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Nitrogen Dioxide Gas Sensor Based on Monolayer SnS: A First-principles Study

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***Abstract*—The sensing behavior of monolayer SnS for four gas molecules (NH_3, NO_2, CO, and H_2O) are studied by first-principles calculation based on density-functional theory. We calculate adsorption energy, adsorption distance, and hirshfeld charge to estimate the adsorption ability of monolayer SnS for these gases. The results demonstrate that all the gas molecules show physisorption nature. We further calculate the current-voltage (I-V) curves using the nonequilibrium Green's function (NEGF) formalism for evaluating the NO_2 gas sensing properties. The monolayer SnS is found to be strongly sensitive to NO_2 molecule dependent on moderate adsorption energy, excellent charge transfer, and significant change of I-V property before and after gas adsorption. Therefore, we suggest that monolayer SnS can be a prominent candidate for application as NO_2 gas sensor.**

***Index Terms*—Density-functional theory, monolayer SnS, nitrogen dioxide, gas sensor.**

I. Introduction

SENSING gas molecules, especially toxic gas, is critical in environmental pollution monitoring, agricultural, and medical applications [1]. NO_2 is recognized as an air pollutant and has been released during many types of fuel combustions. Moreover, NO_2 plays an important role in producing acid rain [2], which does great harm to both human and environment. Great efforts have been made in the development of NO_2 sensors as a safety precaution device [3, 4]. However, some available NO_2 sensors based on metal oxides usually show either poor selectivity or high operation temperature [5, 6]. Therefore, it is in great need of NO_2 gas sensors with considering sensitivity, selectivity, and low-cost.

Two-dimensional (2D) materials have great potential for gas sensors [7, 8] owing to their rapid response and the associated charge transfer between gas molecules and the substrates. Due to the enhanced surface to volume ratio, 2D transition metal dichalcogenides (TMDCs) and transition metal oxides (TMOs) are becoming more prevalent in gas sensing [9, 10]. Wang *et al*. have concluded that only binary TMOs and post-transition metal oxides find their gas sensor application [11]. However, few work has been done on post-TMDC for gas sensor. Recently, a new binary monochalcogenide layered material, tin sulfide (SnS) with topological superconductivity, excellent electronic and optical properties, a potential earth-abundant photovoltaic (PV) material, has been attracted increasing attention for application in photodetector [12] and energy storage [13], etc. Some theoretical studies have reported on the electronic properties of single-layer or multi-layer SnS [14]. The properties of monolayer and few layer SnS are different, such as the optoelectronic properties of the material vary significantly with respect to the number of layers and the band gap is wider for fewer layers. Despite these interesting studies, the sensing behavior of SnS for small molecules, such as NH_3, NO_2, CO and H_2O, is still lacking. In this letter, we investigate the effect of gas adsorption on monolayer SnS in a systematic understanding. And our work confirms the SnS has dramatic performance in gas sensing.

II. Theory and Simulations

First-principles calculations are performed using the DMol^3 package based on density-functional theory (DFT). The exchange correlation interaction is treated by generalized gradient approximation (GGA) with Perdew-Burke-Ernzerh (PBE) functional [15, 16]. We use Grimme [17] custom method for DFT-D to describe tiny van der Waals interaction. The Brillouin zone integration is sampled by 8×8×1 k-grid mesh for a 3×3 supercell (36 atoms) model. Periodic boundary conditions are applied in the x- and y- directions. The vacuum space is set as 20 Å to reduce interaction of the adjacent layers in the z-direction. All of the atomic positions are optimized until the maximum force is less than 0.002 Ha/Å. In order to characterize the adsorption strength between gas molecules and monolayer SnS, the adsorption energy (E_{ad}) defined as $E_{ad}=E_{SnS+gas}-E_{SnS}-E_{gas}$, where $E_{SnS+gas}$, E_{SnS}, and E_{gas} represent the total energy of SnS-gas adsorption system, pristine SnS sheet, and free gas molecules, respectively. The electron localization function (ELF) is calculated by CASTEP code. The electronic transport properties are investigated by the nonequilibrium Green's function (NEGF) formalism [18] within the Atomistix ToolKit

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(ATK) package. The electric current through the contact region is calculated by the following formula:

$$I(V_b) = G_0 \int_{\mu_L}^{\mu_R} T(E, V_b)\, dE \qquad (1)$$

where V_b is the bias voltage, $G_0 = 2e^2h^{-1}$ is the unit of quantum conductance, $\mu_L$and μ_R are the chemical potentials of left and right electrodes and $T(E, V_b)$ represents the bias-dependent transmission coefficient.

