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On MoS\textsubscript{2} TFT Design Consideration for NO\textsubscript{2} Gas Sensor

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Abstract

MoS\textsubscript{2} thin-film transistors (TFTs) are fabricated and simulated to explore NO\textsubscript{2} gas sensing mechanism depending on different device structures. In particular, the role of Al\textsubscript{2}O\textsubscript{3} passivation layer on the MoS\textsubscript{2} channel has been investigated. In the case of non-passivated MoS\textsubscript{2} TFTs, increase of OFF current is observed with NO\textsubscript{2} gas, which has been modeled with the modulation of the effective Schottky barrier height for holes, due to the generation of in-gap states near the valence band as NO\textsubscript{2} gases interact with the MoS\textsubscript{2} channel. The non-passivated MoS\textsubscript{2} TFTs are simulated based on non-equilibrium Green’s function (NEGF) method, and the simulation results do confirm this sensing mechanism. On the other hand, MoS\textsubscript{2} TFTs with the Al\textsubscript{2}O\textsubscript{3} passivation layer has been modeled with a pseudo-double gate structure as NO\textsubscript{2} gases on the capping layer can act like the secondary gate inducing the positive charge state. Our quantum transport simulation shows that significant threshold voltage shift can be achieved with NO\textsubscript{2} gas, which matches the experimental observation, thereby exhibiting completely different sensing mechanism of the passivated device from the non-passivated counterpart. In addition, we also discuss competing device parameters for the passivated MoS\textsubscript{2} TFTs by varying the main and the secondary gate dielectric, suggesting co-optimization to realize high sensitivity and low power consumption simultaneously.
A gas sensor is an essential device for various applications, such as environmental and agricultural monitoring, process control, and diagnostics. Materials for gas sensors require high surface-to-volume ratio, great performance at low operating power, and excellent sensitivity and kinetics. MoS$_2$, which is a well-known two-dimensional (2-D) layered material, exhibits great potential for gas sensors due to their outstanding properties — ultra-high surface-to-volume ratio, effective sensitivity to gases, low power consumption, low operating temperature, and the capability of surface functionality. Recent studies have reported the functionalization of MoS$_2$ surface with metal, metal oxide, and nanoparticles, and the variation in MoS$_2$ morphology to achieve high gas sensitivity with MoS$_2$ thin-film transistors (TFTs). For examples, MoS$_2$/SnO$_2$ nanohybrid sensors can detect NO$_2$ gas concentration ranging from 0.5 ppm to 10 ppm based on change in conductance. Also, Pd quantum-dots-modified MoS$_2$ can enhance its responsivity to NO$_2$ gas 50 times higher than pristine MoS$_2$ by modifying the material’s surface. In addition, vertically standing MoS$_2$ devices were suggested for highly sensitive NO$_2$ gas sensors whose detection limit is 0.1 ppm. These approaches mainly focused on the increase of the surface-to-volume ratio to improve sensitivity; whereas other strategies have also been demonstrated for the same purpose, for example, by using a high temperature treatment to create rapid desorption of gases on the channel surface or a light treatment to heal the surface of MoS$_2$.

To develop highly sensitive gas sensors, it is necessary to understand gas sensing mechanism clearly, which has been briefly discussed in some of previous studies. It was
reported that the resistance and conductance of 2D materials can be changed when they interact with gas molecules due to the charge transfer between the two\textsuperscript{20,21}. Other studies also showed that NO\textsubscript{2} gas can generate sub-gap states, leading to significant change in effective bandgap and increase in leakage current\textsuperscript{22,23}. It should be noted that previous studies mainly focused on the modification of material properties without considering the optimization of device structure. However, the sensitivity of gas sensors strongly depends on not only material properties but also proper design of sensor structure, so it is equally important to consider both material properties and device parameter optimization through systematic studies, which is currently missing from the field.

