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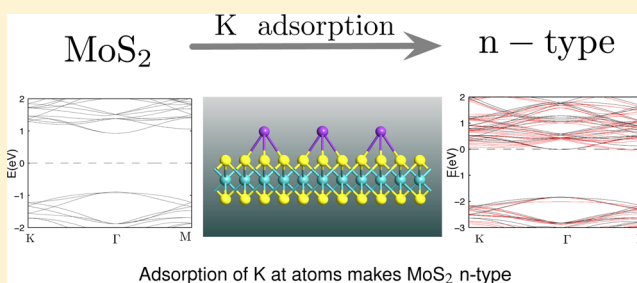
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Doping Strategies for Monolayer MoS₂ via Surface Adsorption: A Systematic Study

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ABSTRACT: Using density functional theory calculations, we have systematically explored the effect of surface adsorption of different atoms on the electronic properties of monolayer molybdenum disulfide (MoS₂). We have chosen a few representative members from each group in the periodic table, ranging from alkali metals (group I) to halogens (group VII), and calculated the electronic band structure of the adatom–MoS₂ system for the most energetically stable location of the adatom adsorbed on MoS₂. The calculated value of charge transfer from the adsorbed adatom to MoS₂ and resultant shifting of the Fermi level to the conduction band suggest that the group I (Li, Na, K) and group II metals (Mg, Ca) are the most effective adatoms to enhance the n-type mobile carrier density in MoS₂. Our calculation is in good agreement with the experimental observation for K [*Nano Lett.* **2013**, *13*, 1991].



1. INTRODUCTION

Increasing cost and process variability of fabrication technology in silicon-based metal oxide semiconductor field effect transistor (MOSFET) devices is straining the boundaries of Moore's "law" of miniaturization¹ and has forced us to investigate alternate materials and technologies to improve transistor performance in terms of speed and power consumption. In this regard, atomistically thin two-dimensional (2D) layered materials have attracted huge interest in recent years due to their useful physical properties and potential applications, particularly in electronics and optoelectronics.^{2–8} Apart from zero bandgap graphene which has a high off current, another class of atomistically thin 2D layered material, namely, transition metal dichalcogenides (TMDs), such as MoS₂, MoSe₂, WS₂, WSe₂, etc., have a direct band gap and are being actively investigated both theoretically and experimentally for a variety of applications. For example, MoS₂-based field effect transistors (FETs)⁹ have been fabricated and are found to have features superior to FETs made of graphene.¹⁰

TMDs have great potential for applications in nanoscale devices due to their novel electronic, physical, and optical properties, which is the outcome of their ultrathin structure.^{3–5} Unlike graphene, which is not suitable for the semiconductor industry due to its zero bandgap, TMDs like MoS₂, WS₂, etc. have an intrinsic (direct or indirect) band gap which depends on the number of layers.¹¹ For example, single-layer MoS₂ has a direct band gap of 1.9 eV,¹² and hence it is very useful for applications in the semiconductor industry. The performance of layered TMDs is comparable to the existing Si transistor for low power applications, due to their ultrathin dimension, highly crystalline nature, and absence of dangling bonds.^{13–16} Monolayer MoS₂ FETs have recently been fabricated, and they have an $I_{\text{ON}}/I_{\text{OFF}}$ ratio of the order of 10^8 , mobility around

200 cm²/(V s), and low standby power dissipation at room temperature.⁹

Intrinsic monolayer MoS₂ has a very low free charge density of 10^{10} cm⁻², and consequently, it has a low drive current.¹⁷ The free carrier concentration can be increased by doping MoS₂ with suitable impurities which can be done either via substitutional doping, i.e., by replacing either Mo or S with other atoms,^{18,19} or via adsorption of surface adatoms.^{20–22} As 2D layered materials have a very high surface area, adatom adsorption can be a very effective strategy for carrier doping and band structure engineering. For example, using hydrogen/halogen, metal, and molecule adsorption, the electronic band structure has been modified to bring versatility to graphene, ranging from metal to semiconductor/insulator.^{23–25} In the case of 2D transition metal dichalcogenides, similar approaches can be adopted to create donor or acceptor levels in between the valence and conduction band of the parent material, leading to doping of a semiconductor like MoS₂ by electrons/holes. To this end, experimental studies of potassium adatom on MoS₂ have been carried out; it has been shown that the adatom dopes MoS₂ with n-type carriers, and the fabricated FET devices have been found to exhibit low contact resistances.²⁶ Other atoms like transition metals are also of practical importance because metallic elements like Sc, Ti, Ni, etc. are used as contacts in MoS₂-based FETs,^{27,28} and metallic impurities like Re are found to occur naturally in MoS₂.²⁹