III. Results and Discussion

To understand the sensing behaviour of monolayer SnS for gas molecules (NH_3, NO_2, CO and H_2O), we calculate different adsorption configurations. The most stable adsorption configurations for NH_3 and NO_2 molecule are shown in Fig. 1. More detailed information from the simulation of different molecule-SnS systems, including adsorption energies (E_{ad}), equilibrium distances (d), and Hirshfeld charge (Q) are listed in Table 1. The d is the shortest distance between the atoms of monolayer SnS and molecule. The negative sign of Q indicates charge transfers from SnS to molecule. The E_{ad} of -0.438 eV is calculated for NH_3 adsorption on monolayer SnS (Fig. 1a) associated with the d of 2.76 Å that is larger than the sum of the covalent radii of N and Sn atoms (2.11 Å)[19], indicating physisorption interaction nature. In the case of NO_2, the most stable adsorption configuration is shown in Fig. 1b. This structure has the E_{ad} of -0.9 eV and the separation distance of 2.47 Å. Because NO_2 is a paramagnetic molecule, the adsorption introduces stronger doping and produces larger E_{ad}. The E_{ad} value is significantly larger than that of NO_2 adsorption on phosphorene (0.5 eV)[20], indicating a higher level detection sensitivity can be achieved using SnS based sensors compared to phosphorene. The adsorption of CO and H_2O on monolayer SnS produces weaker binding energies (-0.190 eV and -0.388 eV) with smaller value of charge transfer (-0.006 eV and -0.055 eV), indicating that SnS is unpromising sensing material of gas sensors to detect the two molecules.

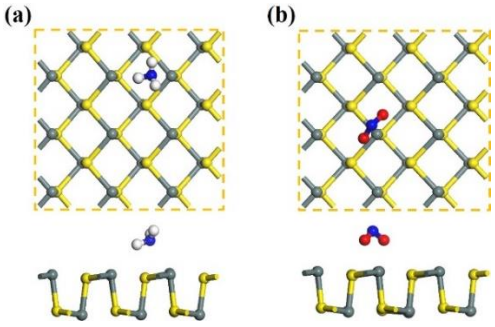

Fig.1. The most stable configuration for (a) NH_3 and (b) NO_2 on monolayer SnS. (The yellow and gray balls represent S and Sn atoms, where blue, white and red represent N,H and O atoms, respectively).

TABLE 1

THE ADSORPTION ENERGY, ADSORPTION DISTANCE AND HIRSHFELD CHARGE OF DIFFERENT GAS ON TIN SULFIDE

gas	E_{ad} (eV)	d (Å)	Q (e)
NH_3	-0.439	2.76	0.085
NO_2	-0.900	2.47	-0.307
CO	-0.190	3.29	-0.006
H_2O	-0.388	2.72	-0.055

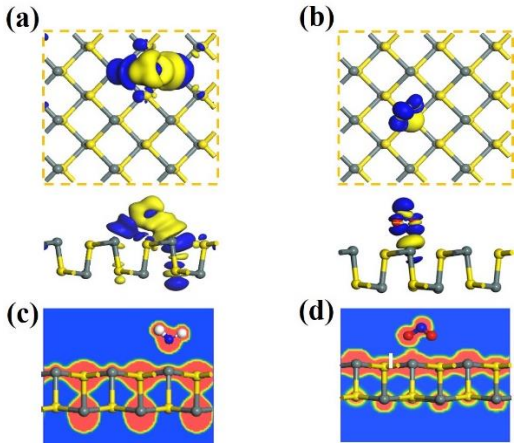

Fig. 2. The CDD for (a) NH_3 and (b) NO_2 adsorbed on monolayer SnS. The isosurface is taken as 0.003 e Å^{-3}. (c) and (d) are the corresponding ELF plots.

