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NO2 gas sensors based on CVD tungsten diselenide monolayer

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ABSTRACT

Two-dimensional (2D) transition metal dichalcogenides (TMDs) are promising for gas sensors owing to their large surface-to-volume ratios, but the long recovery times stemming from the slow molecular desorption have been an important limitation. In this work, we report on a sensor for nitrogen dioxide (NO₂) made with a diselenide (WSe₂) monolayer synthesized via chemical vapor deposition, which functions within a range of concentrations from 100 ppb to 5 ppm and at various temperatures, including room temperature. When operated at an optimized temperature of 250 °C, the WSe₂ sensor exhibited the fastest recovery, with the response (τ_{res}) and recovery (τ_{rec}) times of 18 s and 38 s, respectively, when exposed to 100 ppb NO₂. The sensor also features high selectivity toward NO₂ in the presence of other target gases, in addition to reversibility and long-term stability within 60 days. The overall characteristics of the WSe₂ sensor make it suitable to monitor indoor/outdoor environments, mainly if further optimization is made with sensor design based on a model for the sensing mechanism we present in this paper.

1. Introduction

Human beings and animals are continually exposed to environmental hazards due to air pollution and emission from gas explosion accidents [1-3]. The exposure to toxic gases may lead to cancer and lung and heart diseases, whose early diagnosis requires gas sensing in health monitoring systems [4,5]. Nitrogen dioxide (NO₂) is one of the most hazardous polluting gases, coming mainly from exhaustion. Overexposure to NO2 has caused respiratory problems [6] as the NO2 gas molecules can easily cause inflammation of inner linings of lungs and reduce their immunity to infections, which is particularly harmful to people with asthma. Sensitive and selective NO2 gas sensors are therefore needed for monitoring indoor/outdoor environments to protect human health [7], which can, in principle, be exploited with the variety of materials employed in gas sensors. Selectivity and operation temperature are vital issues of the gas sensor, for example, Metal oxides possess high sensitivity towards toxic gases, but their operating temperature and selectivity are still limited [8]. Graphene-based sensors, on the other hand, exhibit poor performance at low concentrations and low recovery speed [9]. Some strategies, including surface functionalization, designing heterostructures, fabrication of nanocomposite, and utilization of metal oxides, have been employed to improve the selectivity of a sensor [10–12].

Possible alternatives for efficient gas sensors are the two-dimensional (2D) monolayered materials, especially transition metal dichalcogenides (TMDs) with the general formula MX_2 owing to their high surface area to volume ratios and susceptible large surfaces [13,14]. These 2D TMDs have been synthesized directly on silicon or glass substrates by chemical vapor deposition (CVD) [15–20], e.g., WS₂, MoS₂, $MoSe_2$, and WSe₂ were fabricated by CVD and atomic layer deposition (ALD) [21–23]. Recent works have proven that gas sensors made with 2D TMDs are sensitive to NO₂ gas, including at room temperature [24–27]. This has motivated us to institute a project and fabricate large-area and highly crystalline WSe₂ monolayers using the vapor phase reaction of WO₃ and Se carried by flowing gases in a tube furnace [28]. The rationale is to address the various factors that define the suitability of NO₂ gas sensors, namely sensitivity, selectivity, re-

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sponse and recovery rate, and stability. We show that sensors made with WSe_2 may be obtained with low detection limit, reproducibility, and reversibility in a wide range of NO_2 concentrations with the fastest recovery for operation at an optimized temperature.

2. Experimental details

2.1. Synthesis

A single zone furnace is shown in Fig. 1(a) was used for CVD growth of WSe2, with Se Powders (60 mg, 99.5%, Sigma-Aldrich) loaded outside the furnace at the upstream. When the furnace temperature reached 850 °C, the furnace was moved towards the upstream with a distance of 4 cm, where the temperature of Se powders reached 300 °C. WO₃ powders (10 mg, 99.5%, Sigma-Aldrich) were loaded in the center of the furnace. The sapphire substrate was placed on top of the WO₃ upside down. The sapphire substrate was previously treated with plasma to obtain a hydrophilic surface and coated with perylene-3,4,9,10-tetracarboxylic acid tetra potassium salt (PTAS) as the seeding promoter. The tube was pumped to the vacuum of 0.05 Torr and flushed with Ar gas to ambient pressure for three times. The temperature was increased to 250 °C at a rate of 50 °C/min, kept for 20 min, and then increased to 850 °C and kept for 10 min. During the process, Ar/H2, with the volume ratio of 85:15, was used as the carrier gas with a flow rate of 80 sccm at ambient pressure [29].

