however, the zero-bandgap nature of graphene has limited their digital logic applications.¹ Transition-metal dichalcogenides (TMDs) with tunable bandgaps like MoS₂, WSe₂, *etc.* have emerged to be potential materials for digital logic applications in spite of their inferior carrier mobility.² Bulk MoS₂ has a graphene-like layered structure, where the S–Mo–S slabs are stacked together *via* weak van der Waals (vdW) interlayer interaction.³ Few-layer MoS₂ can therefore be mechanically exfoliated⁴ and their bandgaps vary with the number of layers.⁵ Monolayer MoS₂ has a direct bandgap of 1.81 eV,⁶ which endows many excellent properties for nanoelectronics. Monolayer MoS₂ has been regarded as a highly competitive candidate for field-effect transistors (FETs) with a high on/off ratio, and photodetectors based on MoS₂ have been intensively investigated.^{7–9}

A metal contact is required to inject appropriate types of carriers into the host materials for an actual electronic or photoelectronic device using 2D materials as the semi-conducting channel.¹⁰ Abundant researches^{11–14} have shown that the properties for 2D materials based devices can be tuned by substrate selections through interlayer interaction. Copper is the most well-studied metal contact for MoS₂ based devices. Experimentally, Kim D. *et al.* prepared monolayer MoS₂ islands on a copper surface at moderate growth conditions through

sulfur loading of the substrate using thiophenol *via* e-beam evaporation (physical vapor deposition), and obtained high quality MoS₂ monolayer with atomic ordering.¹⁵ Later on, first-principles calculations were demonstrated by Le D. *et al.* to investigate the geometric and electronic structures of monolayer MoS₂ on Cu(111).¹⁶ They predicted chemical interaction between monolayer MoS₂ and the Cu surface atoms instead of physical adsorption.

Au has shown privilege conducting properties, ductility and better interlayer interaction comparing to Cu, is expected to be ideal substrate materials for fabricating monolayer MoS₂.¹⁷ Large area single-layer MoS₂ has been successfully synthesized on the Au(111) surface by physical vapor deposition (PVD) in ultrahigh vacuum.¹⁸ It is interesting to note that B. Radisavljevic *et al.* used a hafnium oxide gate dielectric to demonstrate a room-temperature single-layer MoS₂ mobility of at least 200 cm² V^{−1} s^{−1}, similar to that of graphene nanoribbons, and demonstrated transistors with room-temperature current on/off ratios of 1 × 10⁸ and ultralow standby power dissipation, where Au as the electrode of the transistors. However, calculations by Popov *et al.*¹⁹ suggested that it is rather inefficient for electron injection from Au into single-layer MoS₂ while forming a tunnel barrier at the interface.²⁰ The inefficiency can be caused by the pristine monolayer MoS₂ model adopted in their calculations. However, experimental investigation speculated that the low contact resistance between Au and monolayer MoS₂ was due to defects of pristine monolayer MoS₂ during the preparation process.²¹

The performance of devices is closely related to the quality and defect morphology of the monolayer MoS₂ since defects are evitable during the preparation process. It has been well documented that vacancies in monolayer MoS₂ can have significant

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influence on the electronic and magnetic properties.^{22–26} In addition, vacancies can introduce dangling bonds at the interface between the monolayer MoS₂ and Au, which can enhance adsorption capacity and improve the carrier mobility.¹⁰ Su *et al.*¹⁷ studied the effects of vacancies in monolayer MoS₂ on electronic structure and electronic properties of Au–MoS₂ contact and suggest that defective Au–mMoS₂ top contacts have lower contact resistance and higher electron injection efficiency, whereas Au–MoS₂ contact with Mo-vacancy shows chemisorption interface with ohmic character. Displacement reaction by reactive metals is energetically favourable, which should act to lower resistance contacts.²⁷ However, their researches ignored the stability of the model. The mismatch between monolayer MoS₂ and Au remains large relatively, which may lead to deviations. Only one possible S-vacancy site was concerned in their model, further demonstrations for vacancy effects in Au–MoS₂ system are required.

In this study, first-principles calculations are performed to further illustrate the interface effect induced by intrinsic vacancies. Interface model of Au–mMoS₂ with a relatively small mismatch is therefore built to investigate the electronic structure and electronic properties of the system of Au–mMoS₂ contact. These studies may pave the ways for optimal design of MoS₂-based electronic devices.

