



HAL
open science

Band gap modifications of two-dimensional defected MoS₂

A. V. Krivosheeva, V. L. Shaposhnikov, V. E. Borisenko, J.-L. Lazzari, N. V. Skorodumova, B. K. Tay

► **To cite this version:**

A. V. Krivosheeva, V. L. Shaposhnikov, V. E. Borisenko, J.-L. Lazzari, N. V. Skorodumova, et al.. Band gap modifications of two-dimensional defected MoS₂. International Journal of Nanotechnology, 2015, 12 (8-9), pp.654. 10.1504/IJNT.2015.068886 . hal-03144566

HAL Id: hal-03144566

<https://hal.science/hal-03144566>

Submitted on 17 Feb 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Band gap modifications of two-dimensional defected MoS₂

A.V. Krivosheeva*, V.L. Shaposhnikov
and V.E. Borisenko

Department of Micro- and Nanoelectronics,
Belarusian State University of Informatics and Radioelectronics,
220013 P. Browka 6, Minsk, Belarus
Fax: +375-172-93-88-69
Email: anna@nano.bsuir.edu.by
Email: vs@nano.bsuir.edu.by
Email: borisenko@bsuir.by
*Corresponding author

J-L. Lazzari

Centre Interdisciplinaire de Nanoscience de Marseille (CINaM),
Campus de Luminy, Marseille, France
Email: lazzari@cinam.univ-mrs.fr

N.V. Skorodumova

Multiscale Materials Modelling,
Royal Institute of Technology (KTH),
Stockholm S-10044, Sweden
Email: snv123@kth.se

B.K. Tay

Nanyang Technological University,
Singapore 639798, Singapore
Email: EBKTAY@ntu.edu.sg

Abstract: The changes in structural and electronic properties, occurring in one monolayer of MoS₂ 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.

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

Reference to this paper should be made as follows: Krivosheeva, A.V., Shaposhnikov, V.L., Borisenko, V.E., Lazzari, J-L., Skorodumova, N.V. and Tay, B.K. (2015) 'Band gap modifications of two-dimensional defected MoS₂', *Int. J. Nanotechnol.*, Vol. 12, Nos. 8/9, pp.654–662.

Biographical notes: Anna V. Krivosheeva is a Senior Researcher. She received her PhD Diploma in Nanoelectronics in 2005 at the Belarusian State University of Informatics and Radioelectronics (BSUIR) and continued her work in the Computer Simulation group at the Laboratory of Nanoelectronics and Novel materials (Minsk, Belarus). She worked as researcher at the Institute of Solid State Theory and Theoretical Optics, Jena (Germany), Interdisciplinary Center for Nanotechnology Marseille-CNRS (CINaM-CNRS, France), at the University of Paderborn (Germany) and KTH Royal Institute of Technology (Stockholm, Sweden). Since 2001, she is a member of the organising committee of the International Conference 'Nanomeeting'. She authored more than 35 scientific papers published in refereed international journals and gave talks at different conferences. Her field of interest is related to computer simulation of structural, electronic, optical and magnetic properties of bulk and low-dimensional compounds.

Victor L. Shaposhnikov works as a Senior Researcher in the Computer Simulation group at the Laboratory of Nanoelectronics and Novel materials in Belarusian State University of Informatics and Radioelectronics. He received his PhD Diploma in Condensed Matter Physics in 2000 at the Institute of Solid State and Semiconductor Physics, National Academy of Sciences of Belarus. He authored 50+ scientific papers published in refereed international journals. His primary research field is related to theoretical modelling of electronic and related properties of bulk and nanodimensional semiconducting materials.

Victor E. Borisenko is a Chair of the Micro- and Nanoelectronics Department at the Belarusian State University of Informatics and Radioelectronics (BSUIR). His field of scientific activities: physics of low-dimensional structures and nanoelectronics. He published more than 320 scientific works, among them seven books, nine Conference Proceedings (editor), 51 invention certificates. Since 1995, Chairman of the Organising Committee of the International Conferences on Physics, Chemistry and Application of Nanostructures 'Nanomeeting', held in Minsk (Belarus) every two years.

