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Sensing Behaviour of V-doped 2D MoS₂ in Sarin Detection

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Abstract. Although there are excellent properties in gas sensors, two-dimensional MoS₂ (2D MoS_2) has not been used in the detection of chemical agent sarin. In this paper, pure 2D MoS_2 and V-doped 2D MoS₂ sensors with few and multi-layers (5 and 10 layers, respectively) were prepared by low pressure chemical vapor deposition (LPCVD) method. The results of gas sensing tests show that V-MoS $_2(5 \text{ layers})$ exhibits the best sensing behavior in sarin detection. The low detection limit of V-MoS₂(5 layers) (0.02 mg/m³) meets the requirements of on-site identification and detection of sarin agent at trace level.

1. Introduction

Chemical sensor is the most promising technology in the detection of chemical warfare agents due to its small size, convenience for portability and integration, simple preparation and low cost. At present, most studies on gas sensors are focused on the metal oxide semiconductors¹⁻⁴. Although this type of material shows good sensing sensitivity to most harmful gases, it still cannot meet the requirements in the trace detection of chemical warfare agents.

Since single-layer graphene was successfully deposited by mechanical exfoliation method at 2004 for the first time by Geim and Novoselov et al.⁵, two-dimensional materials have become a hotspot in the scientific community. As a new kind of graphene-like materials, two-dimensional transition metal dichalcogenides (TMDCs), especially 2D MoS₂, show great application potential in gas sensors⁶⁻¹⁴. The chemical gas sensing mechanism is based on the gas adsorption and desorption processes going on the surface of the sensing material. When exposing to the air, the surface of bulk MoS₂ easily adsorbs atmospheric oxygen molecules, resulting in a significant decrease in the concentration and mobility of carriers. This in turn leads to the low gas sensitivity. The performance of gas sensors can be greatly improved by thinning the bulk MoS₂ to 2D MoS₂ thin film, which shows tunable electronic properties. However, one of the biggest hindrances in the application of 2D MoS_2 in the detection of chemical warfare agents is the weak interaction between the host layer and the adsorbates. Although lots of attempts have made to further improve the sensing performance of 2D MoS₂ thin film by creating defects, dopants, and strain, the V-doped 2D MoS₂-gas sensors have not been reported. This paper aims to fabricate V-doped MoS₂-gas sensors to improve the response stability and sensitivity in sarin detection. The sensing performances were studied in detail and the sensing mechanism was clarified.

2. Experimental

2.1. Preparation of MoS₂ and V-doped MoS₂

2D MoS₂ were synthesized by low pressure chemical vapor deposition (LPCVD) using MoO₃ powder and S powder as reactants. As shown in Figure 1, the S powder, MoO₃ powder and silicon thermal

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oxide wafer (Si+SiO₂) were placed in a quartz tube reactor (80 mm inner diameter) in sequence. During VCD process, the S powder was sublimed at 180 °C, and the temperature of chamber, where the MoO₃ powder sublimed and vapor deposition reaction occurred, was maintained at 650 °C. The flow rate of high-purity Ar, which was used as carrier gas, was controlled precisely by a mass flow meter. The principle of CVD is: (1) carried by flowing Ar, the sublimed S vapor enters the high-temperature CVD chamber and reacts with MoO₃ vapor, leading to the reduce of MoO₃ to MoO_{3-x}; (2) MoO_{3-x} was further sulfurized by S vapor to form 2D MoS₂ thin film. The formation of 2D MoS₂ by CVD is a surface diffusion-controlled process. To increase the rate of gas transport and improve the uniformity of the MoS₂ film, a low-pressure chemical deposition environment was employed. Prior to the CVD reaction, the system was vacuumed to remove air by a vacuum pump. The pressure of system was precisely controlled at 2000 Pa in the process of reaction.



Figure 1 Schematic diagram of preparation of 2D MoS₂ by chemical vapor deposition

The preparation of V-doped 2D MoS_2 follows the similar protocols of the preparation of pure 2D MoS_2 as described above. The only difference is that during the preparation of the V-doped sample, a uniform oxide powder (fully mixed and grounded VO_2 , MoO_3 and KCl powder in a mortar) was used as metal sources for VCD reaction. The KCl was added to increase the sublimation rate of VO_2 . The thickness, as well as the number of layers of 2D MoS_2 , was controlled by changing the time of VCD reaction. MoS_2 (few layers) and V- MoS_2 (few layers) samples were obtained through 15 min CVD reaction at the sulfur sublimation temperature of 180 °C, CVD reaction temperature of 650 °C, and the growth pressure of 2000 Pa. MoS_2 (multilayer) and V- MoS_2 (multilayer) were obtained through 20 min CVD reaction at the same conditions as described above.

