Chalcogenide Letters Vol. 14, No. 11, November 2017, p. 475 - 482

ELECTRONIC AND MAGNETIC PROPERTIES OF TRANSITION METAL ATOMS ADSORBED SnS_2 MONOLAYERS

Y. Z. WANG[a*], R. HUANG[a], F. J. KONG[b], B. L. GAO[a], G. HU[a], Y. L. MA[a]
[a]*Department of Applied Physics, Huaiyin Institute of Technology, Jiangsu, 223003, China*
[b]*Department of Physics, Yancheng Institute of Technology, Jiangsu, 224051, China*

The structural, electronic and magnetic properties of transition metal (TM) (from Sc to Zn) atoms adsorbed SnS_2 monolayer have been systematically investigated using density functional theory (DFT). The theoretical results show that the most stable adsorption site is above the Sn atom among the possible adsorption sites, and all the TM atoms are chemically adsorbed on the SnS_2 monolayer. The V, Cr, Mn, Fe and Co adsorbed monolayer SnS_2 exhibit magnetism, while Sc, Ti, Ni, Cu and Zn adsorbed systems are nonmagnetic. Interestingly, the narrow band gap nonmagnetic semiconductor, half semiconductor, bipolar magnetic semiconductor, and nonmagnetic or magnetic metal can be realized in different TM atoms adsorbed SnS_2 monolayers.

(Received September 25, 2017; Accepted November 6, 2017)

Keywords: SnS_2 monolayer, Transition metal, Electronic structure, Magnetic property, Density functional theory

1. Introduction

In recent years, with the successful synthesis of graphene and the rapid development of graphene-based devices[1], analogous atomically thick two-dimensional (2D) layered materials have attracted extensive research attentions for their promising applications in electronic, optoelectronics and spintronics, such as BN[2], GaN[3], MoS_2 and SnS_2[4-10]. Among them, as a typical layered chalcogenide material, SnS_2 is an earth-abundant, nontoxic and environment-friendly semiconductor, which shows distinct electronic, optical, and catalytic properties. Recently, SnS_2 monolayer has been successfully synthesized by liquid and mechanical exfoliation strategies, respectively[8,11]. Many possible applications have been investigated, such as photocatalytic[11-13], field effect emission and lithium-ion batteries[14-18]. On the other hand, previous studies have showed that monolayer SnS_2 is nonmagnetic semiconductor, to explore the monolayer SnS_2-based electronics and spintronics devices, developing approaches to effectively induce and manipulate the magnetic ground states are quite vital. To date, some methods have been investigated to modulate the electronic and magnetic properties of the SnS_2 monolayer, such as various intrinsic defects[19], strain and chemical doping[4,5,7,20,21]. It is well known that chemical adsorption is a promising and effective method to induce and control the electronic and magnetic properties of materials, and it has demonstrated great potential in many materials, such as graphene[22-24], BN monolayer[25-27], ReS_2 and MoS_2 monolayer[28-31]. However, to our knowledge, there are no systematic studies on the structures, electronic and magnetic properties of TM (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn) atoms adsorbed SnS_2 monolayer.

In this paper, the stable structure, adsorption energy, electronic structure and magnetic properties of TM atom adsorbed on the SnS_2 monolayer were explored using density functional theory. Our results show that all the TM atoms prefer to the site above the Sn atom, and the

*Corresponding author: wyzong@hyit.edu.cn

electronic structures and magnetic properties of the SnS_2 monolayer can be effectively tuned by the adsorption of different TM atoms.