Jean-Louis Lazzari works since 1996 as a Senior Researcher in the Centre Interdisciplinaire de Nanoscience de Marseille, Aix-Marseille University (France). His activity is devoted to surfaces, interfaces of heterostructures and nanostructures of semiconductors, electronic, optical and magnetic properties of thin-film compounds for optoelectronic and microelectronic devices. In the past years, he was engaged in investigations of spin-injection in silicon via MIS-structures and design of magnetic memory devices. Nowadays, his research interests are focused on spintronics and photovoltaics. He has published over 70 papers in international scientific journals.

Natalia V. Skorodumova is a Professor at Department of Materials Science and Engineering, KTH, Stockholm, Sweden. She obtained her Doctor degree in science in physics and mathematics in 2003 at Moscow Steel & Alloys Institute, Theoretical Physics Department, Moscow. Since 2004, she has a post-doc position in the Condensed Matter Theory Group, Uppsala University, Sweden. In 2007, she became a docent in Uppsala University. She has more

than 60 papers published in scientific journals, including top-impact journals such as *Science*, *PNAS*, *Phys. Rev. Lett.*, *Applied Phys. Lett.*, has two patents and contributed to more than 30 international conferences with 10 invited talks.

Beng Kang Tay is currently the Deputy Director of the CNRS International NTU Thales Research Alliance (CINTRA) and Associate Dean (Research), College of Engineering. His research work over the years was devoted to thin film technology especially in tetrahedral amorphous carbon, metal oxides, nanocomposites and carbon nanotubes. Up to date he has published more than 300 international journal papers. He has jointly-invented an industrial viable film deposition system based on the filtered cathodic vacuum arc technology and is currently the co-inventor of 28 international patent applications. His research team was awarded the ASEAN Outstanding Engineering Award and National Technology Award in 1997 and 2000 respectively for outstanding R&D contributions on a new Filtered Cathodic Vacuum Arc Technology.

This paper is a revised and expanded version of a paper entitled 'Band gap modifications of two-dimensional defected MoS₂' presented at *NANOTECH-MEET*, Tunisia, 24–26 April, 2014.

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 MoS₂ [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 MoS₂ is indirect and has a value in the range of 1.23–1.29 eV [3,4].

MoS₂ 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 MoS₂ is analogous to graphene [6], but in contrast to the metallic behaviour of the latter it demonstrates semiconducting properties. While MoS₂ 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/MoS₂ or dielectric/MoS₂ gate contacts. Recently McDonnell et al. [7] have shown that intrinsic defects dominate the metal/MoS₂ contact resistance providing a low Schottky barrier independent of metal work function. These natural

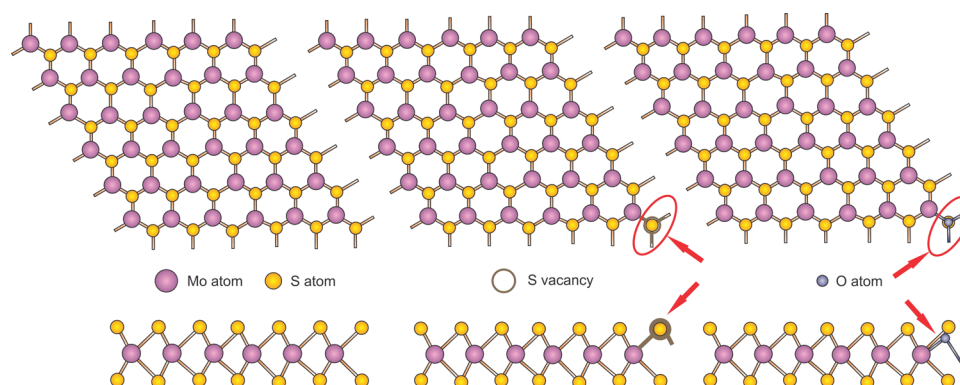
MoS₂ exfoliated sheets exhibit both n-type and p-type conductivity on the same surface with a Fermi level shift as >1 eV over tens of nanometres [7]. Besides, Islam et al. [8] have reported that electrical properties could be tuned from semiconducting to insulating via time-controlled exposure to oxygen plasma and show the creation of insulating MoO₃-rich disordered domains upon the MoS₂ 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 Al₂O₃ and HfO₂ ALD films after oxygen plasma treatment of MoS₂, 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 MoS₂ is considered to have a hexagonal lattice (space group *P*₆*3*/*m**m**c*) 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) MoS₂ 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 × 16 × 1 gamma-centred grid of Monkhorst–Pack points were applied.