2.2. Device fabrication and tests of sensing performance

In this paper, the Pt interdigital electrodes were deposited on silicon slice by DC reactive magnetron sputtering. Then the 2D MoS_2 thin film was deposited with above-mentioned LPCVD method. The gas sensing performance of obtained sensors in sarin detection was tested on a self-made intelligent gas-sensing analysis system. Specifically, the as-prepared gas sensors were located in the chamber of a homemade sensing system. The concentration of sarin was fed into chamber to obtain the response curve. The sensor performance can be evaluated in terms of sensor response (S) and response time. In this study, S is defined by the relative resistance change, as follows:

$$S(\%) = 100 * \frac{\Delta R}{R_0} = 100 * \frac{R_g - R_0}{R_0}$$

where R_0 is the initial resistance of the MoS_2 thin film sensor and R_g is the measured resistance upon gas introduction.

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3. Results and discussion

3.1. Sensing performance tests of four sensors based on the 2D MoS₂ in sarin detection

First, the response curves of four as-prepared gas sensors in a flow of air with 1 mg/m^3 sarin were examined to find the best one that showed the highest sensitivity in sarin detection (see Figure 2). Then, the concentration of sarin in flowing air was gradually decreased to investigate the influence of sarin concentration on the sensing performance. Finally, the repeatability and stability of the optimal sensor in sarin detection were studied.

As shown in Figure 2, all samples were sensitive to sarin and V-MoS₂(few layers) exhibited the highest sensitivity. Therefore, the gas sensing performance of sensor with V-MoS₂(few layers) was studied in detail in subsequent experiments.



Figure 2 The response curves of four as-prepared gas sensors in a flow of air with 1 mg/m³ sarin

3.2. The long-term response curve of sensor with V-MoS₂(few layers) in 1 mg/m³ sarin

The long-term response and recovery curve of sensor with V-MoS₂(few layers) in sarin with 1 mg/m³ concentration was recorded to clarify its sensitive response and recovery properties (see Figure 3). As an electron-donor, Sarin exhibits n-doping characteristics. When a 2D MoS₂ thin film is exposed to sarin-containing gas, adsorbed sarin molecules on the surface of MoS₂ shift the Fermi level to the conduction band, resulting in a resistance decrease consistent with n-type behaviour. As shown in Figure 3, it takes about 1500 s to achieve the adsorption equilibrium of sarin of the surface on V-MoS₂(few layers) and about 2400 s for the complete desorption of sarin. The sensitivities change rapidly in the initial periods of gas on and off and then have a tendency to level off. Considering the requirements of rapid identification and concentration-analysis in the trace detection of chemical warfare agents, the sensitivities of sensor with V-MoS₂(few layers) were obtained when exposing the sample in sarin-containing gas for 100 s to clarify the sensing performances in experiments below.



Figure 3 The long-term response and recovery curve of sensor with V-MoS₂(few layers) in 1 mg/m³ sarin

3.3. Influence of sarin concentration on the sensitivities of sensor with V-MoS₂(few layers)

Figure 4 shows gas sensor response curves of sensor with V-MoS₂(few layers) at various concentrations of sarin-containing gas, from 0.02 to 2 mg/m³ with a bias voltage of 0.5 V. For the sake of comparison, the response curves at six different concentrations of sarin were merged into one graph (see Figure 5). It can be clearly seen that the sensitivity of the sample increases with the sarin concentration. Taking into account the actual requirements in the detection of chemical warfare agents, the more attentions are given to the sensing properties at low concentration of sarin. Obviously, the sensor with V-MoS₂(few layers) still shows legible response curve with 0.73% sensitivity when exposing to the 0.02 mg/m³ sarin-containing air (3.2 ppb). When the concentration of sarin is lower than 0.1 mg/m³, the sensitivity of V-MoS₂(few layers) sample to sarin increases rapidly with the sarin concentration; while when the concentration of sarin is higher than 0.5 mg/m³, the rate of sensitivity change slows down. This phenomenon was the same as the law of gas adsorption on the surface of solid materials. It can be well explained by the fact that the higher concentration of sarin, the more active sites on the surface of V-MoS₂(few layers) are occupied by sarin molecules. At this situation, the increase in sarin concentration has little influence on the adsorption amount of sarin, leading to a smaller change in sensing sensitivity.

The low detection limit of V-MoS₂(few layers) sample in sarin detection shows obvious advantages: (1) At present, detection limit of traditional monitoring alarms based on the principles of electron capture, ion migration, and flame photometry is 1 mg/m^3 (0.16 ppm)¹⁵. However, the sarin-containing air shows great harm to human even that the concentration of sarin is lower than 10^{-2} - 10^{-1} mg/m. From this perspective, the sensor based on the V-MoS₂(few layers) thin film can meet the requirements for on-site identification and detection of sarin at trace levels; (2) the detection limit of sensor with V-MoS₂(few layers) is significant lower than that with the WO₃ thin film ¹⁶.