2. Computational methods

All the calculations in this work were performed using DFT methods with the projector augmented wave (PAW) potentials implemented in Vienna ab initio simulation package (VASP) code[32-34]. The exchange-correlation functional is treated within the generalized gradient approximation (GGA) and parameterized using the Perdew-Burke-Ernzerhofer (PBE) formula[35]. A plan-wave basis set with a cutoff energy of 500 eV was adopted to expand the electronic wave functions. A 4 × 4 × 1 supercell was used to model single TM atom adsorbed on SnS_2 monolayer, which ensure the separation between neighboring adatoms. A vacuum space of more than 15 Å was taken to avoid interactions between the neighboring slabs. The Billouin Zone (BZ) is sampled by the Monkhorst-Pack (MP) scheme with 5 × 5 × 1 and 11 × 11 × 1 for the geometrical optimization and electronic density of states (DOS), respectively[36]. During geometrical optimization, all the atomic positions were relaxed with the convergence thresholds less than 1.0×10^{-5} eV for energy and 0.01 eV/Å for force without any symmetry constraints.

In the present paper, we only consider single TM atom adsorbed on the different high symmetry sites of the SnS_2 monolayer. The configurations of the TM atoms adsorption systems are shown in Fig. 1. The structures of TS, TSn and H are, respectively, that the TM atom occupies the site above the S atom, Sn atom and the hollow site of the hexagonal ring. To explore the magnetic ground state of the adsorption system, we calculate the spin polarization energy (ΔE_{spin}): $\Delta E_{spin} = E_{NSP} - E_{SP}$, the E_{NSP} and E_{SP} are the total energy of the adsorbed system in the non-spin-polarized state and spin-polarized state, respectively. At the same time, to determine the stability of different adsorption systems, we have systematically calculated the adsorption energy (E_{ads}) using the formula[29]: $E_{ads} = E_{monolayer} + E_{atom} - E_{total}$, where, $E_{monolayer}$ is the total energy of the pure SnS_2 monolayer, E_{atom} is the total energy of the isolated TM atom in its ground state. E_{total} is the total energy of the optimized adsorption system. According to the definition of adsorption energy, the positive E_{ads} shows the adsorption process is exothermic. The accuracy of our calculations was carefully checked based on the pristine SnS_2 monolayer, in which the lattice constant was calculated to be 3.696 Å. This value was in good agreement with the previous studies[21,37].

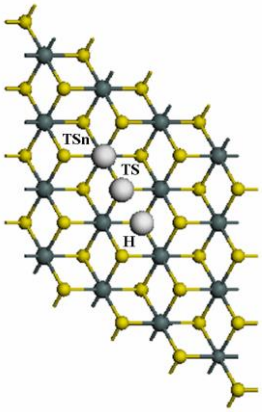

Fig. 1. Top view of three different adsorption sites of SnS_2 monolayer: TS, TSn and H stand for the site above S atom, Sn atom and the center of the hexagonal ring of SnS_2 monolayer, respectively. The yellow, gray and white spheres represent the S, Sn and TM atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article)

3. Results and discussion

To study the stability of TM atoms adsorbed on the SnS_2 monolayer, the adsorption energies of the most stable adsorption configurations are summarized in Table 1. It is shown that the TSn site is the most favorable surface adsorption site for all the TM atoms. At the same time, the adsorption energies also show that all the TM atoms can be chemically adsorbed on the SnS_2 monolayer. These results are some different from those that TM atoms adsorbed on the MoS_2 monolayer[31], which is mainly because of the different crystal structure of them. To investigate the interaction between TM atom and the nearest atom, Fig. 2 shows the comparison of the distance between TM atom and the nearest S (Sn) d_{TM-S} (d_{TM-Sn}) and the sum of the covalent radii $r_{TM}+r_S$ ($r_{TM}+r_{Sn}$). These results show that the bond length between TM atom and S is very close to the sum of the covalent radii for all the TM atom adsorbed system, even the maximum difference for the Mn adsorbed system is only 4.8%. These features indicate that the interaction between all TM atoms and the S atoms are the covalent interaction. At the same time, the bond lengths between TM atoms and Sn atoms for all the TM atoms are also close to the sum of covalent radii. Therefore, it is obvious that all the TM atoms considered can stronger bonding on the SnS_2 monolayer. The variation of the adsorption energies of the TM atoms at the most stable configurations with respect to the number of the 3*d* electrons (N_d) is shown in Fig. 3. The adsorption energies of the Cr and Mn with the half-filled *d* electrons (N_d=5) show the minima between two maxima (except Cu and Zn). The adsorption energy of Sc with the smallest number of *d* electrons (N_d=1) is the maximum. The second local maxima of the adsorption energy occur at N_d=8 (corresponding to Ni), which is smaller than that of V (N_d=3). While the adsorption energies of Cu and Zn with full filled *d* electrons (N_d=10) are small. The overall variation for adsorption energies of TM atoms with respect to the *d* electron is similar with the results of TM atoms adsorbed on the graphene and monolayer MoS_2 [31,38].