In this paper, we fabricate and model two different MoS\textsubscript{2} TFT gas sensors with and without passivation layer on the surface of MoS\textsubscript{2} channel to investigate different operating mechanisms based on the dissimilar device structure. Current-voltage characteristics obtained from each type of gas sensor under NO\textsubscript{2} gas flow exhibit their unique sensing behaviors. Each type of sensor is modelled and simulated to explain the experimental observations. Modulation of effective Schottky barrier (SB) height is adopted to model non-passivated MoS\textsubscript{2} TFTs\textsuperscript{23}, whereas pseudo-double gate device simulation\textsuperscript{24} is used for passivated MoS\textsubscript{2} gas sensors. Our simulations reveal that NO\textsubscript{2} gas can vary OFF-state leakage current of the device when MoS\textsubscript{2} is exposed, while the gas molecules can act as a secondary gate when sitting on the passivation layer. Furthermore, structural optimization is also discussed based on simulations by varying device parameters such as oxide thickness, which makes it possible to achieve higher sensitivity.
Materials and Methods

Device Fabrication

In the case of non-passivated MoS\textsubscript{2} TFTs, a highly-doped Si/SiO\textsubscript{2} wafer was immersed into buffered oxide etch (BOE) for 10 min to reduce SiO\textsubscript{2}. A 40-nm thick high-\textit{k} Al\textsubscript{2}O\textsubscript{3} thin film was deposited on the substrate for a gate insulator using atomic layer deposition (ALD). Multilayer MoS\textsubscript{2} was transferred onto Al\textsubscript{2}O\textsubscript{3} layer from bulk MoS\textsubscript{2}. As-transfer MoS\textsubscript{2} is rinsed in acetone for 1 hour and in isopropyl alcohol (IPA) for 10 min, in order. Then, 10-nm thick Ti and 40-nm thick Au were deposited and patterned using photoresist (PR) and lithography. Before electrical measurement, the transistor was annealed at 200°C for 2 hours under Ar ambient so that the contact resistances between electrodes and MoS\textsubscript{2} can be reduced. In the case of passivated MoS\textsubscript{2} TFTs, as-fabricated non-passivated MoS\textsubscript{2} TFTs were passivated by Al\textsubscript{2}O\textsubscript{3}. As-grown Al\textsubscript{2}O\textsubscript{3} passivation layer was formed about 20 nm-thick and then contact regions on the electrodes were patterned by PR.

Sensor Measurement

Electrical performance and gas-sensing characteristics of MoS\textsubscript{2} TFTs were monitored using a semiconductor analyzer (Keithley Co., SCS 4200). All the electrical measurements and gas-sensing characterizations of devices were conducted in a closed vacuum chamber at room temperature. NO\textsubscript{2} gas was injected towards the MoS\textsubscript{2} channel directly with a sprayer so that we can observe how electrical properties of MoS\textsubscript{2} TFTs will be changed with NO\textsubscript{2}.
gas depending on their structures. The desired concentration and flux of NO$_2$ gas were obtained from mass flow controllers (MFCs) by mixing N$_2$ diluted 2000 ppm NO$_2$ gas and 99.999% N$_2$ gas. The NO$_2$ gas flow is controlled by adjusting the ratio of NO$_2$ gas to N$_2$ gas while the total gas flow is fixed at 100 sccm. The flow of NO$_2$ gas is adjusted from 0 sccm to 0.2 sccm in the flow intervals of 0.05 sccm so that the concentration of NO$_2$ gas can be controlled from 0 ppm and 2000 ppm in the concentration intervals of 500 ppm.