To further explore the interaction between gas molecule and SnS, the charge density difference (CDD) are presented in Fig. 2. The blue and yellow regions show charge accumulation and depletion, respectively. The CDD for NH_3/SnS system shows that the charge is depleted on NH_3 molecule (Fig. 2a) and charge accumulated on SnS surface. As a result, NH_3 acts as a charge donor and provides 0.085 e to monolayer SnS. In the case of NO_2 (Fig. 2b), most charge accumulated on NO_2 molecule surface, while charge depleted on top surface of SnS. The results reveal that NO_2 acts as charge acceptor with larger charge transfer (-0.307 e) because the spin-induced magnetic moment leads to a strong doping. Moreover, the grade of ELF is encoded using a color scheme in which high values correspond to orange and low values to blue. The ELF plot clearly shows that there is no electron sharing between gas molecules (NH_3 and NO_2) and SnS, which proves powerfully the interaction is physical adsorption.

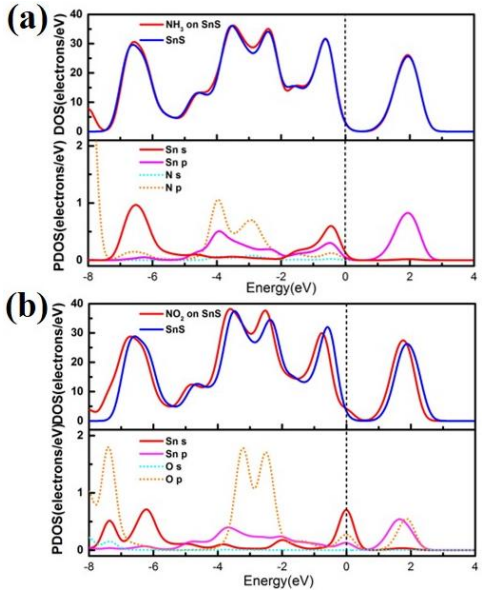

Fig. 3. The total DOS and PDOS for (a) NH_3 and (b) NO_2 adsorbed on monolayer SnS. The Fermi level is set to zero.

The density of states (DOS) and PDOS profiles are presented in Fig. 3. The total DOS of NH_3/SnS system (Fig. 3a) does not change much compared with the pristine SnS, indicating that the outstanding electronic properties of SnS stay unaffected after adsorption. It is find that there is no phenomenon of orbital hybridization in the NH_3/SnS structure. The contribution of NH_3 electronic level to the total DOS is localized between -4 eV to -2 eV in the valence band, which is far away from the Fermi level. For the NO_2 on monolayer SnS (Fig. 3b), the strong interaction causes a dramatic change of the DOS on both sides near the Fermi level. Besides, the Sn s and O p orbitals of the NO_2/SnS system share the similar states just above the Fermi level, indicating the strong orbital hybridization. The change of DOS, is expected to bring about obvious changes in the corresponding electronic properties of the SnS.

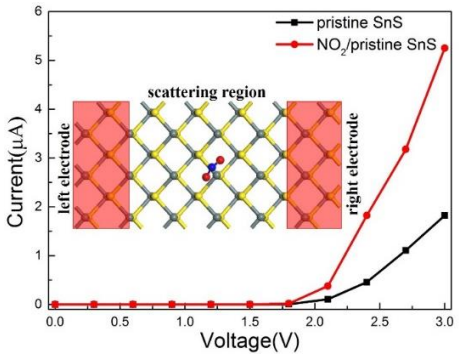

Fig.4. I-V characteristic curves of pristine SnS and NO_2 on SnS.