Table 1. Calculated adsorption energy (E_{ads}) of the TM atom adsorbed on SnS_2 monolayer at the most stable adsorption sites, spin polarization energy (ΔE_{spin}), the total magnetic moments (μ_{total}) of the system, the magnetic moments of the adatom (μ_{adatom}) and the free atom (μ_{atom}), the magnetic moments in the parentheses based on Hund's rule, amounts of charge transferred (CT) from the TM atom to SnS_2 monolayer.

Atom	Site	E_{ads} (eV)	ΔE_{spin} (eV)	μ_{total} (μ_B)	μ_{adatom} (μ_B)	μ_{atom} (μ_B)	CT(e)
Sc	TSn	5.752	0.000	0.000	0.000	1 (1)	1.600
Ti	TSn	5.727	0.000	0.000	0.000	4 (2)	1.347
V	TSn	4.955	0.405	2.707	1.852	5 (3)	1.095
Cr	TSn	3.407	1.096	4.000	3.114	6 (6)	0.892
Mn	TSn	3.468	1.152	4.316	3.659	5 (5)	0.857
Fe	TSn	4.124	0.393	2.000	2.075	4 (4)	0.570
Co	TSn	4.461	0.172	1.000	0.897	3 (3)	0.346
Ni	TSn	4.711	0.000	0.000	0.000	2 (2)	0.282
Cu	TSn	2.798	0.002	0.083	0.009	1 (1)	0.372
Zn	TSn	0.847	0.000	0.000	0.000	0 (0)	0.694

The electronic and magnetic properties of the SnS_2 monolayer can be modified by adsorption of TM atoms. In Table 1, we show the magnetic moments of the adsorption systems, TM adatoms and the ground state free TM atoms. According to the Table 1, we can see that the adsorptions of Sc, Ti, Ni and Zn do not induce any magnetism in these host SnS_2 monolayers. The

total magnetic moments of the V, Cr, Mn, Fe, Co, Cu adsorbed systems are 2.707, 4.000, 4.316, 2.000, 1.000, and 0.083 μ_B, respectively. We find the magnetic moment of Cu adsorbed system is very small. To check the stability of the magnetic ground state, we show the spin polarization energy (ΔE_{spin}) in Table 1. From the results, we can see that Sc, Ti, Ni and Zn adsorbed systems are non-spin polarized. The values of ΔE_{spin} for the V, Cr, Mn, Fe and Co adsorbed systems are much greater than the thermal energy at room temperature, indicating that the magnetism in these systems is stable. While ΔE_{spin} of the Cu adsorbed system is only 0.002 eV, which is smaller than the thermal energy at room temperature. So the magnetism of Cu adsorbed system is not stable. It also can be seen that the sequence of ΔE_{spin} value is similar to that of magnetic moment of the TM atom adsorbed system. At the same time, we find that the local magnetic moments of V, Cr, Mn, Fe and Co are smaller than that of the free TM atoms. To explore the origin of the reduction of the magnetic moment for the TM adatoms, the charge transfer between the TM adatoms and the SnS_2 monolayers are calculated by Bader charge analysis[39], as listed in Table 1. From the results, it can be seen that there are obvious electrons transfer from TM atoms to the SnS_2 monolayer, indicating strong coupling between TM adatoms and the SnS_2 monolayer, which will induce the reduction of magnetic moments of the TM adatoms. At the same time, we find that the number of electrons transferred for all the TM adatoms considered is consistent with the Pauling electronegativity of the TM atoms except for Mn, which mainly attributes to the relative larger distance between Mn atom and the S atom of the surface, as shown in Fig. 2. The contributions of the adatoms V, Cr, Mn, Fe and Co to the total magnetic moments are 68.4%, 77.9%, 84.8%, 103.7% and 89.7%, respectively. So the magnetism of these magnetic systems mainly attributes to the TM adatoms. In order to study the mechanisms of forming magnetic moment, we show the spin density contour of the magnetic system in Fig. 4. It can be seen that the spin density is mainly localized around the TM adatoms, the magnetic moment of the nearest S atom mainly attributes to the *p* orbital. At the same time, the spatial extensions of the spin density in V and Cr adsorbed systems are much larger than that in Mn, Fe and Co adsorbed cases, which is important to achieve long-range magnetic coupling interaction at low adsorption concentrations. In Fig. 4, we also find the nearest S and Sn atoms have opposite spin density with the TM atoms, especially, which induce the total magnetic moment is smaller than the local moment of the Fe adatom for Fe adsorbed system. Fig. 5 shows the projected density of states (PDOS) of TM adatoms. Fig. 5 shows the spin up and spin down PDOS of the Sc, Ti, Ni and Zn adatoms are symmetric, which is also in good agreement with the calculated total magnetic moment of 0 μ_B in these systems. While the PDOS of the Cu adatom shows small spin polarized, even it can be negligible. At the same time, the magnetic moments of the V, Cr, Mn, Fe and Co adatoms are mainly contributed from the 3*d* electron orbital.

