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Band gap modifications of two-dimensional defected MoS_2

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Abstract: The changes in structural and electronic properties, occurring in one monolayer of MoS_2 at different concentrations of oxygen atoms doping and vacancies are investigated by means of *ab initio* computer simulation. The substitution of sulphur atoms by oxygen ones reduces the band gap for high concentrations only, transforming direct-gap semiconductor into an indirect one, whereas a smaller concentration of oxygen practically does not influence the gap. The presence of sulphur vacancies strongly reduces the band gap, leading to bands overlapping at high concentration and appearance of new bands at the gap region, which are determined by Mo 4*d* states with the mixture of S 3*p* states, at low concentrations.

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Keywords: two-dimensional crystals; molybdenum disulphide; electronic properties; oxygen doping; vacancy.

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1 Introduction

Two-dimensional crystals are atomically thin materials possessing strong bonding in one crystal plane, and stacking of atomic planes by much weaker van-der-Waals forces. In recent decades semiconducting two-dimensional transition metal dichalcogenides such as MoS_2 [1] attract much interest as promising materials for a range of applications, as low-power field-effect transistors, logic circuits and phototransistors [1,2]. Electronic properties of these materials go through a dramatic change that makes them ideal for solar energy applications. These materials can be transformed from indirect band gap semiconductors to direct band gap ones when their thickness reduces to a monomolecular layer (ML). The values of the band gap lie in the red to near-infrared spectrum, characteristics that are extremely advantageous for light-harvesting and light-detecting applications. Experimentally determined band gap of bulk MoS_2 is indirect and has a value in the range of 1.23–1.29 eV [3,4].

MoS_2 thin-film transistors were fabricated with ion gel gate dielectrics [5]. They exhibited excellent band transport with a low threshold voltage, high mobility and a high on/off current ratio, as well as remarkably high mechanical flexibility; and no degradation in the electrical characteristics was observed upon significant bending. The structure of 1 ML MoS_2 is analogous to graphene [6], but in contrast to the metallic behaviour of the latter it demonstrates semiconducting properties. While MoS_2 has already proven possibility of its application in different electronic devices [1,2], a tuning of its band gap is important as well as the role of intrinsic defects in view of fabricating controlled metal/MoS_2 or dielectric/MoS_2 gate contacts. Recently McDonnell et al. [7] have shown that intrinsic defects dominate the metal/MoS_2 contact resistance providing a low Schottky barrier independent of metal work function. These natural

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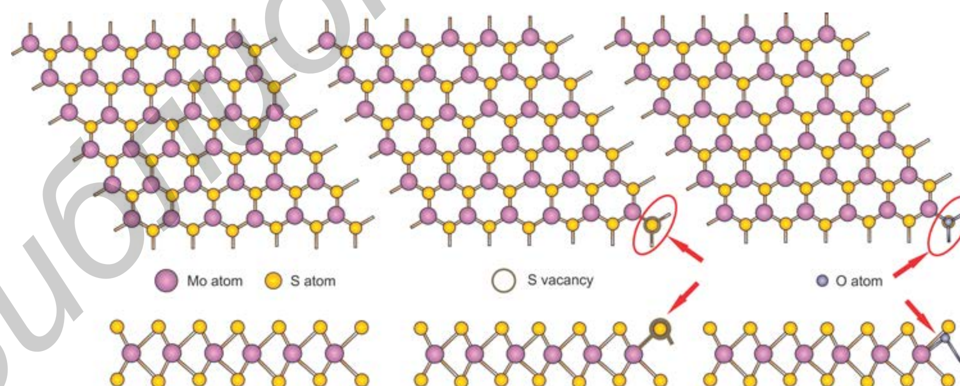
MoS_2 exfoliated sheets exhibit both n-type and p-type conductivity on the same surface with a Fermi level shift as >1 eV over tens of nanometres [7]. Besides, Islam et al. [8] have reported that electrical properties could be tuned from semiconducting to insulating via time-controlled exposure to oxygen plasma and show the creation of insulating MoO_3-rich disordered domains upon the MoS_2 sheet [8]. The formation of an ultrathin Mo-oxide interfacial layer was previously suggested by Yang et al. [9] who observed a significant improvement of the surface conformal coverage by Al_2O_3 and HfO_2 ALD films after oxygen plasma treatment of MoS_2, which supplied sufficient chemical adsorption sites. Thus we have analysed what kind of effects may happen upon oxygen doping, substituting isovalent sulphur atom, and upon removing different number of sulphur atoms.

