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First-Order Time Derivative Response of MoS_2 Nanofilm on TiO_2 Nanotubes to NO_2

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Summary:
ALD grown MoS_2 nanofilm on TiO_2 nanotubes support were studied as NO_2 gas sensor. In addition to traditional relative resistance response, we show that a rarely studied first-order derivative response is an excellent alternative with monotone dependency on concentration and fast response time, avoiding the need for long gas exposure periods to achieve high and stable sensor response.

Keywords: molybdenum dichalcogenides, molybdenum sulphide, nanostructures, gas sensors, derivative response

Background, Motivation and Objective

2D structured molybdenum dichalcogenides are promising materials for chemical sensors devoted to environmental pollutants, such as NO_2, NH_3, CO and volatile organic compounds [1].

We studied ALD grown MoS_2 nanofilm on TiO_2 nanotube supports [2] regarding its gas sensing properties. In order to minimize the sensors response and recovery times we utilized a first-order time-derivative response which was rarely used in gas sensing experiments [3], [4], and can provide better results than routinely used normalized resistance response.

MoS_2 samples fabrication

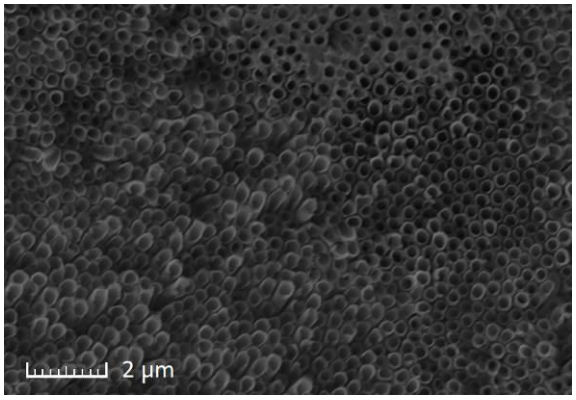

Fig. 1. SEM image of TiO_2 nanotubes decorated with 3 ALD cycles of MoS_2.

TiO_2 nanotubes with 20 µm average thickness and 110 nm in diameter were used as a base, with two dimensional MoS_2 nanostructures grown via Atomic Layer Deposition (ALD) technique (see Fig. 1), resulting in homogenously distributed nanofilm over the entire nanotube layer. The thickness of MoS is determined by the number of ALD cycles, 3 cycles were performed. In detailed fabrication process was described in [2]. Golden electrodes were deposited over the layer to form the electrical connection.

Methodology

Before any characterization, the sample was stabilized under constant 200 sccm synthetic air (SA) flow and 150 °C for a week, until the resistance baseline was stabilized. All gas sensing experiments were performed with sample connected to constant voltage of 0.5 V and constant gas flow of 200 sccm. Desired NO_2 concentration was achieved by mixing 10 ppm NO_2 in SA with pure SA, limiting the obtainable concentrations. Two different sensor responses were evaluated. The relative resistance response was calculated as $R_{rez} = R_{NO2}/R_{SA}$, where R_{SA} is the resistance baseline in SA and R_{NO2} is the maximum resistance reached during the NO_2 exposition. The first-order time derivation was calculated as a slope of linear fit over 20 seconds time period and the maximum was taken as derivative response.

Gas Sensing Characterization

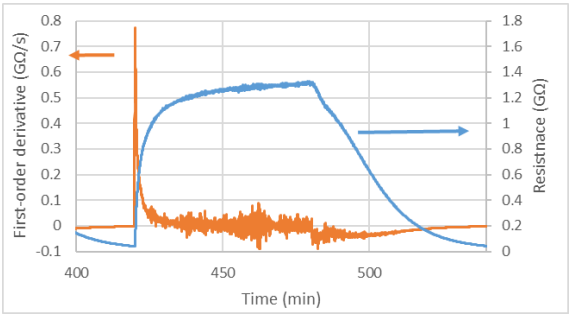

Fig. 2. Time dependence of resistance and its time derivation for 60 min exposure to 2 ppm of NO_2.

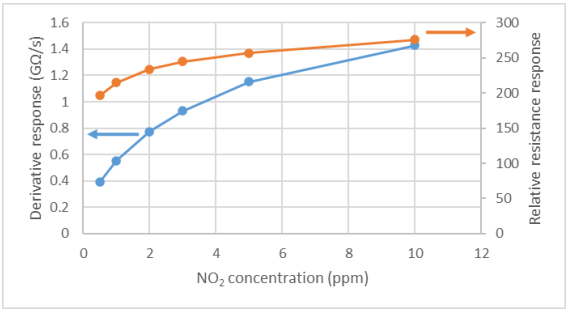

Fig. 3. Dependence of resistive and derivative sensor response on NO_2 concentration, 60 min exposures.

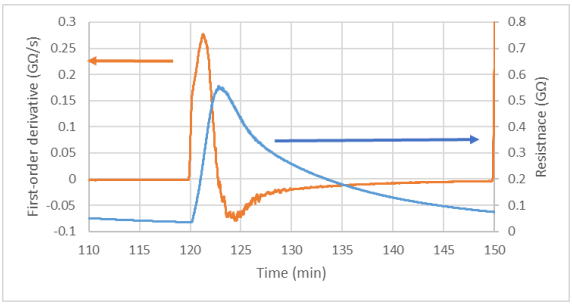

Fig. 4. Time dependence of resistance and its time derivation for 1 min exposure to 2 ppm of NO_2.

Typical experiment comprised of 60 min NO_2, 60 min SA purge cycles, repeated with increasing concentration. The first cycle was discarded as it was significantly distorted by adsorption in the apparatus gas lines and the measurement chamber. Fig. 2 shows the detail of one cycle. While the resistance was rapidly rising for cca 15 minutes followed by slower increase for the rest of the exposure period, the first-order time derivative peaks within the first minute, returning to smaller values for the rest of the gas exposure period. This makes the derivative response a much better choice for fast detections, as the magnitude of the response is not dependent on prolonged gas exposures. Fig. 4 shows the one cycle of 1 min exposure and 19 min SA purge, which is sufficient for the derivative response operation. However, the limitations of our apparatus (mainly the 140 cm^3 volume of the test chamber compared to 200 sccm gas flow) are limiting the precision of these measurements, resulting in smaller derivative response than obtained with longer exposures, as well as being the limiting factor for the recovery.

Adsorption States – Deep and Shallow – Influencing Response and Recovery Times

Sensor response is determined by the NO_2 adsorption on MoS_2 surface. Deep adsorption levels with high adsorption energy traps the molecule on the surface slowing down sensor recovery. However, the ab-initio calculations show that on the pristine surface of MoS_2, there are multiple shallow adsorption states with nearly identical binding energy around 0.20 eV [5]. Although they also discuss the existence of deep adsorption levels on defects and edges, the initial adsorption speed, and consequently the derivative response, would be determined mainly by the shallow adsorption states, which are the most numerous and easily depopulated, reducing the necessity of long recovery periods connected to slow depopulation of deep adsorption levels.

Conclusions

MoS_2 nanosheets responds well to nitrogen dioxide. While the resistive response takes tens of minutes to reach stabilized value, the first-order time derivative response peaks within the first minute, thus being much more suitable response function.

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