Figure 1 Top and side view of MoS₂ 6 × 6 supercell: a) undoped; b) with S vacancy; c) O-doped (see online version for colours)



3 Results and discussions

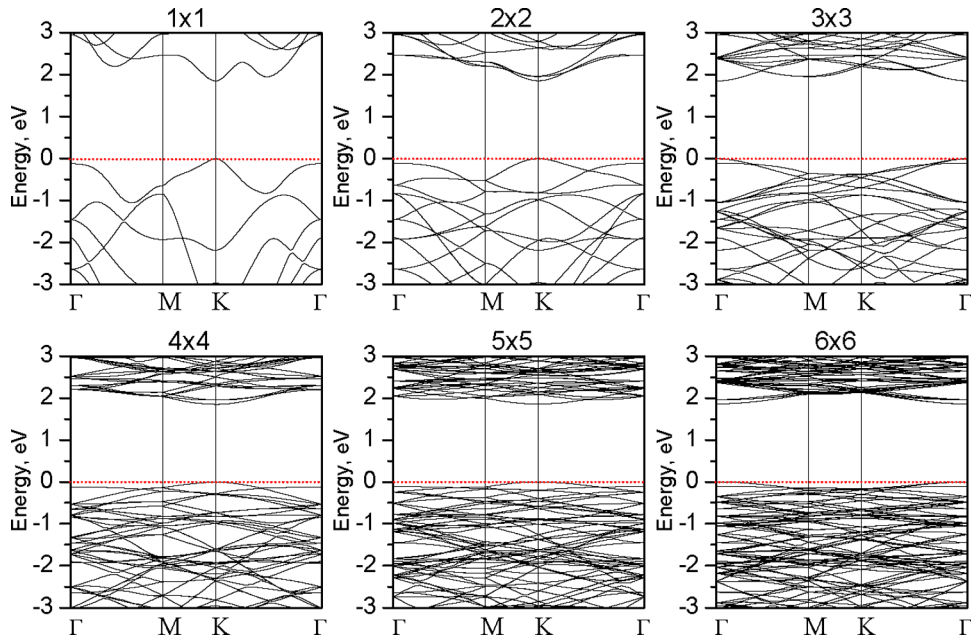
The in-plane lattice constant *a* of the unit cell obtained in our work after full structural relaxation is 3.12 Å that is in rather good agreement with the experimental

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 MoS₂ 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 MoS₂, 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 MoS₂ 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 $E_{\text{form}_{\text{oxy}}} = E_{\text{MoS}_2+\text{oxy}} - E_{\text{MoS}_2} + \mu_{\text{s}} - \mu_{\text{oxy}}$, where $E_{\text{MoS}_2+\text{oxy}}$ is the total energy of structure with oxygen atom, substituting the sulphur atom; E_{MoS_2} is the energy of MoS₂ 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 MoS₂ 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 MoS₂ for different number of translational cells (see online version for colours)



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 $2p$ 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 $4d$ and S $3p$ electrons.

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

Summarising the data obtained for defected 1 ML MoS₂ (Figure 7) we may conclude that the band gap of MoS₂ 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 MoS₂ with one oxygen atom (see online version for colours)

