Proceedings of the 17th
IEEE International Conference on Nanotechnology
Pittsburgh, USA, July 25-28, 2017

Fabrication and Characterization of Humidity Sensors based on CVD Grown MoS_2 Thin Film

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Abstract— **Recent advances in two-dimensional (2D) transition metal dichalcogenides have demonstrated their potential application in chemical sensors. However, the chemical vapor deposition (CVD) grown molybdenum disulfide (MoS_2) humidity sensors are still largely unexplored. In this work, MoS_2 thin films were grown on 1 cm^2 sapphire substrates through sulfurization of e-beam deposited Mo layers. The MoS_2 film morphology, thickness, and crystallinity were characterized by AFM and Raman spectroscopy. The two-terminal devices were fabricated with e-beam evaporated interdigitated electrodes (IDEs) on top of the MoS_2 surface. The water vapor sensing was tested at various humidity levels with the observed increase in the device resistance response to humidity due to the charge transfer mechanism. We found the devices to be reproducible and with excellent dynamic hysteresis. The sensitivity, fast response and recovery proved that CVD growth MoS_2 thin film could be scaled up for humidity and gas sensing applications.**

I. Introduction

Two dimensional (2D) materials such as graphene and molybdenum disulfide (MoS_2), have been extensively studied because of the unique electrical and optical properties introduced by their atomically-thin layer structure. [1]-[3] Various applications such as graphene integrated circuit [3], graphene field-effect transistors (FETs) [4] and MoS_2 photodetectors [5] are reported. Recent studies has shown chemical sensing applications with excellent performance of graphene [6] and graphene oxide [7].

Transition metal dichalcogenide (TMDC) materials are now drawing considerable attention due to their tunable bandgap and low background carrier densities.

*Research partially supported by National Institute of Biomedical Imaging and Bioengineering (NIBIB) of the National Institutes of Health (NIH) under award number U01EB021986. S.K. acknowledges support from the U.S. Department of Commerce, National Institute of Standards and Technology under the financial assistance award 70NANB16H043.

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These properties can potentially provide high sensitivity of the sensors and high selectivity to different analytes. [8]-[11] In particular, sensing capabilities of MoS_2 have recently been studied. Most of the reported sensors are based on mechanically exfoliated flakes of TMDC materials. [12], [13] For example, Late *et al.* fabricated few-layer exfoliated MoS_2 FETs and demonstrated their sensitivity to NH_3, NO_2 and humidity. [14] However, CVD deposited thin films have distinct advantages such as wafer-scale growth and compatibility with conventional semiconductor fabrication processes. [15]

To date, only Liu *et al.* examined the NH_3 and NO_2 gas sensing ability of CVD grown ultra-thin MoS_2 films. [16] In addition, Liu *et al.* reported humidity sensing on the devices fabricated using physical vapor deposition (PVD) of thick MoS_2 polycrystalline films on Si substrate. [17]

To explore the sensing properties of the CVD-grown MoS_2 thin films, we studied two-terminal sensors, which show a resistance change in response to the absorption of water molecules. We measured the current-voltage curves at different humidity levels and recorded a positive response of increased resistivity to higher humidity. Reproducibility and dynamic hysteresis were tested, which proved the promising humidity sensing capacity of ultra-thin MoS_2 films.

II. Experimental

A. Thin Film Growth and Device Fabrication

In this study, we built a MoS_2 thin film sensor prepared by sulfurization of deposited Mo layer. [18] A thin layer of Mo, 4 nm thick, was deposited onto RCA cleaned c-axis sapphire substrates by e-beam deposition. MoS_2 films were then produced by sulfurization of Mo in an $H_2S/H_2/Ar$ gas mixture using a custom-build CVD reactor. The chamber temperature and pressure was set to 1000 °C and 1.33 kPa, respectively. After 20 min of sulfurization, substrates were rapidly cooled to ≈500 °C to prevent re-evaporation of the synthesized material.

Ti (40 nm)/Au (160 nm) bi-layer comb-like IDEs were e-beam deposited on lithographically patterned MoS_2 followed by lift-off. The electrode structure configuration is as follows: the length of each finger is 1200 µm with the gap of 100 µm. The corner contact pads size is 400 µm × 400 µm and the full scale of the device is 2 mm × 2 mm. SEM image of the fabricated device is shown in Figure 1.

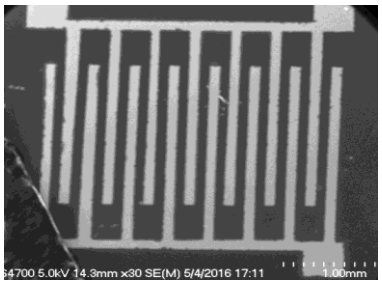

Fig. 1. SEM image of the fabricated structure

The Ti/Au metal contact combination helps narrow the potential barrier at the interface and maximize carrier injection. [19] In general, this structure is shown to provide higher current which improves signal-to-noise ratio and hence sensitivity.