Computational details

First principles calculations were performed based on the density functional theory (DFT) with local density approximation (LDA). The geometry optimizations and electronic structure calculations are performed with the projector augmented wave (PAW) pseudopotential²⁸ and the plane-wave cutoff energy is set to be 450 eV, implemented in the Vienna *ab initio* simulation package (VASP) code.^{29,30} DFT-D2 scheme is included to describe the vdW interactions. The maximum Hellmann–Feynman force between each atom during geometry optimization is less than 0.02 eV Å^{−1}, and energies are converged to within 1.0 × 10^{−5} eV per atom. A 5 × 5 × 1 *k*-mesh based on gamma-centered scheme is applied for relaxation calculations. A vacuum slab of 15 Å is added in monolayer and interface models to avoid spurious interactions between the individual structures. All the calculations were performed under same relaxation criteria and spin-polarized calculations were considered for all defective models.

Results and discussion

A (√3 × √3) supercell of monolayer MoS₂, consisting of 3 Mo atoms and 6 S atoms with one Mo layer arrays between two S layers in a trigonal prismatic layout, is adopted in this study.

The calculated lattice constant of monolayer is 3.160 Å, which is in excellent consistent with the experimental value (3.161 Å).³¹ and the calculated average Mo–S bond length is 2.374 Å. The calculated band gap for pristine monolayer MoS₂ is 1.87 eV, as illustrated in Fig. 1b, agreeing well with the experimental value (1.90 eV).⁶ The schematic of metal–mMoS₂ transistor device is shown in Fig. 2a. Testified four layers of Au

atoms were chosen to simulate the metal contact and a 2 (√3 × √3) monolayer MoS₂ (see Fig. 1a) was absorbed on one side of the Au (111) surfaces, as shown in Fig. 2b and c. The lattice constants of Au (111) surface are kept fixed to simulate the experimental deposition environment, with *a* = *b* = 3.122 Å. Fig. 3a–e show the models of Au–mMoS₂ with five concerned vacancies after structural relaxation.

The structural effects for different types of vacancies on the Au–mMoS₂ can be evaluated by calculating average bond lengths of Mo–S and atomic layer spacing *d*_{S–Au} (as denoted in Fig. 2), which are summarized in Table 1. It can be found that the covalent bond length of Mo–S is slightly increased when contact with Au comparing to pristine monolayer. Moreover, it is obvious that both bond lengths and *d*_{S–Au} (see Fig. 2) with defects are shorter than pristine systems. The shrink can be owed to the surrounding atoms move outwards when a vacancy forms.²³ The formation of either Mo or S vacancy can facilitate the adsorption of gold with monolayer MoS₂ since interface distances are generally decreased.

The structural stability of different vacancies defects can be calculated using the following equation,²²

$$E_f = E_{\text{vacancy}} - E_{\text{perfect}} + \sum N_i \times \mu_i$$

here, *E*_{vacancy} and *E*_{perfect} stand for the total energy of the supercell with and without vacancy, respectively. *N_i* is the numbers of type *i* that have removed from the supercell when vacancy is created. *μ_i* represents the relevant chemical potentials of these atoms. Due to the thermodynamic equilibrium, the chemical of Mo and S must satisfy the stability condition for MoS₂. Therefore, the upper limit of Mo chemical potential is given by the energy of one Mo atom in bulk molybdenum, while the lower limit of Mo chemical potential corresponds to the energy difference between the monolayer MoS₂ unit cell and a S₂ molecule.³² Hence, the extreme S-rich condition is therefore taken as the energy of one S atom in bulk sulfur. The formation energies of monolayer MoS₂ with vacancy can be expressed as a function of S chemical potential, over a wide range of experimental conditions from Mo-rich to S-rich, are plotted in Fig. 4.

The slopes of the energy profiles are proportional to the excess/deficit of S atoms in the defects. It can be seen that with the increase of the sulfur content, the formation energy of a Mo-vacancy in the Au–mMoS₂ contact decreases linearly. This

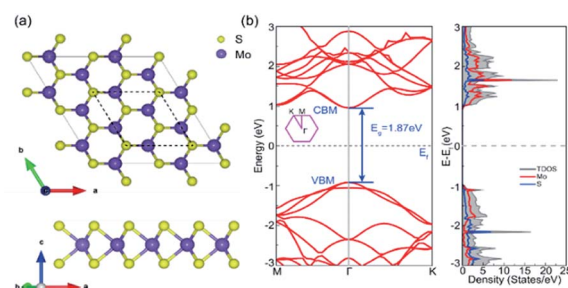


Fig. 1 (a) The atomic structures of monolayer MoS₂ from top view and side view, the dotted lines represent the calculated √3 × √3 cell. (b) Band structure and DOS of monolayer MoS₂ in a √3 × √3 cell.