In this article, using density functional theory (DFT) calculations, we systematically explore the possibility of band structure engineering of monolayer MoS₂ by surface adsorption

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of various adatoms, belonging to different groups of the periodic table. We have chosen a few representative members from each group in the periodic table, ranging from alkali metals (group I) to halogens (group VII), and our aim is to provide a comprehensive guideline for doping strategies of MoS₂ via surface adsorption of adatoms. In addition, we also investigate the most stable configuration for each of the adatoms [see Figure 1(c)] and the amount of charge transfer

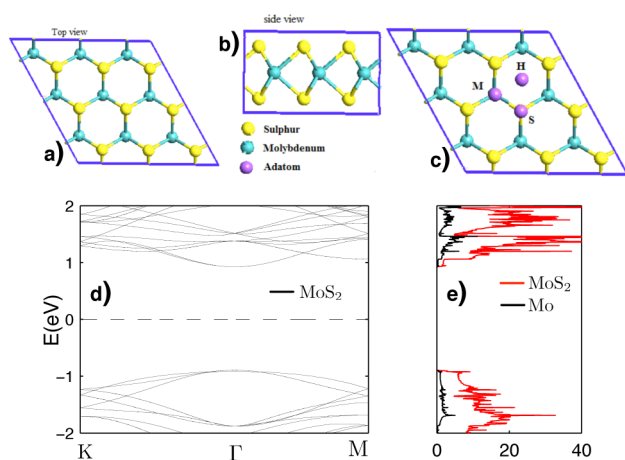


Figure 1. Geometrical view of the MoS₂ monolayer supercell with (a) top view, (b) side view, and (c) top view with adatoms at different locations (M for adatom on top of Mo, S for adatom on top of S, and H for adatom on top of the center of hexagon). Panels (d) and (e) display the band structure and DOS for the pristine MoS₂ supercell (without any adatom).

from the adsorbed adatom to MoS₂ or vice versa. The paper is organized as follows: in Section 2, we present the parameters and other details used for DFT calculation. In Section 3, we briefly review the crystal structure and electronic properties of TMDs. This is followed by systematic presentation of the results and discussion in Section 4. Finally we summarize our findings in Section 5.

2. METHODOLOGY AND SIMULATION DETAILS

We have performed geometry relaxation, total energy calculations, and the electronic structure calculations using the density functional theory (DFT), as implemented in the ATK package.^{30–32} The quasi Newton method is used to optimize the crystal structure.³³ The exchange-correlation energy is treated within the framework of local density approximation (LDA) and given by the Perdew and Zunger (PZ) functional.³⁴ The Brillouin-zone integrations are performed with Monkhorst–Pack K-points with $3 \times 3 \times 1$ Brillouin-zone sampling, along with mesh cutoff of 75 Hartree. We have used a double- ζ polarized basis set for all the calculations performed in this work. We have used a $3 \times 3 \times 1$ MoS₂ super cell with a vacuum region of 20 Å along the *c*-axis, which is sufficient to eliminate interaction among the monolayers. All structures are fully optimized until the force on each atom is less than 0.01 eV/Å, with a tolerance limit of 10^{-5} and a maximum of 200 steps, using the Pulay mixer algorithm³⁵ for the iteration control parameter.

Three possible sites for adatom adsorption [see Figure 1(c)] are named as M (top of molybdenum), S (top of sulfur), and H (center of the hexagon), and we have chosen the most energetically favorable one for the purpose of electronic band

structure calculation. We also have calculated the charge transfer from the adatom to the MoS₂ monolayer using the Mulliken charge transfer method.³⁶ Mathematically, Mulliken charge transfer is given by $\rho^* = Z_a - \rho_a$, where Z_a indicates the valence electron charge of the isolated atom and ρ_a is the calculated electron charge of the atom in the vicinity of the MoS₂ layer. Note that in our notation atom K has $Z_a = -1e$ where $e \approx 1.6 \times 10^{-19}$ C. Thus, $\rho^* < 0$ ($\rho^* > 0$) implies electron transfer from the adatom to the MoS₂ monolayer (to the adatom from the MoS₂ monolayer).

3. TMDs: CRYSTAL STRUCTURE AND ELECTRONIC PROPERTIES

The generic formula for TMDs is given by MX₂, where M is a transition metal atom (Mo, W, Nb, Ti, Zr, etc.) and X is a chalcogen atom (S, Se, Te), respectively. Several transition metal dichalcogenides crystallize in the form of a graphite-like layered structure; for example, MoS₂, WS₂, NbS₂, etc. Each MX₂ layer is approximately 3–4 Å thick because it contains three layers of atoms: M sandwiched between two X layers or X–M–X, arranged in a hexagonal planar lattice [see Figure 1(a)–Figure 1(b)]. The intralayer M–X bonds are predominantly covalent in nature and are much stronger as compared to the weak interlayer coupling, occurring via the van der Waals forces.³⁷ A monolayer or few layers of TMD crystals are then formed via cleaving parallel to the metal dichalcogenide layers.