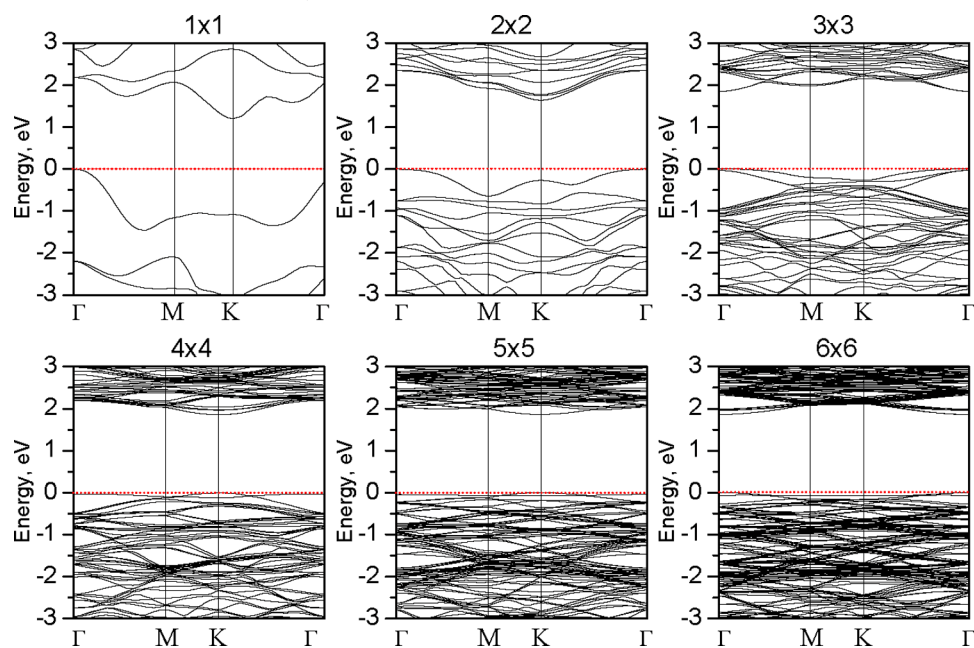


Figure 4 Partial DOSes of 1 ML MoS₂ with one oxygen atom (see online version for colours)

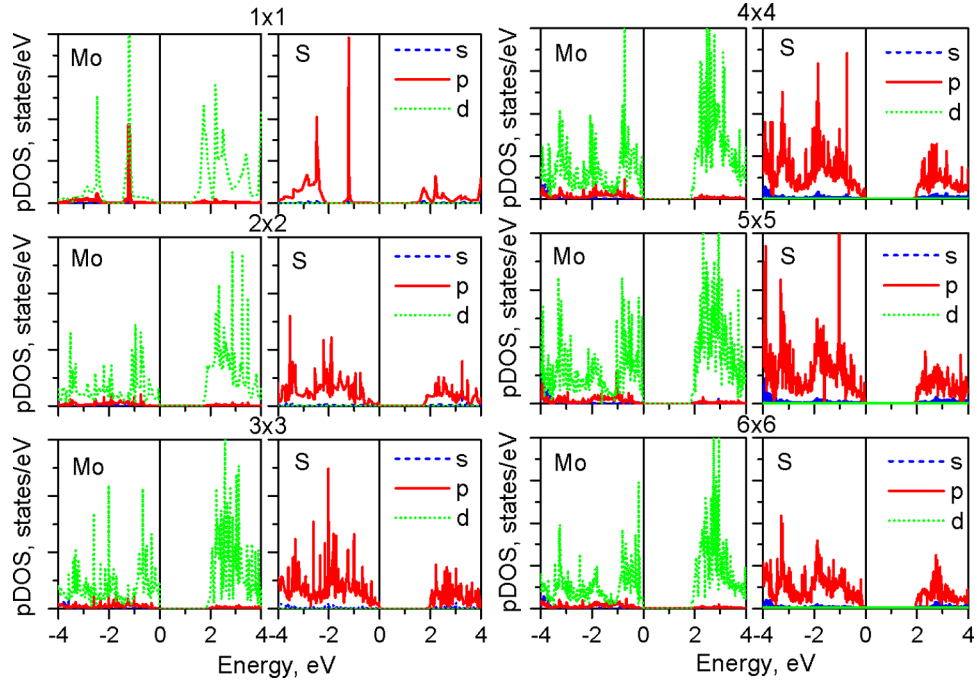


Figure 5 Electron energy band structures of 1 ML MoS₂ with 1 S vacancy (see online version for colours)