2.2. Gas sensing measurements

The gas sensing performance of WSe₂ monolayer films were evaluated in terms of the percentage sensing response, response, and recovery time. A pair of planar gold electrodes were deposited on top of the film by sputtering under a shadow mask with 2 mm spacing between electrodes, as shown in Fig. 1(b). The sensor film was wire-bonded into a dual in-line package (DIP) package and placed in a chamber with a volume of around 1 cm³ for electrical characterization and sensing measurements. The gases used in this study include NO₂ (21 ppm in N₂), H₂ (5% in N₂), CO₂ (2000 ppm in N₂), NH₃ (200 ppm in N₂), CO (500 ppm in N₂), which are calibrated and supplied by Praxair, Inc. A computer-controlled gas delivery system was used to flow individual gas at a constant gas flow rate of 300 sccm to the sensor chamber. In total, 12 mass flow controllers (Bronkhurst) controlled by LabView are used to dilute the gas mixture cylinder with clean air and deliver these gases to the sensor chamber. The stream balance and purge consisted of house air that was dehumidified using a pressure swing adsorption dryer and decontaminated using an activated carbon scrubber. The flow stream temperature and sensor chamber temperature are recorded and are controlled within a few degrees of room temperature. The sensor signal was analyzed using a data acquisition system (Labview) with an open-source Java-based instrument (Zephyr) for controlling and obtaining the data [30]. The sensor measurements were conducted with a Keithley 2602 source meter by applying a bias voltage and recording the current, from which the resistance R was calculated. The concept image of monolayer WSe₂ sensing NO₂ molecules is shown in Fig. 1(c), and the gas sensor response (S) is defined as:

$$\text{Response}(\%) = \left[\frac{\Delta R}{R_a}\right] \times 100$$
[1]

 $\Delta R = R_a - R_g$ for oxidizing gases like nitrogen dioxide (NO₂), where R_g and R_a are the resistance of the sensor film under the exposure of test gas and fresh air, respectively. The response time (τ_{res}) is defined as the time taken to reach 90% of the full response after the exposure of the target gas. The recovery time (τ_{rec}) is defined as the time taken to return to 10% of the baseline resistance after the flow of target gas is stopped. The as-prepared CVD-grown WSe₂ monolayers were characterized by Tapping mode atomic force microscopy (AFM) (Multimode, Bruker, USA), Raman spectroscopy, and photoluminescence (PL) (LabRam ARAMIS, HORIBA, equipped with a 532 nm laser as excitation source). X-ray photoelectron spectroscopy (XPS) was performed using the Scienta Omicron spectrometer (model ESCA +) integrated with monochromatic Al K α radiation (1486.6 eV) as the X-ray source for excitation. Optical microscopy (OM) images were taken using an Olympus DX51.

3. Results and discussion

Fig. 2(a) and (b) show the AFM image and height profile of WSe₂ on a sapphire substrate, where the thickness is 0.73 nm, consistent with data for mechanically exfoliated monolayered WSe₂ [28]. Fig. 2(c) shows the photoluminescence (PL) spectrum at room temperature taken with a micro-PL system (objective, 40X, NA 0.65) integrated with a 532 nm continuous wave (CW) laser, featuring a strong emission at ~ 760 nm assigned to the excitonic absorption. The Raman spectrum taken with excitation of a 473 nm laser shows the characteristic



Fig. 1. (a) Schematic diagram of the fabrication process of CVD-grown WSe₂. (b) Optical image of the 7 mm \times 3 mm gas sensing device. (c) A concept image of monolayer WSe₂ and the sensing behavior of NO₂ molecules (d) Experimental setup for gas sensing measurement.



Fig. 2. Material characterizations. (a) and (b) AFM analysis images of the WSe₂ monolayer. (c) Photoluminescence spectrum for monolayer WSe₂ with a microscopic PL system (excitation wavelength 532 nm). (d) Raman spectrum for the WSe₂ monolayer obtained in a confocal Raman spectrometer excited by a 473 nm laser.

peaks for monolayer WSe₂ at 248 cm⁻¹ assigned to E_{2g}^1 mode and 260 cm⁻¹ assigned to A_{1g} mode [31,32] in Fig. 2(d).

in Fig. 2(d).

The XPS spectra of WSe₂ monolayer for W4f and Se 3d scans are presented in Fig. 3(a) and (b), respectively. The 3d spectra of W and Se provide information on stoichiometry and bonding. The peak energies W4f_{7/2}, W4f_{5/2}, and W4f_{3/2} are located at 31.44, 33.64, and 37.19 eV, respectively, while Se3d_{5/2} and Se3d_{3/2} peak energies appear at 53.59 and 54.44 eV, which are typical of the semiconducting 2H phase[33–35] in WSe₂.