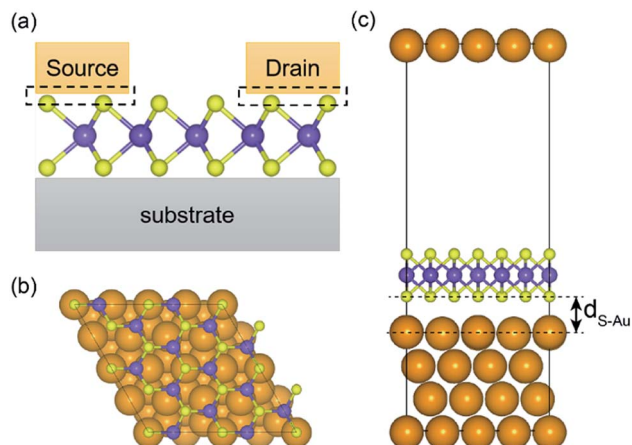


Fig. 2 (a) 2D cross-section schematic of metal-mMoS₂ transistor devices; structural diagram of Au-mMoS₂ contact: (b) the top view; (c) the side view, d_{S-Au} represents the vertical average distance monolayer MoS₂ and Au.

implies that Mo-vacancy is more likely to form under S-rich environment. Similarly, the Au-mMoS₂ with a S-vacancy can be more stable under Mo-rich condition. In addition, the formation energies of four types of S-vacancies can be relatively lower than that of Mo-vacancy under a wide range of sulfur chemical potentials. In most cases, it is easier to form S-vacancy in Au-mMoS₂ top contact than Mo-vacancy. V_{S4} at interface hollow site has the lowest formation energy among the four concerned S-vacancies under Mo-rich environments. The variations in formation energies of a (Mo or S) vacancy in the Au-mMoS₂ contact are consistent with those of a (Mo or S) vacancy

Table 1 Calculated structural parameters for different models after relaxation

Structure	Mo-S (Å)	d_{S-Au} (Å)
mMoS ₂	2.378	—
Au-mMoS ₂	2.432	2.820
V_{S1}	2.387	2.811
V_{S2}	2.387	2.814
V_{S3}	2.386	2.811
V_{S4}	2.387	2.808
V_{Mo}	2.408	2.443

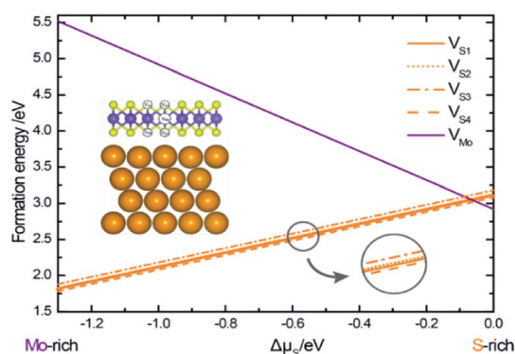


Fig. 4 Formation energies of different vacancies as functions of sulfur chemical potential, plotted in the range $-1.3 \text{ eV} \leq \Delta\mu_s \leq 0 \text{ eV}$, corresponding to the formation of bulk Mo and bulk alpha-S.

in monolayer MoS₂.³¹ The actual experimental conditions of growth for MoS₂ deposited on gold is assumed to be the Mo-rich region since experimental results have shown a sub-