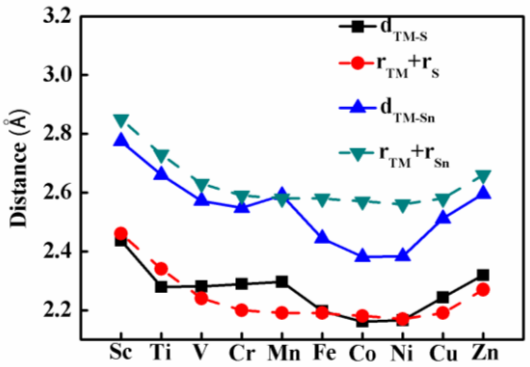

Fig. 2. Calculated the distances (d_{TM-S}, d_{TM-Sn}) between TM adatom and the nearest S (Sn) atom corresponding to the most stable adsorption configurations. The dashed line represents the sum of the covalent radii r_S (r_{Sn}) and r_{TM} for S (Sn) and TM.

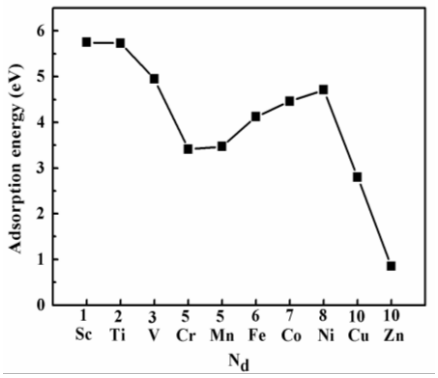

Fig. 3. Variation of the adsorption energies with respect to the number of d electrons in the TM atom

