Abstract

Non-Stationary Gas Sensors Based on WSe$_2$ or MoS$_2$ Calibrated upon NH$_3$ Exposure [†]

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Abstract: We report on the calibration of gas sensors based on two transition metal dichalcogenides, molybdenum disulfide or tungsten diselenide, grown by the thermally assisted conversion of patterned Mo or W. The sensors showed non-stationary behavior when exposed to ammonia (NH$_3$) in the range of 10–100 parts per million at room temperature. This drawback hampered the calibration of the sensors. Applying the time-differential signal output (TDSO) enabled us to overcome the issue since the maxima of TDSO were uniquely and linearly correlated to the NH$_3$ concentration. The outcomes show that TDSO is a powerful, reliable, and valid approach when gas sensors are exposed to both oxidizing and reducing atmospheres.

Keywords: transition metal dichalcogenides; physical vapor deposition; gas sensors; room temperature; calibration curve; NH$_3$; time-differential signal output

1. Introduction

The absence of a detected steady-state signal represents a longstanding hindrance, which affects solid-state gas sensors. Gas sensors based on two-dimensional materials (2DMs) and transition metal dichalcogenides (TMDCs) are not immune from such a drawback. Due to the great potential of 2DMs and TMDCs in the sensing field, especially in terms of extremely low sensitivity, there is an urgent need to treat the lack of a steady-state signal. So far, the approach named time-differential signal output (TDSO) has been a powerful means of overcoming this hindrance, although TDSO has been applied to sensors exposed upon oxidizing analyte, i.e., nitrogen dioxide (NO$_2$) [1]. Here, we present TDSO while exposing the chemiresistors (CRs) based on MoS$_2$ or WSe$_2$ to a reducing analyte, i.e., ammonia (NH$_3$).

2. Materials and Methods

We deposited molybdenum disulfide (MoS$_2$) or tungsten diselenide (WSe$_2$) by thermally assisted conversion (TAC) of patterned Mo or W. The chalcogens' vapors were produced from the solid source at ~115 °C and ~220 °C, for S and Se, respectively. The vapors were then diffused into the metal layers deposited on Si/SiO$_2$ substrate to form MoS$_2$ and WSe$_2$ at 750 and 600 °C, respectively [2]. On the pre-deposited TMDCs, we realized the resistors depositing the metal contacts via hard marks, i.e., Ti/Au for MoS$_2$ and Ni/Au for WSe$_2$ [2].

3. Discussion

Figure 1a illustrates the typical behavior of the signal when the sensors detect NH_3 at room temperature (RT). The current keeps decreasing along the entire exposure without ever reaching the steady state. However, reporting the maxima of TDSO as a function of the NH_3 concentration (Figure 1b,c), we observe linear correlations for both MoS_2- and WSe_2-based chemiresistors, as described in Ref [1]. We reported the absolute values of TDSO peaks because of the decreasing current (black curves) reported in the Insets. The red curves in the Insets show TDSO.

The values of coefficient R^2 show a close agreement between the experimental data and the linear fit, indicating that TDSO is a powerful, reliable, and valid approach when gas sensors are exposed to both oxidizing and reducing atmospheres [3,4]. These outcomes successfully mark a step forward in the treatment of gas sensors showing non-stationary behavior, independently from the investigated analyte.
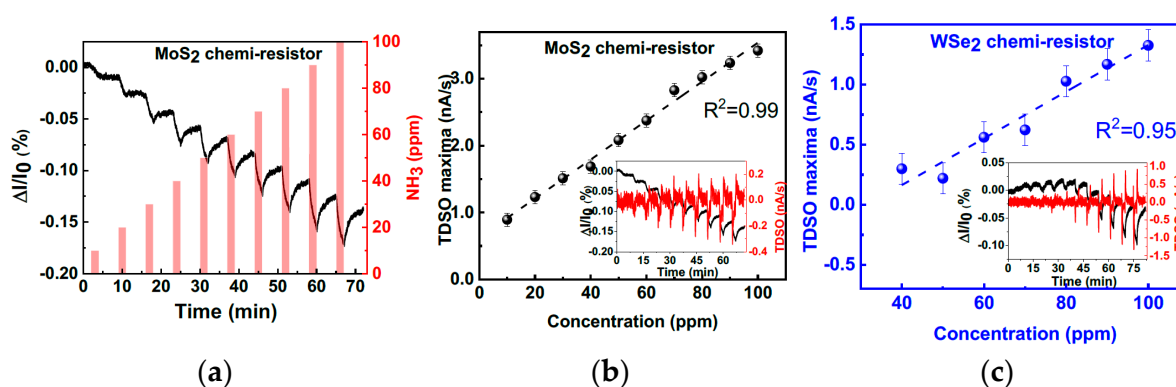

| (a) | (b) | (c) |

Figure 1. (**a**) Real-time percentage current variation (black curve) of MoS_2-sensor exposed to pulses of NH_3 at increasing concentrations (red rectangles). Each pulse lasts 150 s while dry N_2 is used as a buffer gas. Pressure and temperature were kept constant at 150 Torr and RT, respectively. Maxima of the differential curves as a function of the NH_3 concentration for (**b**) MoS_2- and (**c**) WSe_2-based sensors. The WSe_2-based sensor is calibrated in a narrower range because of the scarce response at concentrations lower than 40 ppm and TDSO peaks not being well defined.

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Informed Consent Statement: Not applicable.

Data Availability Statement: Dataset is available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Ricciardella, F.; Polichetti, T.; Vollebregt, S.; Alfano, B.; Massera, E.; Sarro, L. Analysis of a Calibration Method for Non-Stationary CVD Multi-Layered Graphene- Based Gas Sensors. *Nanotechnology* **2019**, *30*, 385501. [CrossRef] [PubMed]
2. Yim, C.; Lee, K.; McEvoy, N.; O'Brien, M.; Riazimehr, S.; Berner, N.C.; Cullen, C.P.; Kotakoski, J.; Meyer, J.C.; Lemme, M.C.; et al. High-Performance Hybrid Electronic Devices from Layered PtSe2 Films Grown at Low Temperature. *ACS Nano* **2016**, *10*, 9550–9558. [CrossRef] [PubMed]
3. Ricciardella, F.; Massera, E.; Polichetti, T.; Miglietta, M.L.; Di Francia, G. A Calibrated Graphene-Based Chemi-Sensor for Sub Parts-per-Million NO_2 Detection Operating at Room Temperature. *App. Phys. Lett.* **2014**, *104*, 183502. [CrossRef]
4. Ricciardella, F.; Lee, K.; Stelz, T.; Hartwig, O.; Prechtl, M.; McCrystall, M.; McEvoy, N.; Duesberg, G.S. Calibration of Non-Stationary Gas Sensors Based on Two-Dimensional Materials. *ACS Omega* **2020**, *5*, 5959. [CrossRef] [PubMed]