Due to change in interlayer coupling and the effect of quantum confinement perpendicular to the X–M–X layer, electronic band structure of 2D TMDs changes significantly compared to their bulk forms.^{37,38} For example, bulk MoS₂ is an indirect bandgap ($E_g \sim 1$ eV) semiconductor;¹¹ not only the bandgap increases as the number of layers reduces but also monolayer MoS₂ is in fact a direct bandgap semiconductor ($E_g \sim 1.9$ eV).¹¹ The valence band maximum (VBM) and conduction band minimum (CBM) are dominated by Mo 4d_{z²} states in monolayer MoS₂, with other Mo states playing a minor role.²⁰ We have calculated the electronic properties of pristine monolayer MoS₂ to validate the parameters used for DFT calculations, as stated in Section 2. The electronic band structure and density of states (DOS) are shown in Figure 1(d) and Figure 1(e), respectively, and the bandgap is in good agreement with the value reported in the literature.¹¹ Thus, having validated the DFT parameters, we then proceed to calculate the electronic properties of monolayer MoS₂ after adatom adsorption and discuss our findings in the following section.

4. RESULTS AND DISCUSSIONS

Among the three possibilities, M, S, and H [see Figure 1(c)], first we have determined the most energetically favorable location for adatom adsorption on MoS₂. For this purpose, we have calculated the binding energy according to the relation

$$E_{\text{binding}} = E_{\text{MoS}_2} + E_{\text{adatom}} - E_{\text{MoS}_2+\text{adatom}} \quad (1)$$

where E_{MoS_2} is the total energy of the $3 \times 3 \times 1$ super cell of pristine monolayer MoS₂; E_{adatom} is the energy of the isolated adatom in the ground state calculated for the same super cell with the same parameters; and $E_{\text{MoS}_2+\text{adatom}}$ is the total energy of the MoS₂ + adatom system after structural relaxation. Thus, by the above definition of binding energy, the higher the value of E_{binding} , the more stable is the atomic configuration. In Table 1, we have reported the most stable configuration (among M, S,

Table 1. Adatom, Preferred Adsorption Site, Binding Energy, and Electronic Charge Transferred to/from the Adatom^a

group	adatom	adsorption site	binding energy (eV)	charge transfer (ρ^*)
1st	Li	M	2.905	−0.109e
	Na	M	1.610	−0.232e
	K	M	1.864	−0.508e
2nd	Be	H	2.738	0.421 e
	Mg	M	1.089	−0.214e
	Ca	M	2.377	−0.244e
3rd	B	M	5.908	0.399e
	Al	M	3.223	0.198e
	Ga	M	2.826	0.081e
4th	C	M	7.742	−0.216e
	Si	H	3.658	0.163e
	Ge	S	2.728	0.007e
5th	N	S	5.658	0.036e
	P	S	3.606	0.171e
	As	S	3.123	0.067e
6th	O	S	6.528	0.069e
	S	S	4.090	0.172e
	Se	S	3.520	0.124e
7th	F	S	3.007	0.170e
	Cl	S	1.888	0.133e
	Br	S	1.614	0.133e
Metals	Ag	H	2.346	−0.165e
	Au	H	2.474	−0.134e
Tr. metals	Ir	M	7.288	−0.099e
	Nb	M	6.112	−0.234e
	Ni	H	7.142	−0.135e
	Pd	M	4.567	0.153e
	Sc	H	4.730	−0.103e
	Ti	M	7.379	−0.102e
	V	H	6.945	0.137e
	Re	M	7.723	−0.371e

^aNote that negative charge transfer implies electronic charge transferred from the adatom to the MoS₂ monolayer; i.e., there is some net positive charge on the adatom (consult the text in Section 2 for the definition of ρ^*).

and H) for each adatom based on the highest binding energy. Interestingly, barring a few exceptions, adatoms belonging to a particular group showed similar behavior. For example, all the adatoms of group I (alkali metals), II (alkaline earth metals), and III are found to prefer the M site over H and S (except Be). On the other hand, adatoms belonging to group V, VI, and VII are more stable when located on the S site, while H is the most favorable site for the noble metals. However, for group IV and transition metals, we have not observed any particular trend in terms of site preference. For example, group IV elements like C, Si, and Ge prefer M, H, and S location, respectively. Similarly, among the transition metals we have studied, Ir, Nb, Pd, Ti, and Re occupy the M site, while Ni, Sc, and V prefer the H site. Our results for the equilibrium site for group I, group VII, and metals like Sc and Pd are consistent with ref 21, in which the authors have studied only group I metals and group VII halogens, in addition to a few other metals. Although our results for Ti are at variance with ref 21, they are consistent with that of ref 20.