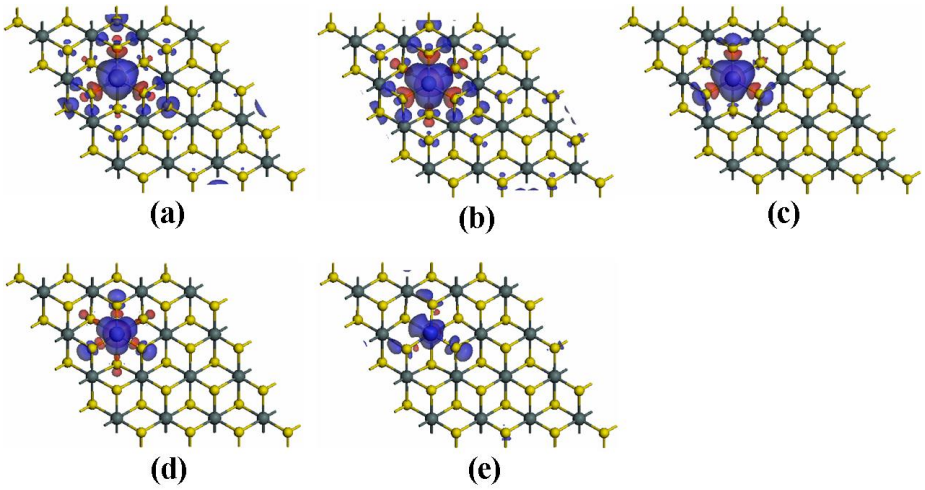

Fig. 4. Spin density distribution of (a) V, (b) Cr, (c) Mn, (d) Fe and (e) Co adsorbed on the monolayer SnS_2 for the most stable configuration. Blue and red distributions correspond to positive (spin up) and negative (spin down) values, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article)

Finally, we study the spin-polarized total density of states (TDOS) for the pristine and TM atoms adsorbed SnS_2 monolayer, as show in Fig. 6. The pristine SnS_2 monolayer is nonmagnetic semiconductor with the band gap of 1.577 eV, which is consistent with the previous reports[37]. The DOSs of spin up and spin down are symmetrical near the Fermi level for the Sc, Ti, Ni, and Zn adsorbed system, which implies the systems should be nonmagnetic. We also find the Sc and Ti adsorbed system are metal, while the Ni and Zn adsorbed system are still semiconductor with the band gap of about 0.628 eV and 0.516 eV, respectively. According to Fig. 6, we can see that the Cu adsorbed system is metal, and the spin splitting is negligible. For the V, Cr, Mn, Fe and Co adsorbed SnS_2 monolayer, the adatoms bring the spin polarized impurity states in the gap. Among them, the valence band and conduction band edges around the Fermi level of the Fe and Co adsorbed systems are contributed by the same spin component, therefore, they are half semiconductors[40]. However, for the Cr adsorbed system, the occupied and unoccupied states near the Fermi level belong to different spins, which shows that the Cr adsorbed SnS_2 is a bipolar magnetic semiconductor (BMS) material[41]. While the Mn adsorbed SnS_2 monolayer is magnetic metal.

