Selective Gas Sensing With *h*-BN Capped MoS_2 Heterostructure Thin-Film Transistors

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***Abstract*— Owing to their ultimate surface-to-volume ratio two-dimensional (2D) van der Waals materials are candidates for flexible gas sensor applications. However, all demonstrated devices had relied on direct exposure of the active 2D channel to gases, which presents problems for their reliability and stability. We demonstrated, for the first time, selective gas sensing with molybdenum disulfide (MoS_2) thin films transistors capped with a thin layer of hexagonal boron nitride (*h*-BN). The resistance change, $\Delta R/R$, was used as a sensing parameter to detect chemical vapors. It was found that *h*-BN dielectric passivation layer does not prevent gas detection via changes in the current in the MoS_2 channel. The detection without direct contacting the channel with analyte molecules was achieved with $\Delta R/R$ ratio as high as 10^3. In addition, we show that the use of *h*-BN cap layers (thickness $H \sim 10$ nm) improves sensor stability and prevents degradation due to environmental and chemical exposure.**

***Index Terms*— Gas sensor, MoS_2, thin-film transistor, BN.**

I. Introduction

GAS sensing technology based on the relative resistance change upon the gas molecule adsorption and desorption enables fast speed and low cost sensors. Two-dimensional *van der Waals materials* such as graphene and MoS_2 are natural candidates for gas sensing applications owing to the ultimately high surface – to – volume - ratio of the 2D materials and the wide-range tunable Femi level [1]–[9]. The molecule adsorption and desorption on the surface of 2D channels tunes the local Fermi level and changes the resistance of the 2D channels. Unlike the zero band-gap graphene MoS_2 has a sizable energy band gap, which ranges from ∼1.1 to 1.9 eV [6]–[8] for the bulk and monolayer MoS_2 samples, respectively. The wide band gap of MoS_2 thin films results in a stronger effect on the source – drain current produced by the analyte molecules attached to the surface. We have recently demonstrated experimentally that the relative resistance change in MoS_2 thin film transistors (TFTs) is a better sensing parameter than that in graphene devices [6]. However, the graphene sensors are more suited for using the low-frequency current fluctuations as an additional sensing parameter [2], [10].

An important question, which arises in the context of the sensor applications of all van der Waals materials, is whether it is possible to use any protective cap layer or surface passivation without degrading the 2D channel sensing ability. All demonstrated devices had relied on direct exposure of the active 2D channel to gases, which presents problems for their reliability and stability. A prolonged exposure of TFTs with channels made of MoS_2 and other 2D materials degrades their sensing performance due to oxidation and surface contamination [11], [12]. Among 2D materials, *h*-BN is one of the most resistive to oxidation [13], [14]. It is rapidly becoming the material of choice for passivation of other 2D materials used in the active channel design [15]. In this Letter, we show that the *h*-BN capped MoS_2 heterostructure thin film transistors (HTFTs) retain their ability for gas sensing while becoming more robust and resistive to degradation.

II. Device Fabrication

For the proof-of-concept demonstration, the thin films of MoS_2 were mechanically exfoliated from the bulk crystal and transfer onto Si/SiO_2 substrate (300-nm thick oxide). The thickness of the resulting films was in the range from 2 nm to 9 nm as confirmed by the atomic force microscopy (AFM) measurements. The capping process was carried out right after identifying the desired MoS_2 layer for the channel fabrication. The selected *h*-BN layers were exfoliated and transferred onto the polydimethylsiloxane (PDMS) stamp. The stamp was then attached to a glass substrate. After the thin *h*-BN layer was identified by an optical microscope, the entire *h*-BN/PDMS/glass stack was mounted on an alignment stage. The stage movement was controlled by a micro-manipulator to accurately position the capping onto the target MoS_2 film [16]. We intentionally used the *h*-BN layers smaller in lateral size than the target MoS_2 channel layers so that the uncapped regions can be used to make contacts to metal electrodes. After the *h*-BN layer was placed on top of MoS_2 film, the PDMS stamp was peeled off leaving behind the *h*-BN capped MoS_2 thin-film channel. A standard electron-beam lithography (EBL) was used to gen-