Out of the three configurations M, S, and H, we have chosen the most stable one (i.e., the location where binding energy is maximum) for presenting the results of the electronic band

structure calculation. Since the alkali (group I) and alkaline earth (group II) metals are highly electropositive, these adatoms are found to be positively charged, as expected [other than Be—see Table 1]. According to the electronic band structure and projected density of states (PDOS, multiplied by a factor of 2 for adatoms) of K-adsorbed MoS₂, shown in Figure 2(a)–2(b), there is neither any significant change near the

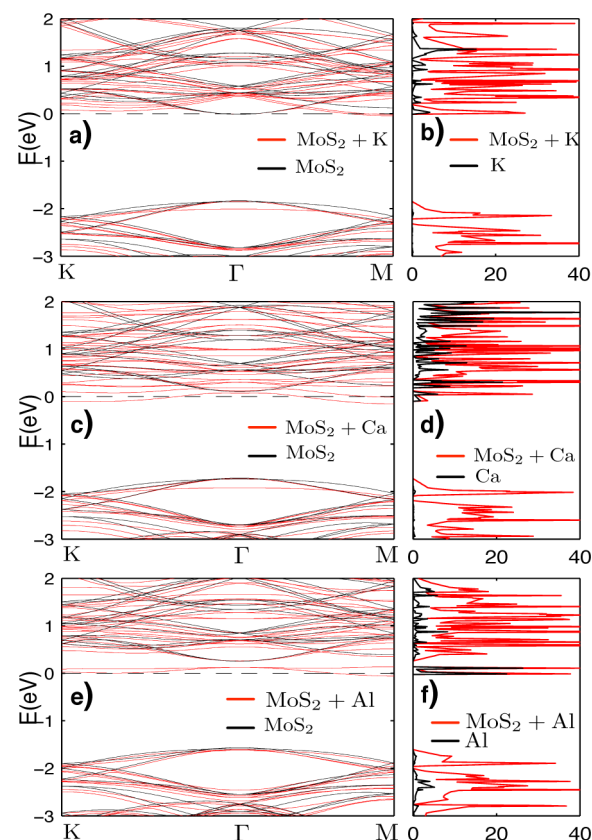


Figure 2. Panels (a), (c), and (e) show the band structure, and panels (b), (d), and (f) display the DOS of MoS₂ with metallic adatoms and two times the projected DOS of the adatom of groups I, II, and III, i.e., K, Ca, and Al, respectively. Fermi level shifts to the conduction band because of the electrons donated by K and Ca adatoms. Al adsorption leads to the creation of a partially filled band very close to the conduction band minimum, from where electrons can easily be excited to the conduction band. Note that the dashed line displays the Fermi level of the MoS₂–adatom system, and the band structure of MoS₂ has been shifted to align the conduction bands of pristine MoS₂ and the MoS₂–adatom system. The same convention is followed in the rest of the diagrams.

band edges (close to the VBM and CBM) nor any modification of band gap. However, due to the electrons donated by adatoms, the Fermi level shifts to the conduction band of MoS₂. Note that the electronic states of K have negligible contribution to the total DOS [see Figure 2(b)] near the CBM. Thus, the adatom donates free mobile electrons to the conduction band of MoS₂, and as a consequence its electrical conductivity is expected to increase significantly. A similar trend has been observed for Li and Na, the other two alkali metals investigated in this paper. In the case of group II adatoms [for example Ca adsorbed MoS₂, band structure, and PDOS shown in Figure 2(c) and Figure 2(d), respectively], there is some noticeable change in electronic band structure near the CBM. However, the overall effect qualitatively remains the same, i.e., group II

adatoms (Mg and Ca) also donate free electrons to the conduction band. As shown in Table 1, the n-type carrier population increases as one moves from top to bottom along group I and II columns in the periodic table.

Unlike groups I and II, adsorption of group III adatoms leads to significant changes in the electronic band structure of MoS₂ [see Figure 2(e)–(f)]. For example, Al adsorption creates midgap energy levels very close to the CBM. Moreover, the adatom (Al) has significant contribution to the total DOS around the energy level close to the Fermi energy; i.e., these states are strongly localized in the vicinity of the adsorbed atoms as evidenced by the projected DOS plots [see Figure 2(f)]. Thus, although the group III adatom like Al does not directly enhance the free electron density, the partially filled midgap energy levels are located very close to the CBM, and these electrons can be excited to the conduction band, effectively increasing the n-type carrier concentration in MoS₂.