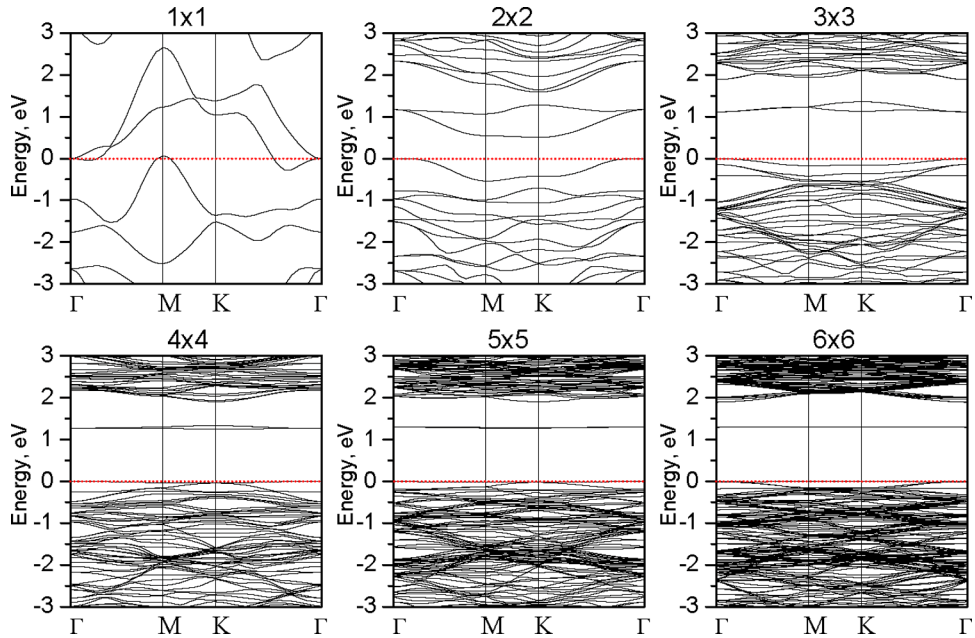


Figure 6 Partial DOSes of 1 ML MoS₂ with 1 S vacancy (see online version for colours)

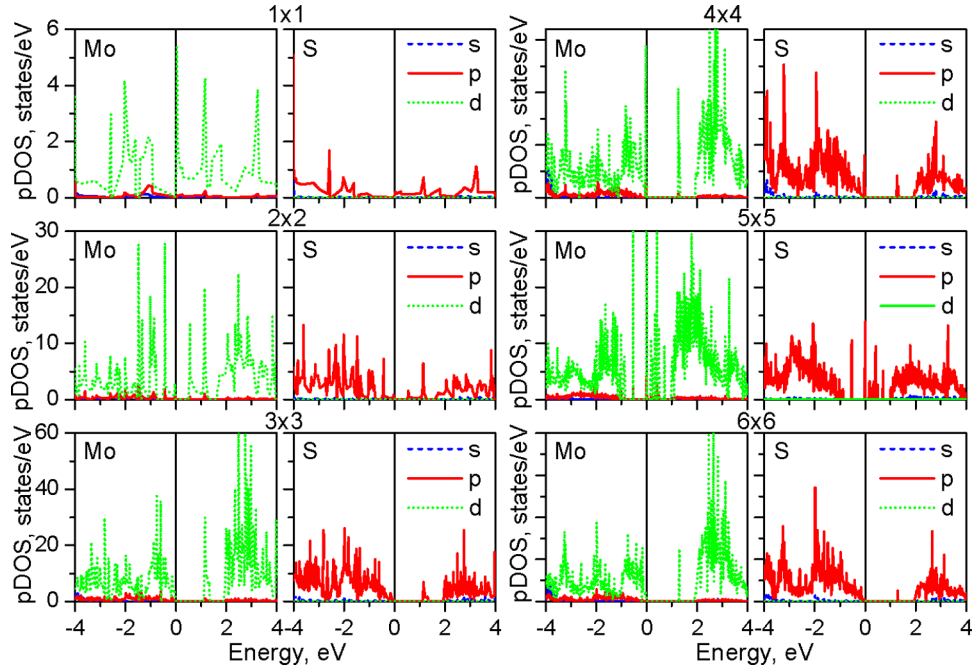
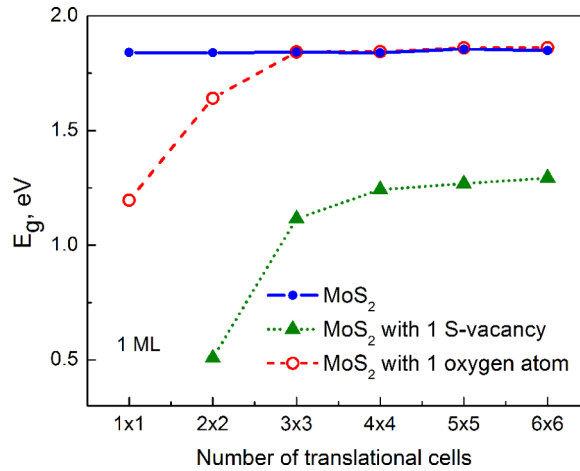