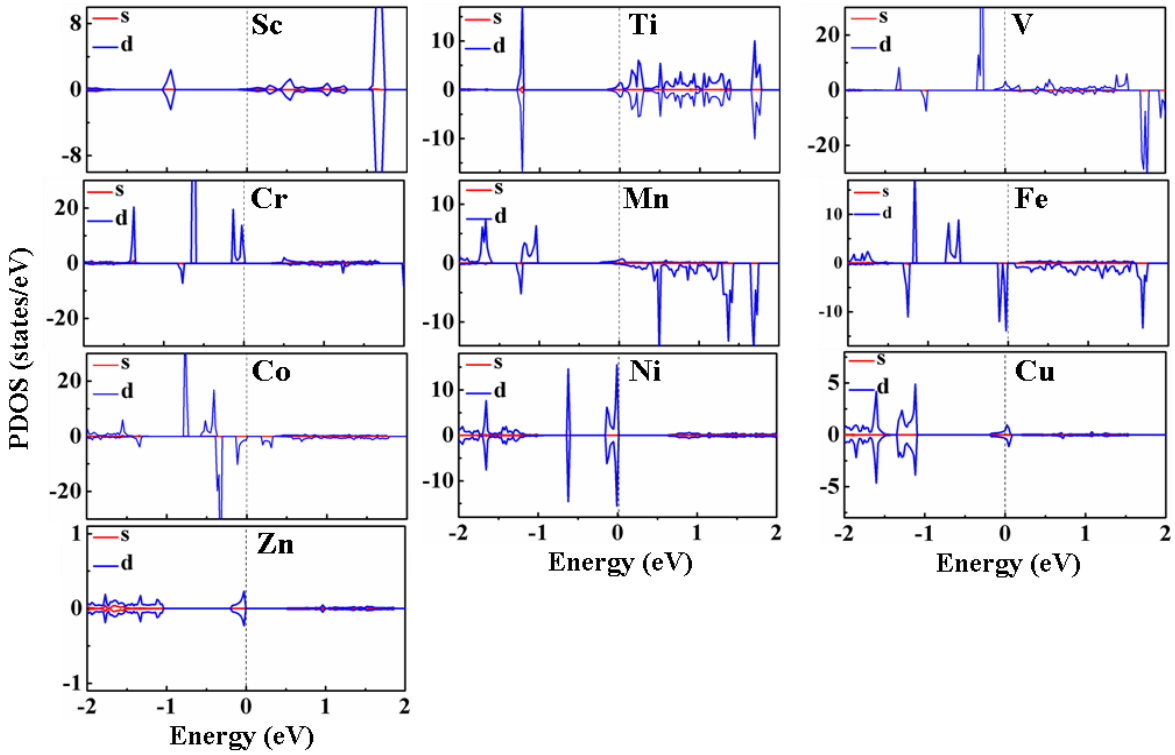

Fig. 5. PDOS of the TM adatoms (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn) for the most stable configurations. The Fermi level is set to zero energy with the vertical black dashed line.

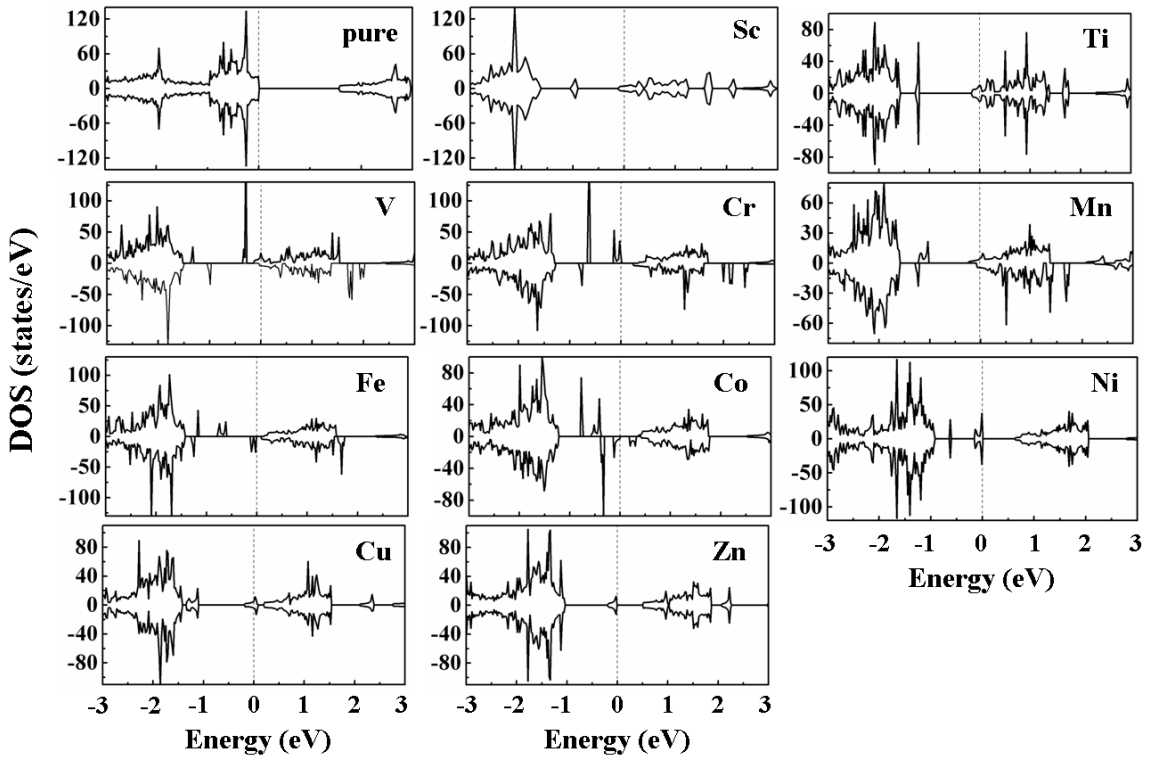

Fig. 6. Calculated spin-polarized TDOS of pristine and TM atom adsorbed SnS_2 monolayer. The Fermi level is set to zero energy with the vertical black dashed line.