**Model and Simulation**

Current-voltage characteristics of both types of MoS$_2$ sensors are calculated based on the non-equilibrium Green’s function (NEGF) ballistic quantum transport simulation using the effective mass approximation, self-consistently with the Poisson’s equation. Schottky contacts is used at the source-channel and the channel-drain junctions with the Schottky barrier height ($\Phi_{Bn}$) of 0.1 eV for electrons$^{25}$. For a nominal device, we use 0.65 nm-thick, 20 nm-long channel with equivalent oxide thickness (EOT) of the bottom gate oxide of 17.3 nm, which matches the experimental value used. Although we have used much a thinner and shorter channel compared to that of the actual devices to save simulation time, it will not change the underlying physics investigated in this study, thereby making our qualitative conclusion unaffected. Note that width information is implicit in the NEGF simulation; hence, the calculated current value is provided in ampere per unit width. A power supply voltage, $V_{DD} = 1$ V was used with the source grounded. To represent the non-passivated device, air is assumed on top of the channel with a floating boundary condition. In this case, NO$_2$ gas molecules introduce in-gap states to the multilayer MoS$_2$,
which can be interpreted as the modulation of effective Schottky barrier height for holes \( \Phi_{Bp} \)^{22,23}. In this study, we have used \( \Phi_{Bp} \) of 1.13–1.23 eV to reproduce the data from experiment. On the other hand, for the passivated MoS\(_2\) TFTs, Al\(_2\)O\(_3\) is used also for the top passivation layer (EOT\(_\text{TOP} = 4.3 \text{ nm for a nominal device} \)). Due to the passivation layer, NO\(_2\) does not have a direct impact on the band structure of the channel MoS\(_2\); instead, the charge transfer occurs between the NO\(_2\) gas and the top passivation layer, resulting in the positive charge state at the surface of Al\(_2\)O\(_3\)^{24,26}. We model this pseudo-double gate structure by introducing the positive charge density \( N \) on the passivation layer for the secondary gate effect caused by the NO\(_2\) gas.

**Design Optimization**

In this work, the optimized sensor design is proposed by engineering two competing parameters – the top and bottom EOTs of passivated MoS\(_2\) TFTs by means of simulation. Moreover, passivated MoS\(_2\) TFTs with different thicknesses of top Al\(_2\)O\(_3\) layer (20 nm and 5 nm) are fabricated and their sensing performance such as \( V_{TH} \) shift and sensitivity is compared by experiment. To facilitate a fair and direct comparison among different sensor structures, sensitivity under NO\(_2\) gas is defined with \( I_{\text{gas}}/I_0 \). For the response/recovery characteristics, the target NO\(_2\) concentrations of 100, 200, 300, 400, and 500 ppm are achieved by controlling the NO\(_2\) flow from 0.1 to 0.5 sccm at the constant total flow of 1000 sccm.
Results and Discussions

Figures 1a and b illustrate the structures of non-passivated and passivated MoS$_2$ TFTs for NO$_2$ gas sensors, respectively. Depending on the structure of TFTs, their responses to NO$_2$ can be significantly different. In order to compare two different devices with regard to the response to NO$_2$ gas, we have chosen devices showing similar electrical properties of pristine MoS$_2$ TFTs as $I_{ON}/I_{OFF}$ of $\sim10^4$ with a surface area of $\sim60$ $\mu$m$^2$. Figure 1c shows $I_{DS}-V_{GS}$ curves of non-passivated MoS$_2$ TFTs with the flow of NO$_2$ gas at $V_{DS} = 1$ V. (The width, length and thickness of the channel are 7.26 $\mu$m, 8.39 $\mu$m and $\sim40$ nm, respectively.) There is a gradual increase in $I_{OFF}$ with the flow of NO$_2$ gas, while $I_{ON}$ and $V_{TH}$ remain almost unaffected. At $V_{GS} = -3$ V, as flow of NO$_2$ gas increases from 0 sccm to 0.2 sccm, $I_{OFF}$ increases from 39.48 pA to 160.86 pA. This response to NO$_2$ gas, showing a trend of proportional increase of $I_{OFF}$ with NO$_2$ gas, is a great accordance with previous studies$^{23}$. On the other hand, the passivated MoS$_2$ TFT with the thickness of $\sim6.3$ $\mu$m, the length of 10.14 $\mu$m and the thickness of $\sim30$ nm exhibits a negative shift of $V_{TH}$ with a negligible change in $I_{OFF}$ with the flow of NO$_2$ gas (see Figure 1d). As the flow of NO$_2$ gas increases from 0 sccm to 0.2 sccm, $V_{TH}$ changes from -0.83 V to -1.05 V towards the negative $V_{GS}$.