Figure 7 Band gap of one monolayer MoS₂ depending on the number of translational cells (see online version for colours)



4 Conclusion

We have established that band gap of MoS₂ 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.

Acknowledgements

This work was supported by joint BRFFR-CNRS project No. F13F-001 and Visby Program: scholarships for PhD studies and postdoctoral research in Sweden.

References

- 1 Wang, Q.H., Kalantar-Zadeh, K., Kis, A., Coleman, J.N. and Strano, M.S. (2012) 'Electronics and optoelectronics of two-dimensional transition metal dichalcogenides', *Nature Nanotechnol.*, Vol. 7, pp.699–712.
- 2 Ho, W., Yu, J.C., Lin, J., Yu, J. and Li, P. (2004) 'Preparation and photocatalytic behavior of MoS₂ and WS₂ nanocluster sensitized TiO₂', *Langmuir*, Vol. 20, pp.5865–5869.
- 3 Kam, K.K. and Parkinson, B. (1982) 'Detailed photocurrent spectroscopy of the semiconducting group VIB transition metal dichalcogenides', *J. Phys. Chem.*, Vol. 86, No. 4, pp.463–467.
- 4 Mak, K.F., Lee, C., Hone, J., Shan, J. and Heinz, T.F. (2010) 'Atomically thin MoS₂: a new direct-gap semiconductor', *Phys. Rev. Lett.*, Vol. 105, pp.136805 (1–4).
- 5 Pu, J., Yomogida, Y., Liu, K.-K., Li, L.-J., Iwasa, Y., Takenobu, T. () 'Highly flexible MoS₂ thin-film transistors with ion gel dielectrics', *Nano Lett.*, Vol. 12, pp.4013–4017.
- 6 Geim, A.K. and Novoselov, K.S. (2007) 'The rise of graphene', *Nature Mater.*, Vol. 6, pp.183–191.
- 7 McDonnell, S., Addou, R., Buie, C., Wallace, R.M. and Hinkle, C.L. (2014) 'Defect-dominated doping and contact resistance in MoS₂', *ACS Nano*, Vol. 8, pp.2880–2888.
- 8 Islam, M.R., Kang, N., Bhanu, U., Paudel H.P., Erementchouk, M., Tetard, L., Leuenberger, M.N. and Khondaker, S.I. (2014) 'Tuning the electrical property via defect engineering of single layer MoS₂ by oxygen plasma', *Nanoscale*, Vol. 6, pp.10033–10039.
- 9 Yang, J., Kim, S., Choi, W., Park, S.H., Jung, Y., Cho, M.-H. and Kim, H. (2013) 'Improved growth behavior of atomic-layer-deposited high-k dielectrics on multilayer MoS₂ by oxygen plasma pretreatment', *ACS Appl. Mater. Interfaces*, Vol. 5, pp.4739–4744.
- 10 Kresse, G. and Furthmüller, J. (1996) 'Efficiency of *ab-initio* total energy calculations for metals and semiconductors using a plane-wave basis set', *Comput. Mater. Sci.*, Vol. 6, pp.15–50; (1996) 'Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set', *Phys. Rev. B*, Vol. 54, pp.11169–11185.
- 11 Zhu, Z.Y., Cheng, Y.C. and Schwingenschlögl, U. (2011) 'Giant spin-orbit-induced spin splitting in two-dimensional transition-metal dichalcogenide semiconductors', *Phys. Rev. B*, Vol. 84, pp.153402 (1–5).