B. Characterization and Measurements

Atomic Force Microscopy (AFM) image (Figure 2(b)) reveals hexagonal grains of MoS_2 film most of which have the same orientation. This is indicative of quasi-epitaxial growth of MoS_2 on sapphire. The thickness of the film was 9 nm (Figure 2(a)). For different samples, surface roughness is estimated between 3.0 nm and 4.2 nm. A representative Raman spectrum (Laser Quantum DPSS, 532 nm) [20] exhibits characteristic lines corresponding to the E_{2g} and A_{1g} modes of MoS_2 with the full width at half maximum (FWHM) between 3.1 cm^{-1} and 3.6 cm^{-1} (Figure 2(c)). Small FWHM values are usually correlated with a high structural quality of the material.

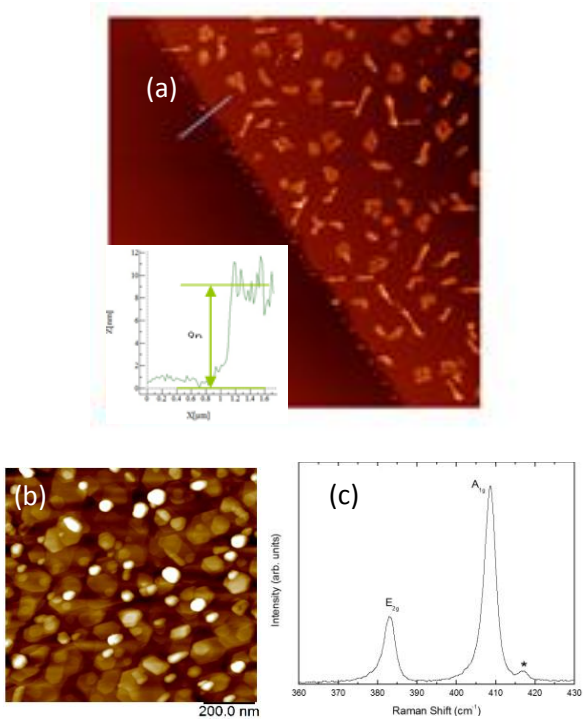

Fig. 2. (a) Low- and (b) high-resolu1tion AFM images of MoS_2 film. Inset in (a) shows an AFM height profile of MoS_2 film. (c) Room-temperature Raman spectrum of MoS_2 film produced by Mo sulfurization. Raman peak at 418 cm^{-1} marked with an asterisk originates from the sapphire substrate.

Current response to changes in the relative humidity (RH) was recorded at a 2 V bias using a NI PXI-1033 instrument. RH was varied by diluting humid air flow (RH = 40 %) with dry air so that 35 %, 30 %, and 25 % RH values were obtained using 20 sccm, 60 sccm, and 100 sccm dry air flow, respectively. The RH was measured by a fast-response commercial humidity probe placed at the exhaust of the sensing chamber. The sensitivity was defined as

$$S = (I_{RH1} - I_{RHE})/I_{RHE}, \quad (1)$$

where I_{RH1} is the current of the device at a certain RH value and I_{RHE} is the current at the base humidity (40 %).

III. Results and Discussion

Dynamic humidity response curves of a MoS_2 thin film sensor under the base humidity and 25 % RH plotted in Figure 3(a) show that current increases for lower RH. A sensitivity of 5.5 % was calculated. We tested the response to dry air and dry N_2 to probe the impact of oxygen. From Figure 3 (b) we can see a 0.3 % change for the two gases, which indicates that the influence of oxygen is much smaller than the humidity. From Figure 4 (b), a response/recovery time of 250 s/250 s was also measured. This parameter is higher compared to some other reported MoS_2 humidity sensors. [11]

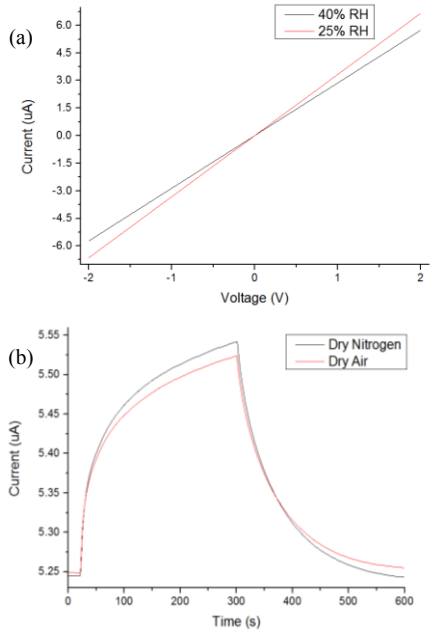

Fig. 3. (a) Typical current-voltage (IV) curves obtained at room humidity and 25 % RH (b) response cycle to dry air and dry N_2.