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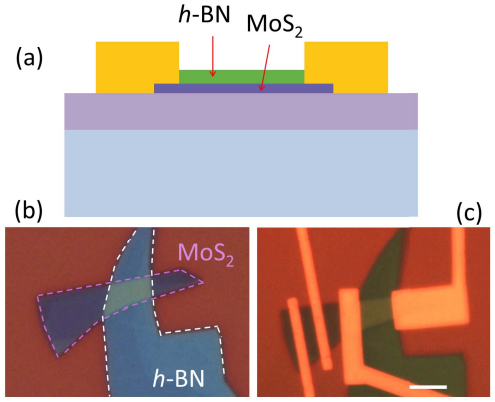

Fig. 1. (a) Schematics of the *h*-BN capped MoS_2 TFT. (b and c) Optical images of a representative *h*-BN capped MoS_2 stack and sensor device. The dash lines outline the *h*-BN and MoS_2 layers. The scale bar is 5 μm.

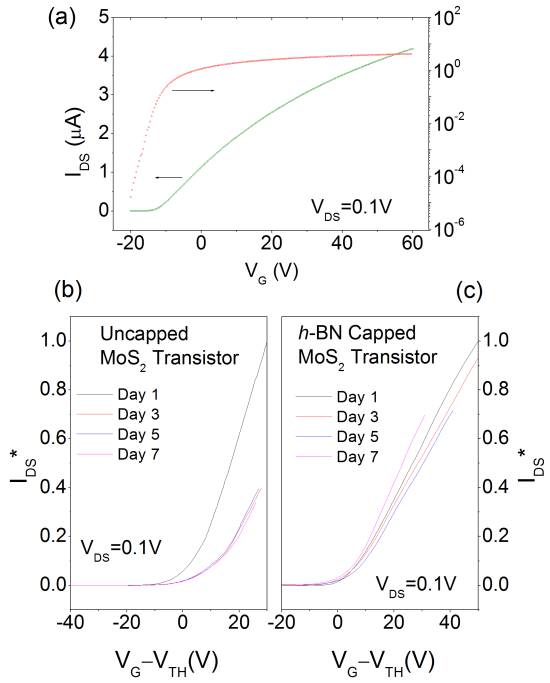

Fig. 2. (a) Typical transfer characteristic of *h*-BN capped MoS_2 TFT. The mobility is around 30-50 cm^2/Vs. The on-off ratio is on the order of 10^5-10^6. The ambient aging comparison of the uncapped and capped device is shown in (b) and (c), respectively. The characteristics of the uncapped device MoS_2 degraded 60% after two days of aging while the capped device did not degrade much within a week. Note that the high gate bias is due to back gating via 300-nm thick SiO_2 layer in these prototype devices.

erate a pattern for the source and drain contacts. The contacts were made by evaporating 60 nm of gold. The device schematics and optical images are shown in Fig. 1. In order to accurately compare the capped and uncapped devices we fabricated both types of structures on the same MoS_2.

The typical transfer characteristics of *h*-BN capped thin film MoS_2 device are shown in Fig. 2(a). The mobility of our devices is the range of 30-50 cm^2/Vs as determined from the formula $\mu = (L/W)(1/C_G V_{DS})(\Delta I_{DS}/\Delta V_G)$, where L and W are the length and width of the channel and C_G is the capacitance per unit area. The on-off ratio was extracted in the range of 10^5-10^6.

Under ambient conditions the uncapped devices started to degrade in the first couple of days as seen in Fig. 2 (b). The source-drain current in transfer *I-V* characteristics decreased by 60% after two days of ambient aging and then stabilized in the following days. To clearly illustrate the aging effect, we normalized the source-drain current I_{DS} to the maximum value (I_{DS} = 1.34 μA at V_G = 50 V of the first day of measurements). We also noticed a minor threshold voltage V_{TH} shift as the ambient environment doped the device p-type. To compensate for the doping effect we plotted V_G-V_{TH} on the *X*-axis.