Figures 2a and b show variations in $I_{OFF}$ (at $V_{GS} = -3$ V) and $\Delta V_{TH}$ (obtained from $\sqrt{I_{DS}}$-$V_{GS}$ curves) depending on the NO$_2$ flow. As clearly seen from Figure 2a, $I_{OFF}$ of the non-passivated MoS$_2$ TFT exhibits a linear response to the NO$_2$ flow while that of the passivated MoS$_2$ TFT shows no changes. On the other hand, Figure 2b shows significant negative $V_{TH}$ shift for the passivated TFT with increase in NO$_2$ flow, which is not the case.
of the non-passivated MoS$_2$ TFT. The distinct characteristics of two devices are attributed to different sensing mechanisms. If NO$_2$ gas molecules are attached to the surface of MoS$_2$ channel in the non-passivated sensors, in-gap states are created close to the valence band of MoS$_2$ as shown in Figure 2c$^{22}$. This can facilitate tunneling as the effective Schottky barrier for holes is lowered, which is modeled by the effective $\Phi_{Bp}$ modulation to capture the off-state leakage current affected$^{23}$. In case of the passivated MoS$_2$ TFT, negative $\Delta V_{TH}$ can be modeled with a secondary gate through the top gate dielectric$^{24}$. If NO$_2$ gas molecules are located on the surface of Al$_2$O$_3$, they can take electrons$^{26}$ and make the passivation layer a positive-charge state. Consequently, the potential barrier of the channel can be lowered as shown in Figure 2d, resulting in the increase of current and the negative $V_{TH}$ shift.

Next, using the models explained above, we have performed numerical simulations. Figure 3a shows the simulated $I_{DS}$–$V_{GS}$ curves of the non-passivated MoS$_2$ device with three different effective $\Phi_{Bp}$ of 1.13, 1.18, and 1.23 eV. Our simulation results show that $I_{OFF}$ increases as $\Phi_{Bp}$ is reduced, which is analogous with experimental observations with the increased gas flow. This indicates that the operating mechanism of non-passivated MoS$_2$ TFTs can be explained by the reduction of effective $\Phi_{Bp}$ as more NO$_2$ gas molecules are attached to the MoS$_2$ channel. Blue asterisks in Figure 3b shows $I_{gas}/I_0$ as a function of $\Phi_{Bp}$ achieved from simulation at $V_{GS} = -3$ V, where $I_0$ is the reference drain current for the pristine MoS$_2$ TFT ($\Phi_{Bp} = 1.23$ eV) and $I_{gas}$ is the current with NO$_2$ gas ($\Phi_{Bp} < 1.23$ eV). Based on the simulation data, we have modeled the relation between $I_{gas}/I_0$ and $\Phi_{Bp}$, leading to
\[
\log_{10}\left(\frac{I_{\text{gas}}}{I_0}\right) = p_1 \Phi_{Bp} + p_2,
\]

where \( p_1 \) and \( p_2 \) are -13.50 eV\(^{-1}\) and 16.56, respectively. The dotted line in Figure 3b represents our model. Next, experimental data for 0 – 0.2 sccm NO\(_2\) gas are also shown in Figure 3b along with the model to derive the relation between the NO\(_2\) gas flow \((F)\) and \( \Phi_{Bp} \). The formula is given by

\[
\Phi_{Bp} = p_3 F^2 + p_4 F + p_5,
\]

where \( p_3 = 1.051 \) eV/sccm\(^2\), \( p_4 = -0.431 \) eV/sccm, and \( p_5 = 1.227 \) eV. The relation between the two is shown in Figure 3c, which represents that effective \( \Phi_{Bp} \) reduces linearly with the NO\(_2\) gas flow of 0 – 0.1 sccm but the effective \( \Phi_{Bp} \) modulation caused by the in-gap state starts to saturate beyond that point.