In the case of group IV, V, VI, and VII, when adsorbed by MoS₂, all the adatoms acquire negative charge [C being the only exception—see Table 1]. Although midgap states are created by group IV, V, and VII adatoms like C, P, and Cl [see Figure 3(a)–(f)], unlike group III adatoms, midgap energy levels are not close to the CBM; rather they are located in the middle of the VBM and CBM. As the midgap energy levels are located quite far (~ 1 eV) from the conduction band edge [see Figure 3(a)–(f)], they are not going to be effective as electron donors. In this regard adsorption of group VI adatom like O is not useful either; neither the Fermi level is shifted to the conduction band nor does it create midgap energy levels [see Figure 3(g),(h)]. Interestingly, despite acquiring some additional negative charge, none of the group IV, V, VI, and VII adatoms are able to hole-dope the underlying MoS₂. This is evident from Figure 3 because neither the Fermi level is shifted to the valence band nor are there any empty midgap states close to the VBM.

Among noble and transition metals, most of the adatoms investigated here (other than Pd and V) are found to be positively charged. Adsorption of noble metals like Au and Ag create partially filled donor levels close to the conduction band edge [see Figure 4(a)–(b)]. In the case of transition metal adatoms, all of them lead to the formation of midgap energy levels. However, unlike other groups, we have not found any general trend as the band structure varies substantially from one transition metal adatom to another. For example, the effect of Nb and Ti adsorption on the band structure and DOS is shown in Figure 4(c)–(d) and Figure 4(e)–(f), respectively. Although midgap energy levels are present, there are neither any filled states close to the conduction band edge nor any empty states near the valence band edge. Moreover, the midgap states are localized to the adatoms, as illustrated by the PDOS plots shown in Figure 4(d) and (f). These localized states are known as trap states, and they effectively behave as additional scattering centers which degrade the mobility of the charge carriers. Thus, the transition metal adatoms create some trap states, and they are not effective for either electron or hole doping in MoS₂. We note, however, that these trap states can speed up the carrier recombination process and can be useful for devices which require fast switch off times.³⁹

5. CONCLUSION

It is not possible to increase charge carriers in MoS₂ via doping using traditional methods such as ion implantation which is very effective for doping silicon. However, the ultrathin

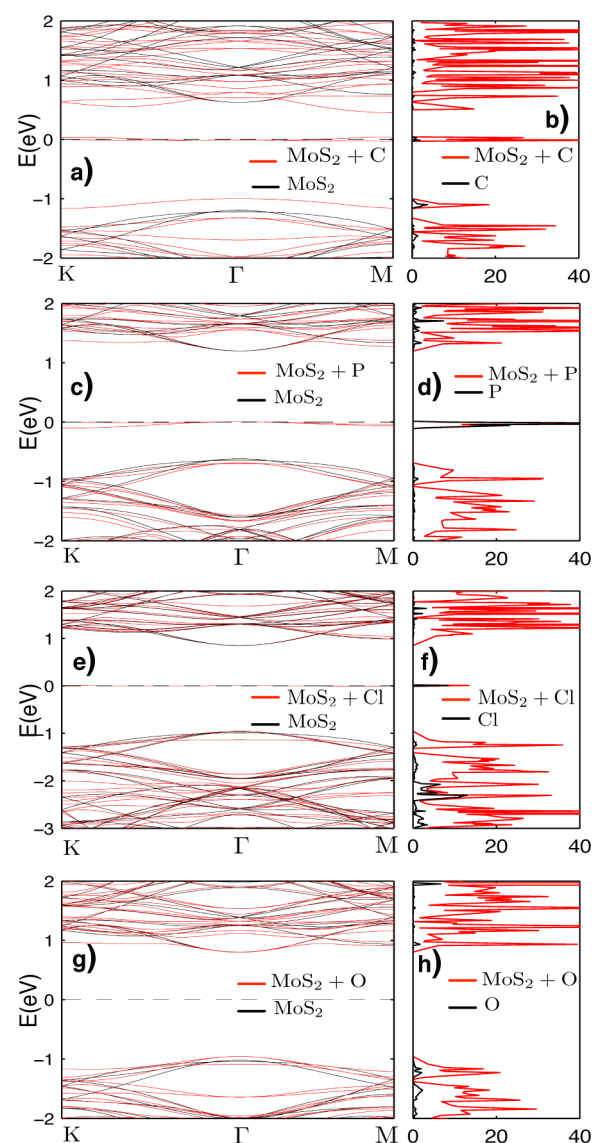


Figure 3. Panels (a), (c), (e), and (g) show the band structure, and panels (b), (d), (f), and (h) display the DOS of MoS₂ with adatoms of group IV, V, VII, and VI, i.e., C, P, Cl, and O, respectively. Except O, the rest of the adatoms create midgap energy levels in the middle of the VBM and CBM. As the midgap levels are ≈ 1 eV away from the CBM, these adatoms are not as effective as group I and II adatoms for the purpose of electron doping.