The *h*-BN capped MoS_2 HTFTs were more robust under ambient condition as can be seen in Fig. 2 (c). The transfer characteristics did not degrade substantially over a week period of time. The I-V curves have been plotted in the same way as for the uncapped devices in Fig. 2 (b). The current is normalized to its maximum value (I_{DS} = 0.96 μA at V_G = 50 V of the first day of measurement). Note that the aspect ratio L/W of the uncapped and capped devices is 0.22 and 1.5, respectively. It is important to note that the capped devices had much larger on-current density than the uncapped ones. Since *h*-BN capping was introduced before EBL process the MoS_2 channel layer was free from e-beam resist contamination. The enhanced performance is therefore might reflect the fact that *h*-BN MoS_2 TFTs are residue free.

III. Gas Sensing Results

To test *h*-BN-MoS_2 HTFT sensor operation, the vapors were produced by bubbling dry air through the respective solvents and diluting the gas flow with the dry air. The resulting concentrations were ~0.5 P/P_0, where P was the vapor pressure and P_o was the saturated vapor pressure. When the device was exposed to the vapors, the vapor molecules were attaching to the channel surface, thus, creating negative or positive surface charges at the *h*-BN capped MoS_2 channel. The molecules introduced n-type or p-type doping effect depending on the vapor species. We selected the same solvents in order to compare with our previous finding of gas sensing on uncapped MoS_2 TF-FETs [6]. Specifically, we used polar solvent: acetonitrile (CH_3CN), ethanol (C_2H_5OH), methanol (CH_3OH), and non-polar solvents: toluene (C_6H_5-CH_3), chloroform ($CHCl_3$).

The source-drain current was monitored as *h*-BN-MoS_2 HTFT sensor was exposed to different gases. For all the measurements, we kept V_{DS} = 0.1 V and V_G = 0 V. Fig. 3 (a) shows the sensitivity ($\Delta R/R$) as the gases turned on and off. The thickness of MoS_2 channel is 9 nm. For all the polar solvents, the resistance sharply increased after the gas was turned on. However, as the gas was turned off, the behavior was quite different. For acetonitrile, the resistance restored to the initial value; whereas for methanol and ethanol, the resistance first increased, and after certain time began to restore at a slow speed. For the two non-polar solvents, the responses also diverged. Under the exposure to chloroform, the resistance kept increasing until the gas was turned off. The resistance partially restored to the initial value. When exposed to toluene, the resistance response was much weaker and slower. As toluene gas was turned off the resistance continued to increase except for a short time of kink. The resistance did not restore after a long waiting time. The measurements were repeated after several days.

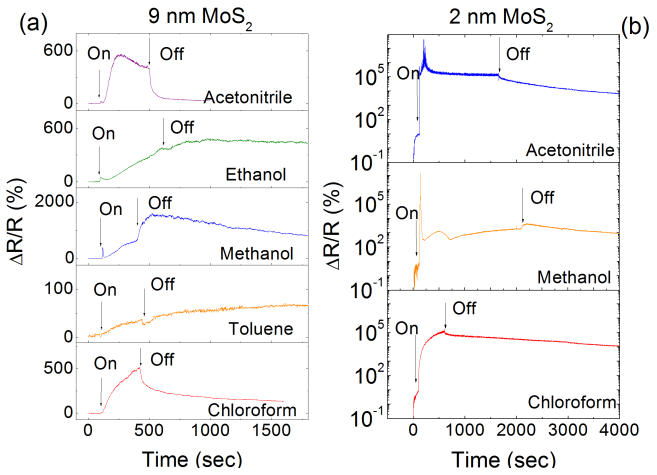

Fig. 3. Response of h-BN capped MoS_2 sensor to different gas vapor. The thickness of MoS_2 channel is 9 nm (a) and 2 nm (b). The current is monitored by applying $V_{DS} = 0.1$ V.

The results were reproducible. The different "gas off" behavior is likely related to different desorption process of the test gas molecules from h-BN surface. Prior studies with MoS_2 and other materials suggest such a possibility [17], [18]. The detailed investigation, which requires more experiments and ab initio simulations, is reserved for future study.