To observing clearly the conductivity modification, we calculate current-voltage (I-V) curves with and without NO_2 adsorption. The simulated I-V curves are plotted in Fig. 4. We find that it is almost no current when bias varies from 0 to 1.8 V due to the existence of band gap. When bias over 1.8 V, the current strats to increase dramatically. Under the bias of 3.0 V, the current passing through the pure SnS is 1.82 μA, while the current of SnS with the NO_2 adsorption under the same bias is increased to 5.25 μA, which is higher than that of silicon carbide nanotube [21] and carbon nanotube [22]. The DOS of SnS without and with NO_2 molecule adsorption is similar in the energy range of 1.8 to 3 eV. Nevertheless, the conductivity of SnS with NO_2 molecule is higher than that of pristine SnS. Because the charge transfer from SnS to NO_2 molecule, which is equivalent to hole doping for SnS and enhance its conductivity. Thus, SnS can be an excellent sensing material to detect NO_2.

IV. Conclusion

In summary, we systemically study the sensing behavior of monolayer SnS for gas molecules (NH_3, NO_2, CO, and H_2O) by using the first-principles calculation, and find the following interesting phenomenon: (1) NO_2 adsorption is a physisorption on monolayer SnS as compared with other gas molecules with the largest adsorption energy (-0.9 eV) and moderate charge transfer (-0.307 *e*), which is suitable for adsorption/desorption of gas molecules on/from SnS surface. Therefore, the excellent reversibility of gas sensor based on SnS is obtained. (2) The transport calculations indicate that NO_2 molecule adsorption on monolayer SnS increase the current, thus changing the resistance, which can be directly measured experimentally. Such sensitivity and selectivity for NO_2 molecule make SnS as a good candidate of a superior NO_2 gas sensor.

References

[1] J. Kong, N. R. Franklin, C. Zhou, M. G. Chapline, S. Peng, K. Cho, and H. *J. Dai*, "Nanotube molecular wires as chemical sensors," *Science*, vol. 287, pp. 622-625, Jan. 2000. doi: 10.1126/science. 287.5453.622

[2] R.Atkinson, "Atmospheric chemistry of VOCs and NO_x," *Atmospheric environment*, vol. 34, pp. 2063-2101, Aug. 1998. doi:10.1016/S1352-2310(99)00460-4

[3] J. Dai, P. Giannozzi, and J. Yuan, "Adsorption of pairs of NO_x molecules on single-walled carbon nanotubes and formation of NO+ NO_3 from NO_2," *Surface Science*, vol. 603, pp. 3234-3238, Sep. 2009. doi: 10.1016/j.susc.2009.09.010

[4] L. Kou, T. Frauenheim, and C. Chen, "Phosphorene as a Superior Gas Sensor: Selective Adsorption and Distinct I-V Response," *J Phys Chem Lett*, vol.5, pp. 2675-81, Aug. 2014. doi: 10.1021/jz501188k

[5] A. Afzal, N. Cioffi, L. Sabbatini, and L. Torsi, "NO_x sensors based on semiconducting metal oxide nanostructures: progress and perspectives," *Sensors and Actuators B: Chemical*, vol. 171, pp. 25-42, Aug-Sep. 2012. doi:10.1016/j.snb.2012.05.026

[6] G. F. Fine, L. M. Cavanagh, A. Afonja, and R. Binions, "Metal oxide semi-conductor gas sensors in environmental monitoring," *Sensors*, vol. 10, pp. 5469-5502, Jun. 2010. doi:10.3390/s100605469

[7] Z. Li, Y. Xiao, Y. Gong, Z. Wang, Y. Kang, S. Zu, and Z.Y.Fang, "Active light control of the MoS_2 monolayer exciton binding energy," *ACS nano*, vol. 9, pp. 10158-10164, Sep. 2015. doi:10.1021/acsnano.5b03764

[8] J. Z. Ou, W. Ge, B. Carey, T. Daeneke, A. Rotbart, W. Shan, and K.K. Zadeh, "Physisorption-based charge transfer in two-dimensional SnS_2 for selective and reversible NO_2 gas sensing," *ACS nano*, vol. 9, pp. 10313-10323, Oct. 2015. doi:10.1021/acsnano.5b04343