monolayer structure of MoS₂ motivates the study of other novel approaches, such as chemical and molecular doping.⁴⁰ In the context of monolayer MoS₂, it has been shown theoretically that substitutional doping shifts the Fermi level into a valence band or conduction band, making it a p-type or n-type semiconductor, respectively.¹⁹ Adatom adsorption has emerged as an alternate way of band structure engineering, as shown by experimental studies of electron doping by potassium adsorption on MoS₂.²⁶ Our calculation is indeed in very good agreement with the experimental observation [see Figure 2(a)–(b)]. As mentioned in Section 4, this is found to be a generic feature for all the group I and II adatoms (Be being the only exception) which add mobile charge carriers to the MoS₂ monolayer. Interestingly, the n-type carrier population increases as one moves from top to bottom along the groups I and II column in the periodic table [see Table 1]. Among the other

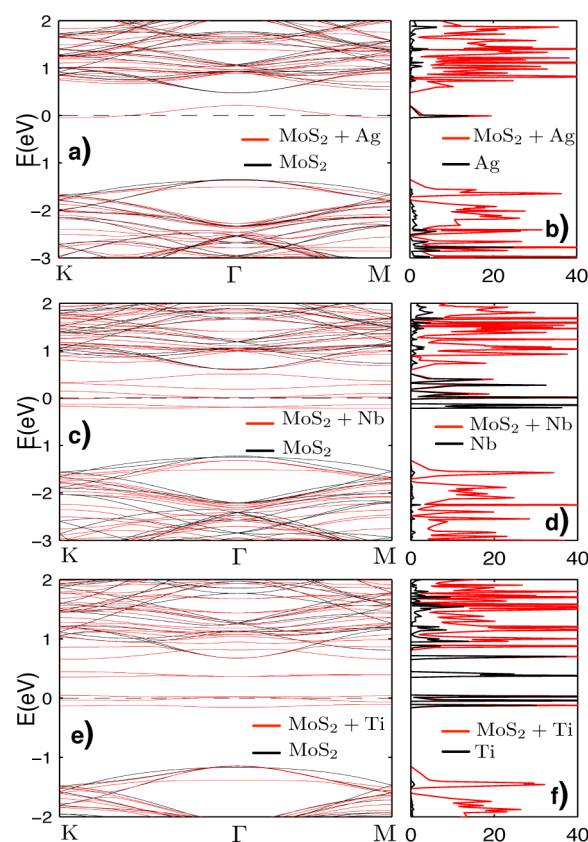


Figure 4. Panels (a), (c), and (e) show the band structure, and panels (b), (d), and (f) display the DOS of MoS₂ with noble and transition metallic adatoms, i.e., Ag, Nb, and Ti, respectively. While Ag creates some partially filled band close to the CBM, that can be somewhat effective as an electron donor, both Nb and Ti create some trap states in between the VBM and CBM and are not effective as either an electron or hole donor.