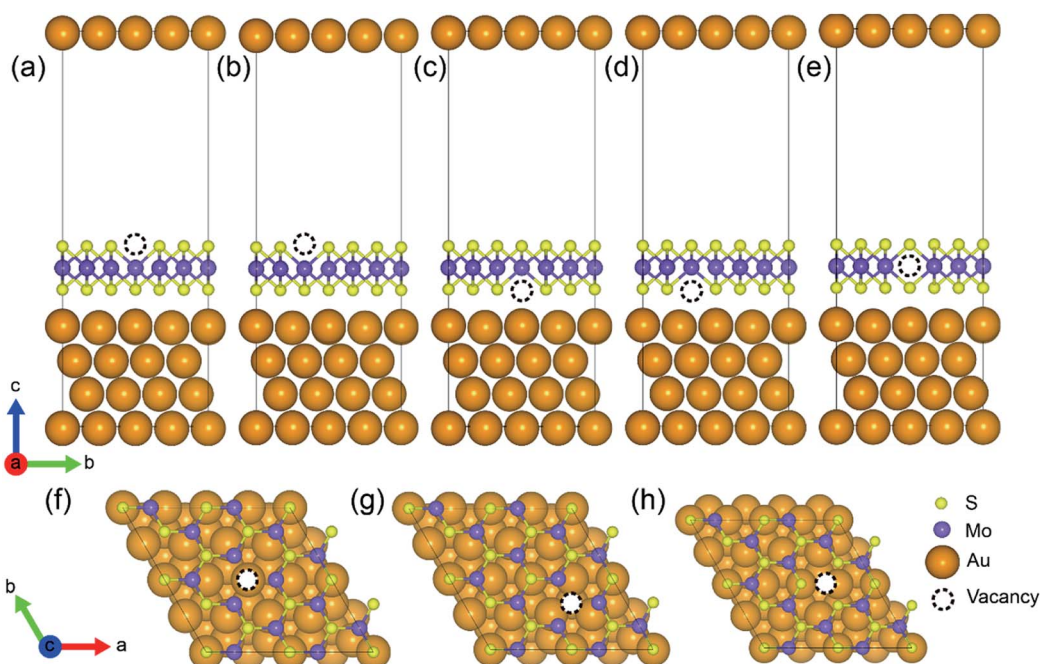


Fig. 3 Schematic diagram of Au-mMoS₂ top contact with (a)–(d) S-vacancy and (e) Mo-vacancy: V_{S1} , V_{S2} , V_{S3} , V_{S4} and V_{Mo} ; (f) corresponds to the top view of (a) and (c); (g) corresponds the top view of (b) and (d); and (h) is the top view of (e).



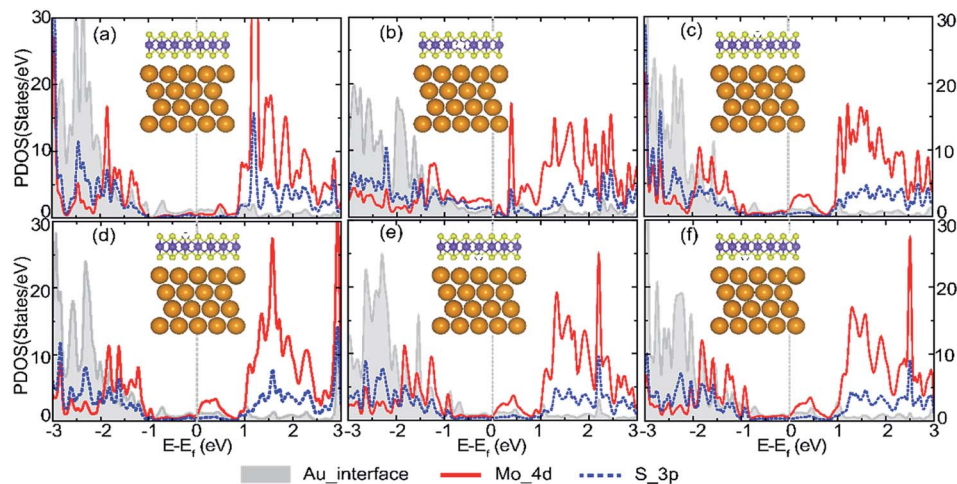


Fig. 5 Calculated PDOS of (a) perfect Au-mMoS₂ contact, (b) V_{Mo}, (c) V_{S1}, (d) V_{S2}, (e) V_{S3}, and (f) V_{S4}. The fermi levels are set at zero level as denoted by dashed grey lines.

stoichiometric Mo/S ratio higher than 0.5, suggesting a loss of S atoms.³³ Formation energies for double S-vacancies (V_{2S}) are calculated using the same equation. Five different configurations of V_{2S} with various vacancy distances are considered. The calculated formation energy of V_{2S} is roughly twice of a single

V_S, suggesting weak tendency of dimerization of S-vacancies under the Mo-rich conditions.