2 Method

According to the experimental data, bulk MoS_2 is considered to have a hexagonal lattice (space group P_63/mmc) with a unit cell consisting of two alternating S-Mo-S layers attached to each other through Van-der-Waals forces. However, to suppress the influence of Van-der-Waals interaction in our work we used only one monolayer (1 ML) MoS_2 with three atoms in the unit cell.

For modelling of the different concentrations of vacancies and oxygen atoms, we considered 1 ML supercell enlarged from 1×1 up to 6×6 translations (Figure 1) with 21 Å vacuum width for suppression of the influence of neighbouring layers. For structural optimisation and calculation of electronic properties, we used PAW-LDA approximation, realised in VASP code [10]; 4*p* semi-core states of Mo were treated as valence. The energy cut-off of 520 eV and $16 \times 16 \times 1$ gamma-centred grid of Monkhorst–Pack points were applied.

Figure 1 Top and side view of MoS_2 6×6 supercell: a) undoped; b) with S vacancy; c) O-doped (see online version for colours)



3 Results and discussions

The in-plane lattice constant *a* of the unit cell obtained in our work after full structural relaxation is 3.12 Å that is in rather good agreement with the experimental

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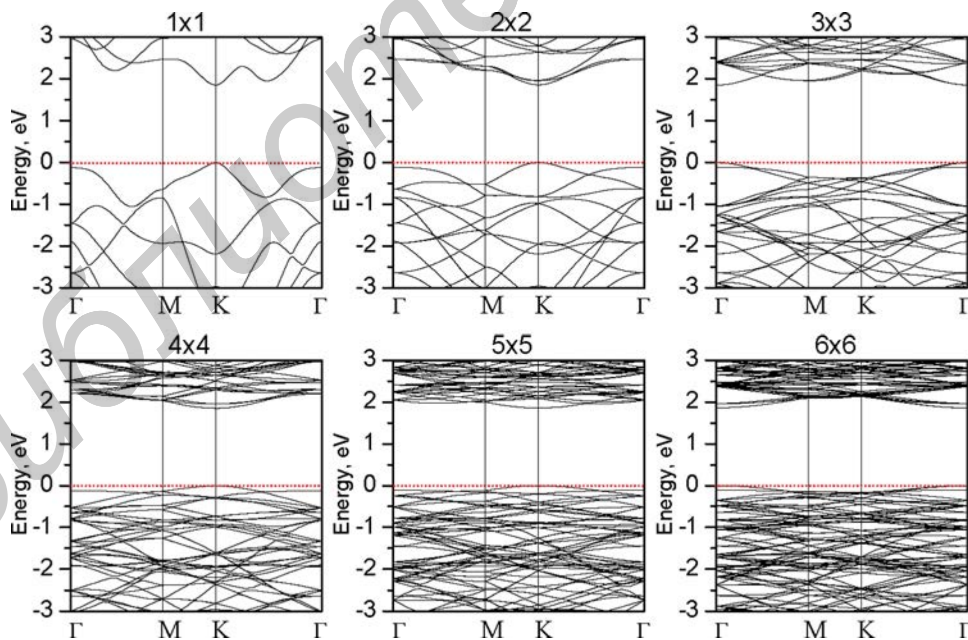
value of 3.16 Å [11]. The 1 ML structure is shown to be stable and to have a direct gap of 1.84 eV at the K-point, while bulk material is characterised by an indirect gap of 1.29 eV.

The band structures of 1 ML MoS_2 for cells translated up to 6×6 are presented in the Figure 2. The differences observed for 3×3 and 6×6 cells occur due to the symmetry of hexagonal cell; however, the gap value remains unchanged. Unlike bulk MoS_2, 1 ML material is direct gap semiconductor with the first direct transition in the K point.