Similarly, Figure 3d shows the simulated \( I_{DS}-V_{GS} \) curves of the passivated MoS\(_2\) TFT with three different conditions: positive charge density \( (N) \) of 0, \( 2 \times 10^{23} \), and \( 4 \times 10^{23} \) m\(^{-3}\). Our simulation results show that more negative \( V_{TH} \) is achieved as \( N \) increases. Consequently, \( \Delta V_{TH} \) due to the secondary gate effect, with respect to the case with no gas condition, becomes negative. Blue asterisks in Figure 3e shows \( \Delta V_{TH} \) as a function of \( N \), which can be described by

\[
\Delta V_{TH} = q_1 N^2 + q_2 N + q_3,
\]

where \( q_1 = 5.3229 \times 10^{-49} \) V \( \cdot \) m\(^6\), \( q_2 = -8.8428 \times 10^{-25} \) V \( \cdot \) m\(^3\), and \( q_3 = 0.069907 \) V. To find the relation between \( N \) and NO\(_2\) gas flow \((F)\) giving the same threshold voltage shift, 0 – 0.2 sccm NO\(_2\) gas from experiments (red open squares) are also shown in Figure...
3e along with the model (dotted line), resulting in the following relation:

\[ N = q_4 F + q_5, \]

where \( q_4 = 1.4727 \times 10^{24} \, \text{m}^3\text{scm}^{-1} \) and \( q_5 = 1.6203 \times 10^{23} \, \text{m}^3 \). As shown in Figure 3f, \( N \) exhibits a linear relation to the gas flow \( F \) for the entire range considered in this study (0 to 0.2 sccm).

So far, we have investigated different operational mechanisms of non-passivated and passivated MoS\(_2\) TFTs. Next, we will further extend our discussion for sensitivity improvement through design optimization. For non-passivated MoS\(_2\) TFTs, NO\(_2\) gas directly interacts with the MoS\(_2\) channel, so there exists less room for optimization. However, for passivated MoS\(_2\) TFTs, we can engineer two competing parameters: namely, the main bottom gate and the secondary top gate, by carefully tuning top and bottom EOTs. Therefore, we will focus on the optimization of the passivated MoS\(_2\) TFTs below. It is expected that \( \Delta V_{\text{TH}} \) of the passivated MoS\(_2\) TFTs can be more sensitive if thinner EOT\(_{\text{TOP}}\) is used. Figure 4b exhibits how \( \Delta V_{\text{TH}} \) varies with different EOT\(_{\text{TOP}}\) for a fixed EOT\(_{\text{BOT}}\) (17.3 nm) and \( N = 3 \times 10^{23} \, \text{m}^3 \). It shows that \( \Delta V_{\text{TH}} \) can be improved from -0.15 V to -0.37 V by changing EOT\(_{\text{TOP}}\) from 4.3 nm to 1.3 nm. On the other hand, EOT\(_{\text{BOT}}\) can provide another design freedom to achieve higher sensitivity. Figure 4c shows \( \Delta V_{\text{TH}} \) as a function of EOT\(_{\text{BOT}}\) with EOT\(_{\text{TOP}}\) = 1.3 nm for the same gas flow assumed. \( \Delta V_{\text{TH}} \) can be significantly larger by 3.8 times if EOT\(_{\text{BOT}}\) is changed from 7.3 nm to 27.3 nm. However, at the same time, subthreshold swing (SS) is significantly increased with the same change in EOT\(_{\text{BOT}}\) (with a fixed EOT\(_{\text{TOP}}\)) as it can be seen in Figure 4d. It should be noted that
devices with smaller SS is desirable for lower leakage current and less power consumption, which could be important particularly for mobile device applications. The observed trade-off between sensitivity and SS can be explained by the channel potential modulation through the device’s main (bottom) gate. Thinner EOT\textsubscript{BOT} results in better gate control, which can lower SS; however, such a strong control screens the secondary gate effect induced by the NO\textsubscript{2} gas, resulting in lower sensitivity, and vice versa. On the other hand, SS will be less susceptible to EOT\textsubscript{TOP} as long as EOT\textsubscript{BOT} will not be changed, as NO\textsubscript{2} gas on the top passivation layer provides only the secondary effect on the switching characteristics. Therefore, it is suggested that sensitivity and fundamental device performance should be considered simultaneously in optimizing parameters of the passivated TFT structure.