The real-time resistance response of the WSe₂ film at an operating temperature of 250 °C is shown in Fig. 4(a), where the resistance decreased after exposure to NO₂ gas in a p-type semiconductor behavior[36]. Fig. 4(b) depicts linear plots for current (I) vs. voltage (V) with the WSe₂ sensor at room temperature (RT) and 250 °C, in both cases with an Ohmic contact between the WSe₂ film and the electrodes. The resistance decreases at the higher temperature, as expected for a semiconductor. Fig. 4(c) shows the sensor response for the WSe₂ film as a function of NO₂ concentrations from 0 to 5 ppm at the working temperature of 250 °C. The sensor response increases as the gas concen-

3.1. Gas sensing performance of WSe₂ monolayer film



Fig. 3. The XPS spectra with fitted curves for (a) $WSe_2 W4f$ and (b) $WSe_2 Se3d$ scan.

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Fig. 4. (a) NO₂ gas sensing response for WSe₂ as a function of gas exposure at an operating temperature of 250 °C. (b) Linear I/V plots of the WSe₂ sensor at RT and 250 °C, respectively. (c) Sensor response versus gas concentration in the range of 0.1–5 ppm NO₂. (d) Gas sensing response of WSe₂ exposed to 5 ppm NO₂ at different operating temperatures.

tration increases, and the saturation level is almost the same as that highest concentration allowed by the current setup of the mass flux controller (MFC). For the exposure of 5 ppm NO₂, the sensor response achieves its maximum at 250 °C, according to Fig. 4(d). The sensor response achieves its maximum at 250 °C, with the appearance of a maximum being explained as follows. The reaction of NO₂ gas with chemisorbed oxygen sites increases with increasing temperatures, but above 250 °C, the desorption rate surpasses the adsorption rate. Therefore, we consider 250 °C as the optimal operating temperature where the adsorption and desorption processes reach an equilibrium. Table 1 shows a comparison of NO₂ sensing with WSe₂ and other NO₂ gas sensing materials, including MoS₂, WS₂, WSe₂, and WS₂ with graphene aerogel (GA) [24–29]. The sensor presented here is competitive with the most efficient for room temperature and displays the fastest recovery at an optimized temperature (250 °C).

For completeness, we show the gas sensing responses to NO₂ (5 and 2 ppm) at room temperature in Figure S1, as well as the reversibility and stability of the WSe₂ film sensor. Figure S2 depicts the dynamic electrical response for several NO₂ exposures (5, 5, 1, 0.1, and 5 ppm) at an operating temperature of 250 °C. After the sensor was exposed to 5 ppm NO₂ for 5 sensing cycles, it could still detect lower NO₂ concentrations, as shown in Figure S3. Since more NO₂ molecules interacted with adsorbed oxygen ions at the low concentration (0.1 ppm), a faster response time of 38 s was measured compared to that at a higher concentration (2 ppm). There was an irreversible chemical reaction, and the baseline resistance did not change. Fig. 5(a) shows enlarged response and recovery curves for the WSe₂ sensor at 5 ppm NO₂, for

Materials	NO ₂ concentration (ppm)	Recovery speed (min.)	Sensor res
comparison of N	O_2 gas sensor parameters for a WSe ₂ com	pound with other 2D materials.	

Materials	NO ₂ concentration (ppm)	Recovery speed (min.)	Sensor response (%)	Reference	Operating Temp. (⁰ C)
WS_2	10	-	84.7	[27]	RT
MoS_2	100	No Recovery	~14	[37]	RT
WS ₂ /GA	2	5	3	[38]	180
WS ₂ /GA	2	Incomplete	6.5	[38]	RT
WSe ₂	500	85	4140	[25]	RT
WSe ₂	500	21.5	_	[25]	100
WSe ₂	0.05	17.5	5.06	[39]	RT
WSe ₂	2	_	~10	[39]	RT
WSe ₂	0.5	-	238.35	[40]	RT
WSe ₂	2	24.5	18.8	this work	RT
WSe ₂	1	4.8	13.45	this work	250
WSe ₂	0.1	0.63 (38 s)	6.15	this work	250



Fig. 5. (a) Typical response-recovery characteristics of WSe₂ sensor at an operating temperature of 250 °C. (b) Sensing histogram of the WSe₂ sensor exposed to common gases present in the atmosphere to show good selectivity with NO₂ (c) Long-term stability of WSe₂ monolayer to 5 ppm of NO₂ at 250 °C for 60 days.