By means of computer simulation we analyse the changes, which take place in 1 ML MoS_2 at different doping concentrations of oxygen atoms and vacancies. First, we replaced one sulphur atom from the top of the slab by an oxygen atom and analysed the atomic configurations obtained, consecutively enlarging the size of the cell. Obtained formation energy of oxygen dopant is –2.3 eV and it was determined as $Eform_{oxy} = E_{MoS2+oxy} - E_{MoS2} + \mu_s - \mu_{oxy}$, where $E_{MoS2+oxy}$ is the total energy of structure with oxygen atom, substituting the sulphur atom; E_{MoS2} is the energy of MoS_2 without defects; μ_s and μ_{oxy} are the chemical potentials of sulphur and oxygen atoms, determined from the bulk elemental phases. Oxygen reduces the band gap of MoS_2 for 1×1 and 2×2 cells, transforming direct-gap semiconductor into an indirect-gap one (Figure 3). Nevertheless, this effect is sizable only at very high oxygen concentrations (50 at.% and 25 at.%, corresponding to 1×1 and 2×2 cells, respectively), smaller concentrations of oxygen atoms practically does not change the gap; 3×3 structure demonstrates already direct-gap behaviour. The gap varies from 1.2 eV for 1×1 to 1.86 eV for 6×6 cells.

Figure 2 Electron energy band structures of 1 ML MoS_2 for different number of translational cells (see online version for colours)



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Upon modelling of S vacancy introduction, different vacancy sites (on the top and at the bottom of the slab) were considered (Figure 1), but no changes in electronic properties as a function of the defect position were observed. The analysis of electronic band structures shows that the presence of S vacancy strongly reduces the band gap, leading to bands overlapping at high concentrations (>25 at.%) and appearance of new bands at the gap region (Figure 4) at low concentration.

To understand which states are mainly responsible for such behaviour of the defect contained structures, the partial densities of states (DOSes) for each case have been analysed. In the case of oxygen doping (Figure 5), we have found that 2*p* states of oxygen give a sizable contribution only for the 1×1 cell, when concentration of oxygen atoms is maximal (50 at.%). In all other cases its impact is not meaningful, thus not shown at the Figure. The main contributions in the electronic states near the Fermi level are composed by Mo 4*d* and S 3*p* electrons.

Analogously, the new bands appearing ~1 eV at the gap region of band structures with S vacancy are determined mainly by Mo 4*d* states with the small mixture of S 3*p* states (Figure 6).

Summarising the data obtained for defected 1 ML MoS_2 (Figure 7) we may conclude that the band gap of MoS_2 is changing upon introducing oxygen atoms or vacancy. The doping by oxygen sizably reduces the gap for 1×1 and 2×2 cells only. Concentrations of oxygen atoms smaller than 25 at.% practically do not change the gap. The sulphur vacancy strongly reduces the band gap, leading to no gap at high concentrations.

Figure 3 Electron energy band structures of 1 ML MoS_2 with one oxygen atom (see online version for colours)

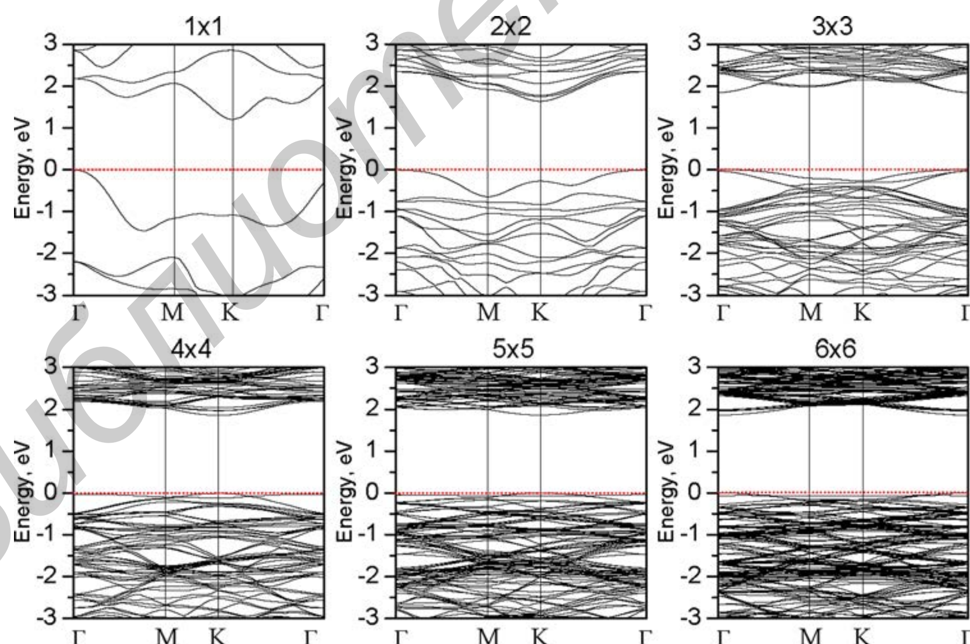

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Figure 4 Partial DOSes of 1 ML MoS_2 with one oxygen atom (see online version for colours)