As suggested by the numerical simulation, we have also fabricated a passivated MoS\textsubscript{2} TFT with a thinner (5 nm) passivation layer to improve the sensor performance. With 5 nm-thick Al\textsubscript{2}O\textsubscript{3}, the $V_{TH}$ shift becomes -0.52 V (Figure 5a) and the resulting sensitivity can be $\sim$ 18 (Figure 5b) under 500 ppm of NO\textsubscript{2} gas, which is huge improvement as compared to the sensor with a thicker (20 nm) passivation layer (see Figures 5a and 5b).

Next, time-resolved NO\textsubscript{2} sensing behaviors have been investigated for two different types of MoS\textsubscript{2} TFTs. Figures 6a and 6b present time-resolved current responses of the non-passivated and the passivated MoS\textsubscript{2} TFT with 5 nm-thick Al\textsubscript{2}O\textsubscript{3} with different NO\textsubscript{2} gas concentration. After NO\textsubscript{2} gas was injected for 10 min (color lines in Figures 6a and 6b; not scaled) to stabilize the chamber condition, drain currents were measured in real-time. The
non-passivated MoS$_2$ TFT shows the higher $I_{\text{OFF}}$ with increasing NO$_2$ concentration; however, the current increase is insufficient, and $I_{\text{OFF}}$ after NO$_2$ exposure is gradually degraded over time as shown in Figure 6a. In contrast, the passivated MoS$_2$ TFT with 5 nm-thick top oxide layer exhibits much more distinguishable current depending on NO$_2$ concentration, and their signals are cleaner with no noticeable decline in the current level over time (Figure 6b).

Finally, time-resolved ON-OFF switching responses at a NO$_2$ gas concentration of 500 ppm have been examined. In the ON state, currents were measured in real-time 10 min after NO$_2$ gas was injected (color lines in Figures 6c and 6d; not scaled). In the OFF state, each device was first recovered for 1 min at $V_{\text{GS}} = 30$ V, which is opposed to the measurement bias, while injecting only N$_2$ gas (gray lines in Figures 6c and 6d; not scaled), and then current has been measured at the same $V_{\text{GS}}$ as in the ON state$^{23,27}$. As shown in Figure 6c, the non-passivated MoS$_2$ TFT shows relatively poor ON-OFF switching characteristics, and the signal is unstable over time. On the contrary, the passivated MoS$_2$ TFT with 5-nm top oxide layer shows superior ON-OFF switching responses with stable and clean signals (Figure 6d). Our results indicate that the passivated MoS$_2$ TFTs with a thin top oxide have great potential for gate-refreshable, high-performance NO$_2$ gas sensors.

**Conclusions**

We have investigated structure-dependent NO$_2$ gas sensing mechanism of MoS$_2$ TFTs based on both experiment and theory. Fabricated non-passivated MoS$_2$ TFTs showed that
OFF current increases as the sensor is exposed to more NO$_2$ gases. We have modeled the sensing mechanism of the non-passivated MoS$_2$ TFT with the in-gap states induced by NO$_2$ gas on the MoS$_2$ surface and the modulation of the effective Schottky barrier height for holes. Our numerical device simulation results are in good agreement with the experiment, thereby confirming the validity of our model for the non-passivated MoS$_2$ gas sensors. On the other hand, fabricated passivated MoS$_2$ TFTs exhibit negative $V_{TH}$ shift as the flow of NO$_2$ gas increases. We have modeled the sensing mechanism by introducing a secondary gate with positive charges on the capping dielectric surface. Our simulation on the pseudo-double gate MoS$_2$ TFT showed the same negative $V_{TH}$ shift as experiment, indicating that the NO$_2$ sensing mechanism of the passivated structure is completely different from that of the non-passivated MoS$_2$ TFT. Furthermore, we have also discussed the design strategy to optimize sensitivity and power consumption simultaneously by careful investigation of the main and the secondary gate dielectric of the passivated MoS$_2$ TFT. Lastly, as suggested by the numerical simulation results, we have fabricated a passivated MoS$_2$ TFT with a thinner top passivation layer to further improve the sensor performance, which exhibited significant enhancement not only in $V_{TH}$ shift and sensitivity but also in response/recovery behaviors through design optimization.