We also checked the gas sensing with thinner MoS_2 devices ($H = 2$ nm), shown in Fig. 3 (b). Owing to even higher surface-to-volume ratio the $\Delta R/R$ in the 2-nm thick channel HTFT upon exposure to gas vapors is 10–100 times higher than that in the 9-nm thick devices. However, the resistance restoration was much slower than in the 9-nm device. The increased sensitivity can be understood from the point of view of the screening length, which is 5-7 nm for MoS_2 [19], [20]. In the thicker 9-nm film the surface charge cannot affect the current through the entire channel thickness. In the thinner 2-nm films, which the thickness much smaller than screening length, the current in the channel can be influenced by the surface charge.

The responses of h-BN-MoS_2 HTFTs on gases were different than those of the uncapped MoS_2 TFTs [6]. In the uncapped MoS_2 TFTs devices the resistance decreased when exposed to polar solvent and increased when exposed to non-polar solvent. This difference might reflects the fact that instead of direct charge transferring from molecules to MoS_2 channel, the dielectric h-BN behaves as a charge mirror and induces the charging effect with reversed polarity of the original molecule charge.

IV. Conclusion

This work demonstrates that h-BN capped MoS_2 TFTs can be used for sensitive and selective gas detection without direct contact of MoS_2 channel with analyte molecules. The use of h-BN cap layers in MoS_2 gas sensors improves the stability of the devices and still preserves the gas sensing capability.

References

[1] F. Schedin, A. K. Geim, S. V. Morozov, E. W. Hill, P. Blake, M. I. Katsnelson, and K. S. Novoselov, "Detection of individual gas molecules adsorbed on graphene," *Nature Mater.*, vol. 6, no. 9, pp. 652–655, Jul. 2007. DOI: 10.1038/nmat1967

[2] S. Rumyantsev, G. Liu, M. S. Shur, R. A. Potyrailo, and A. A. Balandin, "Selective gas sensing with a single pristine graphene transistor," *Nano Lett.*, vol. 12, no. 5, pp. 2294–2298, Apr. 2012. DOI: 10.1021/nl3001293

[3] F. K. Perkins, A. L. Friedman, E. Cobas, P. M. Campbell, G. G. Jernigan, and B. T. Jonker, "Chemical vapor sensing with monolayer MoS_2," *Nano Lett.*, vol. 13, no. 2, pp. 668–673, Jan. 2013. DOI: 10.1021/nl3043079

[4] L. Kou, A. Du, C. Chen, and T. Frauenheim, "Strain engineering of selective chemical adsorption on monolayer MoS_2," *Nanoscale*, vol. 6, pp. 5156–5161, Feb. 2014. DOI: 10.1039/C3NR06670C

[5] K. Lee, R. Gatensby, N. McEvoy, T. Hallam, and G. S. Duesberg, "High-performance sensors based on molybdenum disulfide thin films," *Adv. Mater.*, vol. 25, no. 46, pp. 6699–6702, Sep. 2013. DOI: 10.1002/adma.201303230

[6] R. Samnakay, C. Jiang, S. L. Rumyantsev, M. S. Shur, and A. A. Balandin, "Selective chemical vapor sensing with few-layer MoS_2 thin-film transistors: Comparison with graphene devices," *Appl. Phys. Lett.*, vol. 106, no. 2, pp. 023115-1–023115-5, Jan. 2015. DOI: 10.1063/1.4905694

[7] R. Ganatra and Q. Zhang, "Few-layer MoS_2: A promising layered semiconductor," *ACS Nano*, vol. 8, no. 5, pp. 4074–4099, Mar. 2014. DOI: 10.1021/nn405938z

[8] K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, "Atomically thin MoS_2: A new direct-gap semiconductor," *Phys. Rev. Lett.*, vol. 105, no. 13, pp. 136805-1–136805-4, Sep. 2010. DOI: 10.1103/PhysRevLett.105.136805

[9] D. J. Late, Y.-K. Huang, B. Liu, J. Acharya, S. N. Shirodkar, J. Luo, A. Yan, D. Charles, U. V. Waghmare, V. P. Dravid, and C. N. R. Rao, "Sensing behavior of atomically thin-layered MoS_2 transistors," *ACS Nano*, vol. 7, no. 6, pp. 4879–4891, May 2013. DOI: 10.1021/nn400026u