adatoms, only group III and noble metals can be somewhat effective as electron donors, as they create partially filled energy levels very close to the CBM [see Figure 2(e)–(f) and Figure 4(a)–(b)], and these electrons can easily be excited to the conduction band of MoS₂, enhancing the n-type carrier concentration. However, none of the other adatoms proved to be effective as electron or hole donors; rather they give rise to midgap trap states, which act as scattering centers and can reduce the performance of MoS₂-based FETs.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) The International Technology Roadmap for Semiconductors (ITRS). Semiconductor Industry Association, 2013; <http://www.itrs.net/>.
- (2) Novoselov, K. S.; Jiang, D.; Schedin, F.; Booth, T. J.; Khotkevich, V. V.; Morozov, S. V.; Geim, A. K. Two-dimensional Atomic Crystals. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 10451–10453.
- (3) Butler, S. Z.; Hollen, S. M.; Cao, L.; Cui, Y.; Gupta, J. A.; Gutierrez, H. R.; Heinz, T. F.; Hong, S. S.; Huang, J.; Ismach, A. F.; et al. Progress, Challenges, and Opportunities in Two-Dimensional Materials Beyond Graphene. *ACS Nano* **2013**, *7*, 2898–2926.
- (4) Wang, Q. H.; Kalantar-Zadeh, K.; Kis, A.; Coleman, J. N.; Strano, M. S. Electronics and Optoelectronics of Two-dimensional Transition Metal Dichalcogenides. *Nat. Nanotechnol.* **2012**, *7*, 699–712.
- (5) Neto, A. H. C.; Novoselov, K. New Directions in Science and Technology: Two-dimensional Crystals. *Rep. Prog. Phys.* **2011**, *74*, 82501–82509.
- (6) Maiti, U. N.; Lee, W. J.; Lee, J. M.; Oh, Y.; Kim, J. Y.; Kim, J. E.; Shim, J.; Han, T. H.; Kim, S. O. 25th Anniversary Article: Chemically Modified/Doped Carbon Nanotubes & Graphene for Optimized Nanostructures & Nanodevices. *Adv. Mater.* **2014**, *26*, 40–67.
- (7) Yun, J. M.; Park, S.; Hwang, Y. H.; Lee, E. S.; Maiti, U.; Moon, H.; Kim, B. H.; Bae, B. S.; Kim, Y. H.; Kim, S. O. Complementary p- and n-Type Polymer Doping for Ambient Stable Graphene Inverter. *ACS Nano* **2014**, *8*, 650–656.
- (8) Li, D. J.; Maiti, U. N.; Lim, J.; Choi, D. S.; Lee, W. J.; Oh, Y.; Lee, G. Y.; Kim, S. O. Molybdenum Sulfide/N-Doped CNT Forest Hybrid Catalysts for High-Performance Hydrogen Evolution Reaction. *Nano Lett.* **2014**, *14*, 1228–1233.
- (9) Radisavljevic, B.; Radenovic, C. A.; Brivio, J.; Giacometti, V.; Kis, A. Single-layer MoS₂ Transistors. *Nat. Nanotechnol.* **2011**, *6*, 147–150.
- (10) Schwierz, F. Graphene Transistors. *Nat. Nanotechnol.* **2010**, *5*, 487–496.
- (11) Splendiani, A.; Sun, L.; Zhang, Y.; Li, T.; Kim, J.; Chim, C. Y.; Galli, G.; Wang, F. Emerging Photoluminescence in Monolayer MoS₂. *Nano Lett.* **2010**, *10*, 1271–1275.
- (12) Mak, K. F.; Lee, C.; Hone, J.; Shan, J.; Heinz, T. F. Atomically Thin MoS₂: A New Direct-Gap Semiconductor. *Phys. Rev. Lett.* **2010**, *105*, 136805.
- (13) Ayari, A.; Cobas, E.; Ogundadegbe, O.; Fuhrer, M. S. Realization and Electrical Characterization of Ultrathin Crystals of Layered Transition-metal Dichalcogenides. *J. Appl. Phys.* **2007**, *101*, 014507.
- (14) Liu, K. K.; Zhang, W.; Lee, Y. H.; Lin, Y. C.; Chang, M. T.; Su, C. Y.; Chang, C. S.; Li, H.; Shi, Y.; Zhang, H.; et al. Growth of Large-Area and Highly Crystalline MoS₂ Thin Layers on Insulating Substrates. *Nano Lett.* **2012**, *12*, 1538–1544.
- (15) Yoon, Y.; Ganapathi, K.; Salahuddin, S. How Good Can Monolayer MoS₂ Transistors Be? *Nano Lett.* **2011**, *11*, 3768–3773.
- (16) Liu, L.; Bala Kumar, S.; Ouyang, Y.; Guo, J. Performance Limits of Monolayer Transition Metal Dichalcogenide Transistors. *IEEE Trans. Electron Devices* **2011**, *58*, 3042–3047.
- (17) Wu, C. C.; Jariwala, D.; Sangwan, V. K.; Marks, T. J.; Hersam, M. C.; Lauhon, L. J. Elucidating the Photoresponse of Ultrathin MoS₂ Field-Effect Transistors by Scanning Photocurrent Microscopy. *J. Phys. Chem. Lett.* **2013**, *4*, 2508–2513.
- (18) Komsa, H. P.; Kotakoski, J.; Kurasch, S.; Lehtinen, O.; Kaiser, U.; Krasheninnikov, A. V. Two-Dimensional Transition Metal Dichalcogenides under Electron Irradiation: Defect Production and Doping. *Phys. Rev. Lett.* **2012**, *109*, 035503.
- (19) Dolui, K.; Rungger, I.; Pemmaraju, C. D.; Sanvito, S. Possible Doping Strategies for MoS₂ Monolayers: An Ab Initio Study. *Phys. Rev. B* **2013**, *88*, 075420.
- (20) Ataca, C.; Ciraci, S. Functionalization of Single-Layer MoS₂ Honeycomb Structures. *J. Phys. Chem. C* **2011**, *115*, 13303–13311.
- (21) Chang, J.; Larentis, S.; Tutuc, E.; Register, L. F.; Banerjee, S. K. Atomistic Simulation of the Electronic States of Adatoms in Monolayer MoS₂. *Appl. Phys. Lett.* **2014**, *104*, 141603.