The partial density of states (PDOS) projection onto Au, S and Mo atom orbits are presented in Fig. 5a-f for the perfect and defective Au-mMoS₂ contact (V_{Mo}, V_{S1}, V_{S2}, V_{S3}, and V_{S4}) to

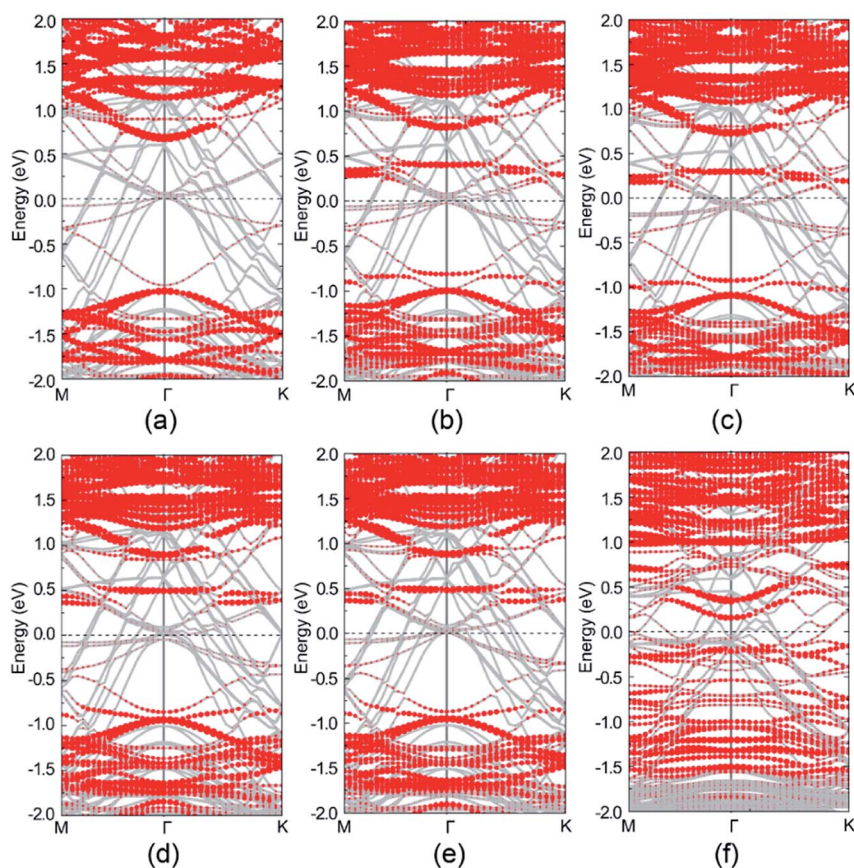


Fig. 6 Band structure of Au-mMoS₂ and Au-mMoS₂ with defects. (a) Represents perfect Au-mMoS₂; (b)–(f) correspond to V_{S1}, V_{S2}, V_{S3}, V_{S4} and V_{Mo}, respectively. Fermi level is at zero energy; the grey lines and red dotted lines represent the total band structure and contributions from MoS₂, respectively.



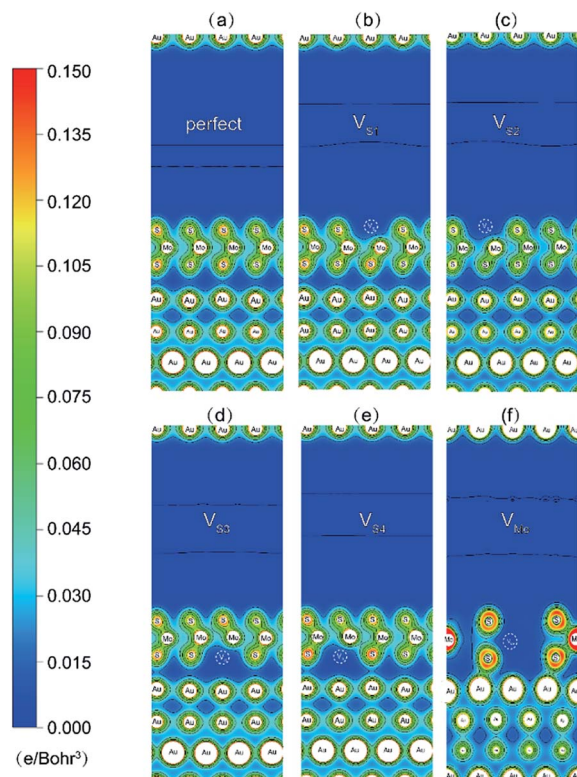


Fig. 7 Contour plots of total charge density of Au–mMoS₂ contact: (a) perfect Au–MoS₂ contact, (b)–(e) defective Au–MoS₂ contact with various S-vacancy. (f) Defective Au–MoS₂ contact with a Mo-vacancy.

investigate the effect of vacancies on the electronic properties. We selected the Au atoms at the interface to eliminate the influence of the Au atoms in the bulk phase. It can be found that the top of the valence bands and the bottom of the conduction bands of monolayer MoS₂ are dominated by the hybridization of anti-bonding and bonding between Mo_4d and S_3p states. Upon contact with Au, both Mo_4d and S_3p states of monolayer MoS₂ (in Fig. 1b) are shifted almost 0.3 eV in the direction of negative axis and spread across the original band gap of pristine monolayer MoS₂. Besides, Fermi level is mainly occupied by Mo_4d states, where PDOS corresponds to a low carrier density. No obvious overlap of the concerned interfacial orbitals can be found near the E_F , indicating weak bonding between interfacial atoms. A physisorption of Au/MoS₂ interface is predicted.