[10] S. L. Rumyantsev, C. Jiang, R. Samnakay, M. S. Shur, and A. Balandin, "$1/f$ noise characteristics of MoS_2 thin-film transistors: Comparison of single and multilayer structures," *IEEE Electron Device Lett.*, vol. 36, no. 5, pp. 517–519, Mar. 2015. DOI: 10.1109/LED.2015.2412536

[11] W. Park, J. Park, J. Jang, H. Lee, H. Jeong, K. Cho, S. Hong, and T. Lee, "Oxygen environmental and passivation effects on molybdenum disulfide field effect transistors," *Nanotechnology*, vol. 24, no. 9, pp. 095202-1–095202-5, Feb. 2013. DOI: 10.1088/0957-4484/24/9/095202

[12] S. KC, R. C. Longo, R. M. Wallace, and K. Cho, "Surface oxidation energetics and kinetics on MoS_2 monolayer," *J. Appl. Phys.*, vol. 117, no. 13 pp. 135301-1–135301-9, Apr. 2015. DOI: 10.1063/1.4916536

[13] Z. Liu, Y. Gong, W. Zhou, L. Ma, J. Yu, J. C. Idrobo, J. Jung, A. H. MacDonald, R. Vajtai, J. Lou, and P. M. Ajayan, "Ultra-thin high-temperature oxidation-resistant coatings of hexagonal boron nitride," *Nature Commun.*, vol. 4, Oct. 2013, Art. ID 2541. DOI: 10.1038/ncomms3541

[14] L. H. Li, J. Cervenka, K. Watanabe, T. Taniguchi, and Y. Chen, "Strong oxidation resistance of atomically thin boron nitride nanosheets," *ACS Nano*, vol. 8, no. 2, pp. 1457–1462, Jan. 2014. DOI: 10.1021/nn500059s

[15] R. A. Doganov, E. C. T. O'Farrell, S. P. Koenig, Y. Yeo, A. Ziletti, A. Carvalho, D. K. Campbell, D. F. Coker, K. Watanabe, T. Taniguchi, A. H. C. Neto, and B. Özyilmaz, "Transport properties of pristine few-layer black phosphorus by van der Waals passivation in an inert atmosphere," *Nature Commun.*, vol. 6, Sep. 2014, Art. ID 6647. DOI: 10.1038/ncomms7647

[16] C.-H. Lee, G.-H. Lee, A. M. van der Zande, W. Chen, Y. Li, M. Han, X. Cui, G. Arefe, C. Nuckolls, T. F. Heinz, J. Guo, J. Hone, and P. Kim, "Atomically thin p–n junctions with van der Waals heterointerfaces," *Nature Nanotechnol.*, vol. 9, no. 9, pp. 676–681, Aug. 2014. DOI: 10.1038/nnano.2014.150

[17] G. Korotcenkov, "Metal oxides for solid-state gas sensors: What determines our choice?" *Mater. Sci. Eng., B*, vol. 139, no. 1, pp. 1–23, Apr. 2007. DOI: 10.1016/j.mseb.2007.01.044

[18] Q. Yue, Z. Shao, S. Chang, and J. Li, "Adsorption of gas molecules on monolayer MoS_2 and effect of applied electric field," *Nanosc. Res. Lett.*, vol. 8, p. 425, Oct. 2013. DOI: 10.1186/1556-276X-8-425

[19] S. Das and J. Appenzeller, "Where does the current flow in two-dimensional layered systems?" *Nano Lett.*, vol. 13, no. 7, pp. 3396–3402, Jun. 2013. DOI: 10.1021/nl401831u

[20] Y. Li, C.-Y. Xu, and L. Zhen, "Surface potential and interlayer screening effects of few-layer MoS_2 nanoflakes," *Appl. Phys. Lett.*, vol. 102, no. 14, pp. 143110-1–143110-4, Apr. 2013. DOI: 10.1063/1.4801844