an improvement in the recovery time. The transient responses under 5 ppm of NO₂ also reveal the stable response and recovery characteristics. The corresponding response (τ_{res}) and recovery (τ_{rec}) times were 150.9 s and 669.8 s for 5 ppm, and 18 s and 38 s for 0.1 ppm NO₂ concentration, respectively. The response and recovery time as a function of NO₂ concentrations shows in Fig. S4, it can be seen that the response time increases with increasing ozone concentration. The response time increases from 18 to 150.9 s while recovery time also increases from 38 to 669.8 sec as the concentration increases from 0.1 to 5 ppm. However, at low concentration, more NO₂ molecules easily interact with adsorbed oxygen ions providing a fast response compared to higher concentration [41,42].

Fig. 5(b) indicates the selectivity of the WSe₂ sensor toward NO₂ gas when exposed to 2000 ppm of CO₂ and H₂, 200 ppm of NH₃, and 30 ppm of CO gases and 5 ppm of NO₂ gas at 250 °C. The response to NO₂ is higher than for other oxidizing and reducing gases because of its higher adsorption energy and degree of charge transfer [25,43], as expected from density functional theory (DFT) calculations [43]. The long-term stability of WSe₂ nanosheets is confirmed in Fig. 5(c) for ten measurements for two months with 5 ppm NO₂. It can be seen that

no apparent decline in the response in day one and day 60 (inset Fig. 5(c)).

Regarding the gas sensing mechanism, exposure to the oxidizing gas (NO₂) induced a decrease in resistance, which indicates a typical p-type sensing behavior [44] and an increase in resistance, which indicates n-type sensing behaviour [45,46]. There is also an unpaired electron on the nitrogen atom, which works as an electron acceptor, which allows us to propose the mechanism of Fig. 6. Electrophilic NO₂ molecules and oxygen species are spontaneously adsorbed and capture electrons from the conduction band, thus causing an increase in the concentration of holes, the majority carriers in p-type WSe₂ A hole-accumulation layer is created at the surface of WSe2 due to chemisorption of NO₂, and the resistance decreases. The scheme depicted in Fig. 6 also explains the slow recovery of WSe₂ at room temperature. With the high adsorption energy and charge transfer, the sensor resistance starts recovering slowly because of defects on the surface of WSe₂ exposed to NO₂ molecules. Hence, the slow recovery is due to the strong adsorption of NO₂ and WSe₂ [25,47]. The scheme we present here is only pictorial since other effects from chemisorption, physisorption, defect sites, and transduction should be considered to determine the whole adsorption/ desorption mechanism [48].

 $NO_{2 (gas)} + e^{-} \rightarrow NO^{-}_{2 (ads)}$



Fig. 6. Schematic picture of the sensing mechanism of WSe_2 monolayer exposed to NO_2 gas.

4. Conclusion

In this work, we reported on a high-performance WSe₂ gas sensor for NO₂, which was synthesized with the CVD process and evaluated at room temperature and high temperatures. While the sensor was competitive with other chemiresistive sensors [13,25,49,50] at room temperature, it exhibited the fastest recovery at an optimized temperature of 250 °C, also featuring fast recovery, reproducibility, and selectivity. The WSe₂ sensor works within the detection range from 0.1 to 5 ppm, thus being suitable to monitor the environment, especially when rapid detection is required, and power consumption is not a limitation. Taken together, our results confirm the expectation from the recent literature that WSe₂ is highly promising, but further studies are necessary not only to enhance the performance at room temperature but also to understand the sensing mechanisms in detail. Herein we provided a physical model that can explain qualitatively the decrease in resistance induced by the adsorption of NO2 molecules on the WSe2 surface, but other phenomena must be taken into account. Furthermore, new studies may be done to design WSe₂ sensors for other reducing and oxidizing gases, probably using different catalysts or tuning reaction parameters such as temperature and controlling morphology.

CRediT authorship contribution statement

Yichuan Wu: Writing - original draft, Methodology, Writing - review & editing. Nirav Joshi: Writing - original draft, Validation, Conceptualization, Writing - review & editing, Supervision, Investigation. Shilong Zhao: Methodology, Writing - original draft. Hu Long: Methodology, Software, Validation, Writing - review & editing. Liujiang Zhou: Writing - review & editing, Validation. Ge Ma: Writing - review & editing, Validation. Bei Peng: Writing - review & editing, Validation. Osvaldo N Oliveira Jr: Writing - review & editing, Supervision, Project administration. Alex Zettl: Writing - review & editing, Supervision, Project administration. Liwei Lin: Writing - review & editing, Supervision, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.apsusc.2020.147110.

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