4. Conclusions

In summary, we have systematically studied the most stable adsorption configurations, electronic structures and magnetic properties of the TM atoms adsorbed SnS_2 monolayer by density functional theory. It is found that the most favorable adsorption site is above the Sn atom for all the TM atoms considered, and all these adatoms can be chemically adsorbed on the SnS_2 monolayer. The variation of the adsorption energy may be related to the number of the *d* electrons for the TM adatoms. The Sc, Ti, Ni, Cu and Zn adsorbed SnS_2 monolayer is nonmagnetic, while the V, Cr, Mn, Fe and Co adsorbed monolayer SnS_2 produce magnetism. The magnetic moments of the adsorbed systems are mainly contributed by the TM adatoms. Interestingly, the electronic structure of the SnS_2 monolayer can be widely modulated by the TM adatoms. The narrow gap nonmagnetic semiconductor, half semiconductor, bipolar magnetic semiconductor, and nonmagnetic or magnetic metal can be obtained in different TM atom adsorbed SnS_2 monolayer. These results suggest that the TM atoms adsorbed SnS_2 monolayers are the potential material for future optoelectronic and spintronic devices.

Acknowledgements

This work was supported by the Foundation for the National Natural Science Foundation of China (11604113) and Jiangsu Overseas Research & Training Program for University Prominent Young & Middle-aged Teachers and Presidents.

References

[1] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, Science **306**, 666 (2004).
[2] D. Golberg, Y. Bando, Y. Huang, T. Terao, M. Mitome, C.C. Tang, C.Y. Zhi, ACS Nano **4**, 2979 (2010).
[3] D.C. Camacho-Mojica, F. López-Urías, Sci. Rep. **5**, 17902 (2015).
[4] W. Zhou, N. Umezawa, Phys. Chem. Chem. Phys. **18**, 7860 (2016).
[5] L.L. Sun, W. Zhou, Y.Y. Liu, D.D. Yu, Y.H. Liang, P. Wu, RSC Adv. **6**, 3480 (2016).
[6] C.X. Xia, Y.T. Peng, H. Zhang, T.X. Wang, S.Y. Wei, Y. Jia, Phys. Chem. Chem. Phys. **16**, 19674 (2014).
[7] Y.M. Liu, F. Wang, D.C. Kong, B. Hu, C.X. Xia, J.X. Su, Phys. Lett. A **381**, 1732 (2017).
[8] Y. Huang, E. Sutter, J.T. Sadowski, M. Cotlet, O.L.A. Monti, D.A. Racke, M.R. Neupane, D. Wickramaratne, R.K. Lake, B.A. Parkinson, P. Sutter, ACS Nano **8**, 10743 (2014).
[9] S. Manzeli, A. Allain, A. Ghadimi, A. Kis, Nano Lett. **15**, 5330 (2015).
[10] L. Yang, X.D. Cui, J.Y. Zhang, K. Wang, M. Shen, S.S. Zeng, S.A. Dayeh, L. Feng, B. Xiang, Sci. Rep. **4**, 5649 (2014).
[11] Y.F. Sun, H. Cheng, S. Gao, Z.H. Sun, Q.H. Liu, Q. Liu, F.C. Lei, T. Yao, J.F. He, S.Q. Wei, Y. Xie, Angew. Chem. Int. Ed. **51**, 8727 (2012).
[12] H.L. Zhuang, R.G. Hennig, Phys. Rev. B **88**, 115314 (2013).
[13] J. Yu, C.Y. Xu, F.X. Ma, S.P. Hu, Y.W. Zhang, L. Zhen, ACS Appl. Mater. Interfaces **6**, 22370 (2014).
[14] T.S. Pan, D. De, J. Manongdo, A.M. Guloy, V.G. Hadjiev, Y. Lin, H.B. Peng, Appl. Phys. Lett. **103**, 093108 (2013).