Defect energy levels can be introduced when there is a vacancy. Strong interaction between S_3p and Au_5d states is observed in Au–mMoS₂ contact with a Mo-vacancy, (Fig. 5b) which implies a higher electron injection efficiency compared to a perfect Au–mMoS₂ contact. Furthermore, some peaks of the PDOS occur near the top of original valence bands of the monolayer MoS₂, indicating the defective contact is p-type. Fig. 5c–f illustrate the PDOS of Au–mMoS₂ contact with different types of S-vacancies. There is no evident difference of the PDOS when S-vacancy locates in the same atomic layer. However, stronger hybridization between S_3p and Au_5d orbitals of S-vacancy in top S layer (V_{S1} or V_{S2}) is found than that

of vacancies in bottom layer of monolayer MoS₂ (V_{S3} or V_{S4}). A n-type Au–mMoS₂ contact is expected with all kinds of S-vacancies.

Band structure analysis on selected atoms of perfect and defective Au–mMoS₂ contact are shown in Fig. 6. Despite the energy bands of MoS₂ and Au are mostly hybridized together, the majority bands of the MoS₂ can be recognized clearly. The monolayer MoS₂ still presents semiconducting nature in the perfect contact as shown in Fig. 6a, further confirming the physisorption of the Au/MoS₂ interface. However, the Fermi level of the Au–mMoS₂ generally moves upward and the band gap slightly reduces comparing with single monolayer MoS₂. Fig. 6b–e present the band structures of four types of Au–mMoS₂ contact with S-vacancy. It is obvious that defect bands can be introduced and band gap shall be reduced, therefore stronger interaction between Au and monolayer MoS₂ than pristine contact is expected. Fermi levels of the defective contact always lie in the band gap region of MoS₂, contributing to the formation of Schottky barrier heights, which can be evaluated by the energy differences between the conduction band minimum and the Fermi levels. V_{S1} and V_{S2} located at the top layer are predicted to have smaller band gap and lower Schottky barrier heights at interface than the bottom vacancies due to stronger hybridization of interfacial Au and MoS₂. Au–mMoS₂ contact with a Mo-vacancy has a narrower and more active band gap than S-vacancies as shown in Fig. 6f and better chemical contact with substrate is therefore expected.

To further illustrate the interfacial bonding and electronic properties, the total electron distributions of the Au–mMoS₂ contacts were plotted in Fig. 7. Electron redistributions can be observed around the defective areas, which result in stronger binding between the monolayer and substrate. The electron accumulations around interfacial S and Au atoms in defective contacts imply a transition from physisorption into chemisorption and formation of weak Au–S covalent bonds. The Au–S bonds in system with Mo-vacancy is more covalent than others, consisted with their band structure analysis. The defective systems can therefore exhibit higher electron injection efficiency than pristine ones.

Conclusions

In summary, the interfacial properties of Au–mMoS₂ contact with possible vacancies were systematically investigated through first-principles calculations. Based on the afore discussed results, we found that the formation energies of four types of S-vacancy are generally lower than Mo-vacancy over a wide range of S chemical potential. The actual experimental growth condition is assumed to be Mo-rich where S-vacancies are more likely to form. Density of states, band structures and electron density of states analysis of the systems indicate a lower contact resistance and higher electron injection efficiency of defective Au–MoS₂ contacts than perfect one. Notably, the S-vacancy locates on the top layer of monolayer MoS₂ shows better performance than that on the bottom layer. Mo-vacancy is beneficial for obtaining high quality p-type Au–mMoS₂ contact, whereas n-type contacts can be achieved by S-vacancies.



These findings can bring new ideas for design and fabrication of novel nanoelectronics devices with monolayer MoS₂ through defect engineering.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors would like to thank the financial support from the Natural Science Foundation of Hunan Province (No. 2019JJ50795). The computational resource at the High-Performance Computing Center of Central South University is also gratefully acknowledged.

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