[9] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, and M. S. Strano, "Electronics and optoelectronics of two-dimensional transition metal dichalcogenides," *Nature nanotechnology*, vol.7, pp.699-712, Nov.2012. doi: 10.1038/NNANO.2012.193

[10] K. Kalantar-zadeh, J. Z. Ou, T. Daeneke, A. Mitchell, T. Sasaki, and M. S. Fuhrer, "Two dimensional and layered transition metal oxides," *Applied Materials Today*, vol.5, pp.73-89, Dec. 2016. https://doi.org/10.1016/j.apmt.2016.09.012

[11] C. Wang, L. Yin, L. Zhang, D. Xiang, and R. Gao, "Metal oxide gas sensors: sensitivity and influencing factors," *Sensors*, vol.10, pp.2088-2106, Mar. 2010. doi:10.3390/s 100302088

[12] G. Ozin and R. Bedard, "Adsorption and sensing properties of microporous layered tin sulfide materials," *Journal of Materials Chemistry*, vol. 8, pp. 1649-1656, Aug. 1998. doi:10.1039/A801501E

[13] M. Jayalakshmi, M. M. Rao, and B. Choudary, "Identifying nano SnS as a new electrode material for electrochemical capacitors in aqueous solutions," *Electrochemistry communications*, vol. 6, pp. 1119-1122, Sep. 2004. doi:10.1016/j.elecom.2004.09.004

[14] G. A. Tritsaris, B. D. Malone, and E. Kaxiras, "Optoelectronic properties of single-layer, double-layer, and bulk tin sulfide: A theoretical study,"*Journal of Applied Physics*,vol.113,p.233507, Jun.2013. doi: http://dx.doi.org/10.1063/1.4811455

[15] J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple," *Physical review letters*, vol. 77, p. 3865, Oct.1996. doi:10.1103/PhyRevLett.77.3865

[16] Q. Yang, R.-S. Meng, J.-K. Jiang, Q.-H. Liang, C.-J. Tan, M. Cai, and X.P. Chen, "First-Principles Study of Sulfur Dioxide Sensor Based on Phosphorenes," *IEEE Electron Device Letters*, vol. 37, pp. 660-662, Mar. 2016. doi:10.1109/LED.2016.2543243

[17] S. Grimme, "Semiempirical GGA-type density functional constructed with a long-range dispersion correction," *Journal of*

computational chemistry, vol. 27, pp. 1787-1799, Sep. 2006. doi:10.1002/jcc.20495

[18] X.-f. Yu, Y.-c. Li, J.-b. Cheng, Z.-b. Liu, Q.-z. Li, W.-z. Li, and B. Xiao, "Monolayer Ti_2CO_2: A Promising Candidate for NH_3 Sensor or Capturer with High Sensitivity and Selectivity," *ACS applied materials & interfaces*, vol. 7, pp. 13707-13713, Jun. 2015. doi:10.1021/acsami.5b03737

[19] A. Rodin, A. Carvalho, and A. C. Neto, "Strain-induced gap modification in black phosphorus," *Physical review letters*, vol. 112, p. 176801, Jan. 2014. doi: http://dx.doi.org/10.1103/Phys RevLett. 112.176801

[20] Y. Cai, Q. Ke, G. Zhang, and Y.-W. Zhang, "Energetics, charge transfer, and magnetism of small molecules physisorbed on phosphorene," *The Journal of Physical Chemistry C*, vol. 119, pp. 3102-3110, Jun. 2015. doi:10.1021/jp510863p

[21] D. Ruixue, Y. Yintang, and L. Lianxi, "Working mechanism of a SiC nanotube NO_2 gas sensor," *Journal of Semiconductors*, vol. 30, p. 114010, Nov. 2009. doi:10.1088/1674-4926/30/11/114010

[22] S. Sivasathya, D. J. Thiruvadigal, and S. M. Jaya, "Electron transport through metallic single wall carbon nanotubes with adsorbed NO_2 and NH_3 molecules: A first-principles study," *Chemical Physics Letters*, vol. 609, pp. 76-81, Jun. 2014. doi:http://dx.doi.org/10.1016/j.cplett.2014.06.038