The reproducibility of the device is shown in Figure 4(a). In this test, the device was exposed to a step-like increased flow of dry air with an exposure time of 500 s for each RH level to reach a current saturation. The test result demonstrated a remarkable reproducibility with three different humidity levels and only a small baseline drift of 0.3 % is observed for each cycle. The sensitivity curve of humidity from 25 % RH to 40 % RH is demonstrated in

Figure 4(b), from which we can conclude that the device performance is better for lower humidity values.

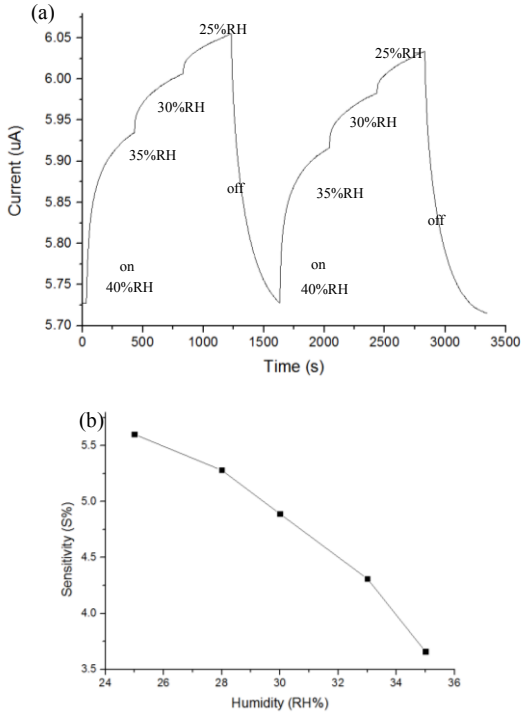

Fig. 4. (a) The reproducibility of the device at 25 % RH, 30 % RH and 35 % RH (b) The sensititivity curve of humidity from 25 % RH to 40 % RH

Humidity sensors are often affected by the history of its environment conditions, and the dynamic hysteresis is also one of the most important figures of merit of the humidity sensors. The humidity hysteresis of MoS_2 sensor was tested by increasing the dry air flow rate from 20 sccm to 120 sccm at a 20 sccm increment and then decreasing to 80 sccm and further to 40 sccm. The dynamic humidity hysteresis curve is plotted in Figure 6 with a hysteresis about 1 % RH, which is better than for some other 2D materials humidity sensors. Wang et al. proposed that the hysteresis in I-V characteristics is caused by the charge injection at the surface and the charge transfer between neighboring adsorbates. [21]

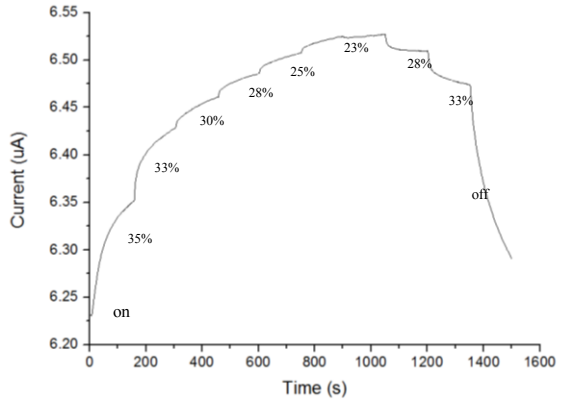

Fig. 5. Dynamic hysteresis curve of the device

In general, the positive impedance response of MoS_2 thin film humidity sensor can be explained according to the charge transfer concept: the surface absorbed water molecules act as electron acceptors, resulting in pinning of the Fermi level closer to the valence-band edge. [12], [22] The free electrons in MoS_2 interact with the water molecules according to the reaction:

$$H_2O + e^- = \frac{1}{2}H_2 + OH^-. \quad (2)$$

In this way, the free electrons are consumed which leads to the decrease of the current. From the mechanism described above, we can speculate that the sensitivity might be influenced by the thickness of the sample and by the operating conditions, for example the surface oxidation of the film could cause a drift of the device.

IV. Conclusions

In this work, humidity sensors fabricated using large-area CVD-grown MoS_2 thin films are presented. A positive resistance response of the sensors to the humidity was observed with a high sensitivity (≈5.5 % for a 15 % RH difference), a low hysteresis (≈ 1 %), and response and recovery time of ≈250 s. The sensing mechanism is explained by electron transfer from MoS_2 to the water molecules, which results in a decrease of current with increasing humidity.

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