- (22) Rastogi, P.; Kumar, S.; Bhowmick, S.; Agarwal, A.; Chauhan, Y. S. Ab-initio Study of Doping Versus Adsorption in Monolayer MoS₂. *Proc. Int. Conf. Emerging Electron. (Bangalore, India)* **2014**, accepted.
- (23) Sofo, J. O.; Chaudhari, A. S.; Barber, G. D. Graphane: A Two-dimensional Hydrocarbon. *Phys. Rev. B* **2007**, *75*, 153401.
- (24) Valencia, H.; Gil, A.; Frapper, G. Trends in the Adsorption of 3d Transition Metal Atoms onto Graphene and Nanotube Surfaces: A DFT Study and Molecular Orbital Analysis. *J. Phys. Chem. C* **2010**, *114*, 14141–14153.
- (25) Chan, K. T.; Neaton, J. B.; Cohen, M. L. First-principles Study of Metal Adatom Adsorption on Graphene. *Phys. Rev. B* **2008**, *77*, 235430.
- (26) Fang, H.; Tosun, M.; Seol, G.; Chang, T. C.; Takei, K.; Guo, J.; Javey, A. Degenerate n-Doping of Few-Layer Transition Metal Dichalcogenides by Potassium. *Nano Lett.* **2013**, *13*, 1991–1995.
- (27) Das, S.; Chen, H. Y.; Penumatcha, A. V.; Appenzeller, J. High Performance Multilayer MoS₂ Transistors with Scandium Contacts. *Nano Lett.* **2013**, *13*, 100–105.
- (28) Popov, I.; Seifert, G.; Tománek, D. Designing Electrical Contacts to MoS₂ Monolayers: A Computational Study. *Phys. Rev. Lett.* **2012**, *108*, 156802.
- (29) Sachs, B.; Britnell, L.; Wehling, T. O.; Eckmann, A.; Jalil, R.; Belle, B. D.; Lichtenstein, A. I.; Katsnelson, M. I.; Novoselov, K. S. Doping Mechanisms in Graphene-MoS₂ Hybrids. *Appl. Phys. Lett.* **2013**, *103*, 251607.
- (30) Atomistix ToolKit version 13.8.1. QuantumWise A/S (www.quantumwise.com).
- (31) Brandbyge, M.; Mozos, J. L.; Ordejón, P.; Taylor, J.; Stokbro, K. Density-functional Method for Nonequilibrium Electron Transport. *Phys. Rev. B* **2002**, *65*, 165401.
- (32) Soler, J. M.; Artacho, E.; Gale, J. D.; Garcia, A.; Junquera, J.; Ordejón, P.; Portal, D. S. The SIESTA Method for Ab Initio Order- N Materials Simulation. *J. Phys.: Condens. Matter* **2002**, *14*, 2745–2779.
- (33) Sheppard, D.; Terrell, R.; Henkelman, G. Optimization Methods for Finding Minimum Energy Paths. *J. Chem. Phys.* **2008**, *128*, 134106.
- (34) Perdew, J. P.; Zunger, A. Self-interaction Correction to Density-Functional Approximations for Many-electron Systems. *Phys. Rev. B* **1981**, *23*, 5048–5079.
- (35) Pulay, P. Convergence Acceleration of Iterative Sequences. The Case of SCF Iteration. *Chem. Phys. Lett.* **1980**, *73*, 393–398.
- (36) Mulliken, R. S. Electronic Population Analysis on LCAO - MO Molecular Wave Functions. II. Overlap Populations, Bond Orders, and Covalent Bond Energies. *J. Chem. Phys.* **1955**, *23*, 1841–1846.
- (37) Chhowalla, M.; Shin, H. S.; Eda, G.; Li, L. J.; Loh, K. P.; Zhang, H. The Chemistry of Two-dimensional Layered Transition Metal Dichalcogenide Nanosheets. *Nat. Chem.* **2013**, *5*, 263–275.
- (38) Xu, X.; Yao, W.; Xiao, D.; Heinz, T. F. Spin and Pseudospins in Layered Transition Metal Dichalcogenides. *Nat. Phys.* **2014**, *10*, 343–350.
- (39) Streetman, B. G.; Banerjee, S. K. *Solid State Electronic Devices*; Prentice-Hall series in solid state physical electronics; Pearson Prentice Hall: New York, 2006.
- (40) Du, Y.; Liu, H.; Neal, A. T.; Si, M.; Ye, P. D. Molecular Doping of Multilayer MoS₂ Field-Effect Transistors: Reduction in Sheet and Contact Resistances. *Electron Device Lett., IEEE* **2013**, *34*, 1328–1330.