[15] H.S. Song, S.L. Li, L. Gao, Y. Xu, K. Ueno, J. Tang, Y.B. Cheng, K. Tsukagoshi, Nanoscale **5**, 9666 (2013).
[16] D.S. Guan, L.L. Ma, D.Q. Pan, J.Y. Li, X.F. Gao, Y.Y. Xie, M. Qiu, C. Yuan, Electrochim. Acta **242**, 117 (2017).
[17] Z.X. Liu, H.Q. Deng, P.P. Mukherjee, ACS Appl. Mater. Interfaces **7**, 4000 (2015).
[18] Y.C. Huang, C.Y. Ling, X. Chen, D.M. Zhou, S.F. Wang, RSC Adv. **5**, 32505 (2015).
[19] L.L. Sun, W. Zhou, Y.Y. Liu, Y.L. Lu, Y.H. Liang, P. Wu, Comp. Mater. Sci. **126**, 52 (2017).
[20] D.D. Yu, Y.Y. Liu, L.L. Sun, P. Wu, W. Zhou, Phys. Chem. Chem. Phys. **18**, 318 (2016).
[21] H. Xiang, B. Xu, Y.D. Xia, J. Yin, Z.G. Liu, Sci. Rep. **6**, 39218 (2016).
[22] M. Sargolzaei, F. Gudarzi, J. Appl. Phys. **110**, 064303 (2011).
[23] C. Cao, M. Wu, J.Z. Jiang, H.P. Cheng, Phys. Rev. B **81**, 205424 (2010).
[24] F. Shayeganfar, J. Beheshtiyan, M. Neek-Amal, R. Shahsavari, Nanoscale **9**, 4205 (2017).
[25] D.W. Ma, Z.S. Lu, W.W. Ju, Y.A. Tang, J. Phys.: Condens. Matter **24**, 145501 (2012).
[26] J. Li, M.L. Hu, Z.Z. Yu, J.X. Zhong, L.Z. Sun, Chem. Phys. Lett. **532**, 40 (2012).
[27] M. Forster, J.E. Parker, A. Inaba, C.A. Murray, N.A. Strange, J.Z. Larese, T. Arnold, J. Phys. Chem. C **120**, 25796 (2016).
[28] X.O. Zhang, Q.F. Li, J. Appl. Phys. **118**, 064306 (2015).
[29] Z.Y. Huang, G.L. Hao, C.Y. He, H. Yang, L. Xue, X. Qi, X.Y. Peng, J.X. Zhong, J. Appl. Phys. **114**, 083706 (2013).
[30] C. Gonzalez, B. Biel, Y.J. Dappe, Phys. Chem. Chem. Phys. **19**, 9485 (2017).
[31] Y.Z. Wang, B.L. Wang, R. Huang, B.L. Gao, F.J. Kong, Q.F. Zhang, Physica E **63**, 276 (2014).
[32] P.E. Blöchl, Phys. Rev. B **50**, 17953 (1994).
[33] G. Kresse, J. Furthmüller, Comp. Mater. Sci. **6**, 15 (1996).
[34] G. Kresse, J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
[35] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[36] H.J. Monkhorst, J.D. Pack, Phys. Rev. B **13**, 5188 (1976).
[37] L. Ao, A. Pham, H.Y. Xiao, X.T. Zu, S. Li, Phys. Chem. Chem. Phys. **18**, 25151 (2016).
[38] H. Valencia, A. Gil, G. Frapper, J. Phys. Chem. C **114**, 14141 (2010).
[39] G. Henkelman, A. Arnaldsson, H. Jónsson, Comp. Mater. Sci. **36**, 354 (2006).
[40] X.X. Li, J.L. Yang, J. Mater. Chem. C **2**, 7071 (2014).
[41] X.X. Li, X.J. Wu, Z.Y. Li, J.L. Yang, J.G. Hou, Nanoscale **4**, 5680 (2012).