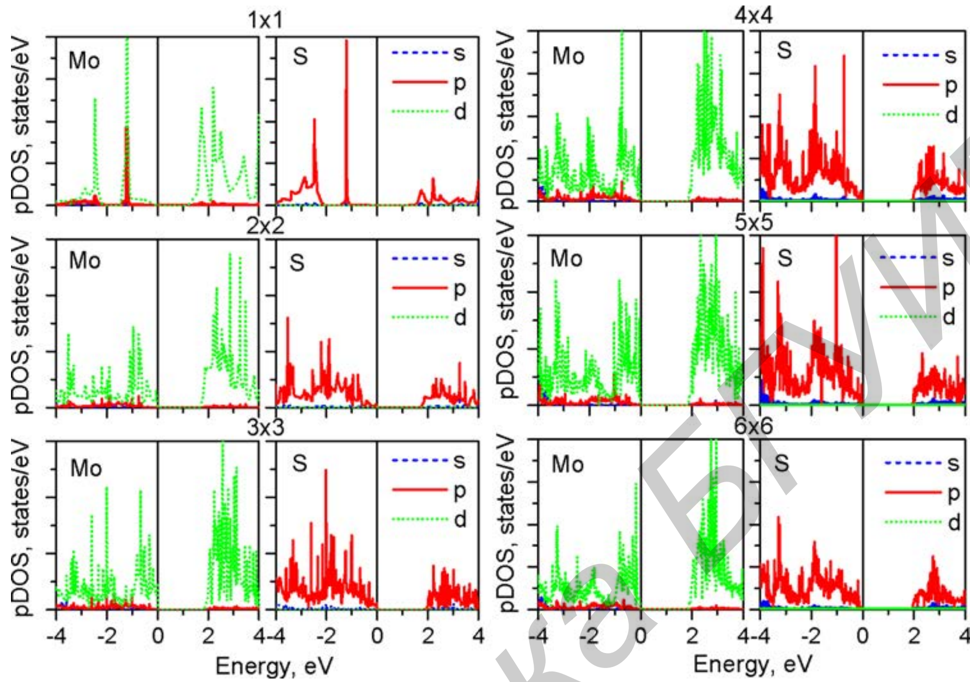

Figure 5 Electron energy band structures of 1 ML MoS_2 with 1 S vacancy (see online version for colours)

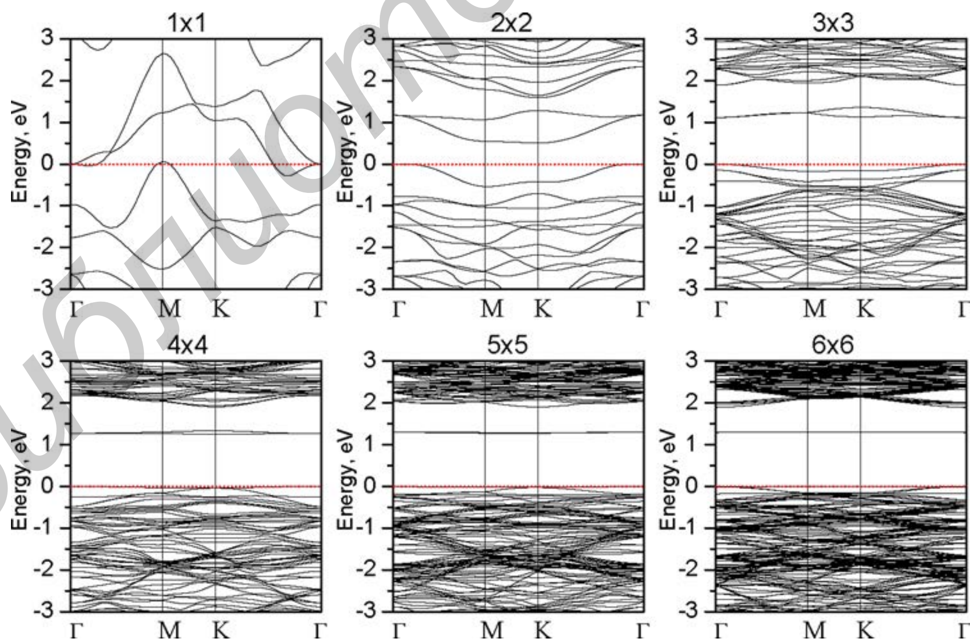

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Figure 6 Partial DOSes of 1 ML MoS_2 with 1 S vacancy (see online version for colours)