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**Author Contributions**

H. Im and A. AlMutairi equally contributed to this work.
References


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(21) Yuan, W.; Liu, A.; Huang, L.; Li, C.; Shi, G. High-Performance NO$_2$ Sensors Based on Chemically


Figure 1. Schematic images of (a) a non-passivated MoS$_2$ TFT and (b) a passivated MoS$_2$ TFT. $I_{DS}$–$V_{GS}$ curves showing the response of (c) the non-passivated MoS$_2$ TFT and (d) the passivated MoS$_2$ TFT to NO$_2$ gas.
Figure 2. Device structure-dependent response of MoS$_2$ TFTs to NO$_2$ gas. (a) OFF-state current vs. NO$_2$ flow. (b) $\Delta V_{TH}$ vs. NO$_2$ flow. Energy band diagrams of (c) the non-passivated MoS$_2$ TFT and (d) the passivated MoS$_2$ TFT in the presence of NO$_2$ gas.
Figure 3. (a) Simulated $I_{DS} - V_{GS}$ for the non-passivated device with the effective Schottky barrier height for holes ($\Phi_{Bp}$) of 1.13, 1.18 and 1.23 eV (red, green and blue, respectively). (b) $I_{gas}/I_0$ vs. $\Phi_{Bp}$ calculated at $V_{GS} = -3$V from the simulation results (blue asterisks) and the experimental results (red squares). The dotted blue line is the fitting to the simulation data. (c) The relation between $\Phi_{Bp}$ and NO$_2$ gas flow, showing decrease in $\Phi_{Bp}$ in response to the increase of NO$_2$ flow. (d) Simulated $I_{DS} - V_{GS}$ of the passivated device with the positive charge density of $N = 0$ (blue), $2 \times 10^{23}$ m$^{-3}$ (green), and $4 \times 10^{23}$ m$^{-3}$ (red) on the secondary gate dielectric. (e) $V_{TH}$ shift ($\Delta V_{TH}$) as a function of the charge density, $N$. The simulated results are shown in blue asterisks and experimental data in red squares. The dotted blue line is the fitting to the simulation data. (f) The relation between $\Delta V_{TH}$ and NO$_2$ gas flow.
Figure 4. (a) Cross-section of the passivated device showing the parameters $EOT_{\text{TOP}}$ and $EOT_{\text{BOT}}$ varied for optimization. (b) $\Delta V_{\text{TH}}$ as a function of $EOT_{\text{TOP}}$ (at a fixed $EOT_{\text{BOT}} = 17.3$ nm). (c) Effect of $EOT_{\text{BOT}}$ variation on the $V_{\text{TH}}$ shift (at a fixed $EOT_{\text{TOP}} = 1.3$ nm). (d) Subthreshold swing (SS) plotted as a function of $EOT_{\text{TOP}}/EOT_{\text{BOT}}$ for the case shown in Figure 4c.
Figure 5. Responses to NO2 gas with different device structures. (a) $V_{TH}$ shift and (b) $I_{gas}/I_0$ as a function of NO2 concentration.
Figure 6. Time-resolved current responses of (a) non-passivated MoS$_2$ TFT and (b) passivated MoS$_2$ TFT with 5 nm-thick Al$_2$O$_3$ with different NO$_2$ gas concentration (vertical color lines depict 10 min of exposure time; not scaled). Time-resolved ON-OFF switching responses of (c) non-passivated MoS$_2$ TFT and (d) passivated MoS$_2$ TFT with 5 nm-thick Al$_2$O$_3$ at a NO$_2$ gas concentration of 500 ppm (vertical color lines depict 10 min of exposure time; gray lines 1 min of NO$_2$ gas removal from MoS$_2$ TFTs by applying $V_{GS}$ of 30 V; not scaled).
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