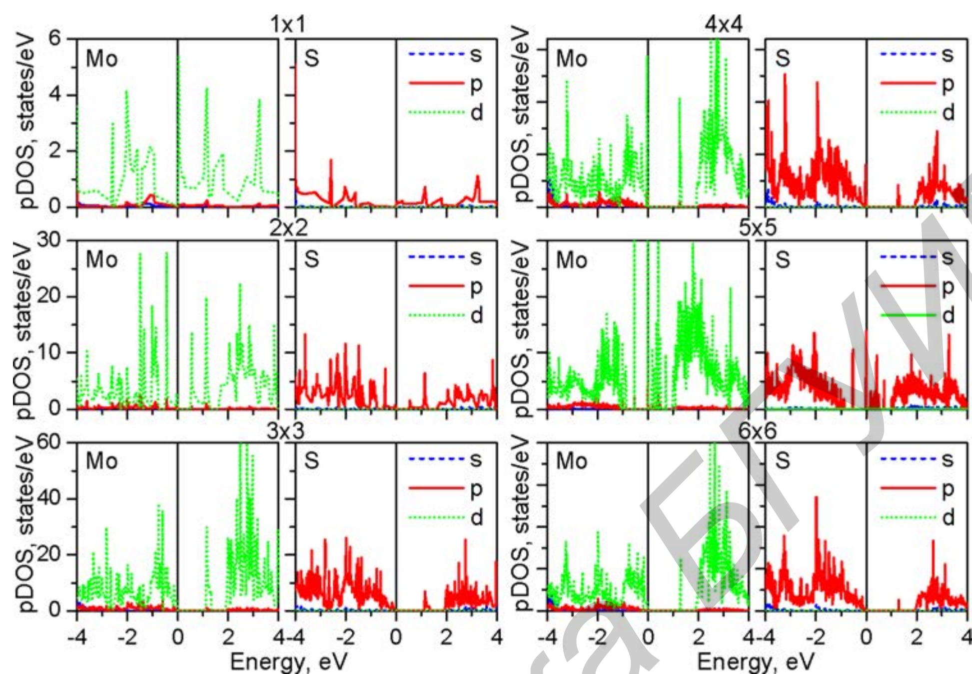
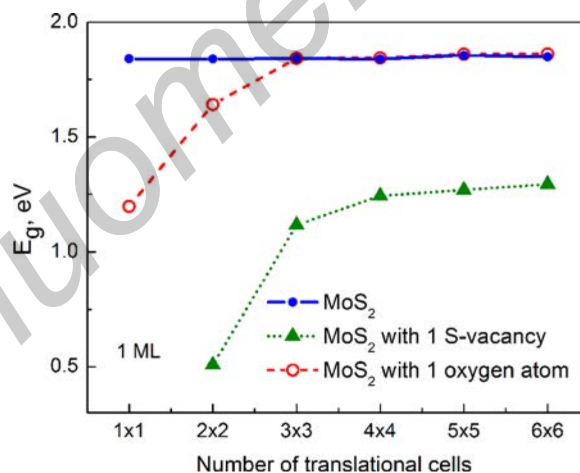


Figure 7 Band gap of one monolayer MoS_2 depending on the number of translational cells (see online version for colours)



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4 Conclusion

We have established that band gap of MoS_2 can be changed by oxygen doping or introduction of vacancies. Oxygen reduces the gap for 1×1 and 2×2 cells, transforming the direct-gap semiconductor into an indirect one. Nevertheless, this effect is sizable only at very high defects concentrations (>25 at.%), the smaller concentrations of oxygen

practically do not change the gap. The presence of vacancies strongly reduces the band gap, leading to bands overlapping at high concentrations (50 at.%) and appearance of new energy levels in the gap region.

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