Figure 4 The response and recovery curves of sensor with V-MoS₂(few layers) in different concentration of sarin



Figure 5 The comparison of response and recovery curves of sensor based on the V-MoS₂(few layers) thin film in different concentration of sarin

To obtain the concentration of sarin from sensing sensitivity, the numerical fitting between the sarin concentration and response sensitivity was performed. We obtain:

S = -4.136 - 1.003Ln(C + 0.011)

Where, C is the sarin concentration in sarin-containing air, mg/m^3 ; S is the corresponding response sensitivity, %. As shown in Figure 6, there is a good logarithmic relationship between response sensitivity and sarin concentration. Therefore, the sarin concentration can be quantitatively calculated by above equation within the concentration range of 0.02-2 mg/m³.



Figure 6 The result of numerical fitting between the sarin concentration and response sensitivity

3.4. Repeatability investigation of sensor with V-MoS₂(few layers) in sarin detection

In order to test the repeatability of the response properties of V-MoS₂(few layers) sample, the response curve was measured for 5 times repeatedly. As shown in Figures 7 and 8, V-MoS₂(few layers) sample shows good repeatability (< 5% of fluctuation) both in 0.1 and 2 mg/m³ sarin containing air after baseline subtraction.



Figure 7 Sensing repeatability of sensor with V-MoS₂(few layers) in 0.1 mg/m³ sarin detection





3.5. Stability investigation of sensor with V-MoS₂(few layers) in sarin detection

The response curves of the sensor with V-MoS₂(few layers) in 1 mg/m³ sarin detection were recorded after exposing in in ambient room air for 3 months and 6 months to investigate the stability of sample. As shown in Figure 9, the sensing properties have little change after exposing in the atmosphere for different time. The variation amplitudes of sensitivity are always lower than 10%, indicating the excellent stability of this type sensor.



Figure 9 Sensing stability of sensor with V-MoS₂(few layers) in 1 mg/m³ sarin detection

3.6. Mechanism analysis of gas sensing of V-MoS₂(few layers)

The gas sensing response of semiconductor sensors is a complex process involving the interaction between gas molecules and the surface of V-MoS₂(few layers) thin film. On one hand, the oxygen molecules in the air adsorb on the active sites of the semiconductor surface and capture electrons in the conduction band of semiconductor to form oxygen ions. On the other hand, the adsorption and desorption of gas molecules on the surface of semiconductor lead to the complex transfer of electrons between adsorbents and surface. Above electron transfer phenomena lead to a reversible change in resistance of V-MoS₂(few layers) thin film during the adsorption and desorption process of sarin molecules. The change of resistance value strongly depends on the concentration of sarin in air. Therefore, the physico-chemical properties of gas-sensing material have great influences on the chemisorption, reaction, and electron transfer of sarin molecules with the surface of semiconductor, which determines the sensing properties of gas-sensing material. This can be understood from the following points: (1) the strong adsorption of sarin molecules on the surface of gas-sensing material leads to the difficulty in reaction and desorption, which results in the poor sensitivity and repeatability; (2) the weak adsorption of sarin molecules on the surface of gas-sensing material has a negative effect on the electron transfer between sarin molecules and the surface of semiconductor, which also results in the decrease of response sensitivity. Therefore, the ideal response sensitivity is obtained under the situation of optimal coverage and reactivity of sarin molecules on the surface of gas-sensing material, when the adsorption energy of sarin molecules on the surface of gas-sensing material is moderate.

It is worth mentioning that of V-MoS₂ (few layers) thin film prepared in this paper exhibits much better gas-sensing properties in sarin detection than traditional metal oxide materials, as discussed below. (1) Compared with metal oxide, V-MoS₂(few layers) thin film shows higher response sensitivity and faster response rate in sarin detection. In this study, the sensing limit of sensor with V-MoS₂ (few layers) thin film in sarin detection is lower than 0.02 mg/m³, which is much lower than that of binary precious metal modified metal oxide (0.053 mg/m³, Pt-Pd modified WO3). V acts as an efficient acceptor in MoS₂ and results in the formation of Schottky barriers, which leads to the high hole density and relatively high mobility and gives rise to the high sensing response at low sarin concentration. (2) V-MoS₂(few layers) thin film shows excellent sensing response in sarin detection even at room temperature. However, the optimal working temperature of metal oxide materials is 350-400 °C. Thus, V-MoS₂(few layers) thin film meets the requirement of real-time application at room temperature in the trace detection of chemical warfare agents. (3) Sarin molecules adsorbed on the 2020 International Conference on Energy Science and Engineering ThermophysicsIOP PublishingIOP Conf. Series: Earth and Environmental Science 605 (2020) 012012doi:10.1088/1755-1315/605/1/012012

surface of V-MoS₂(few layers) thin film can completely desorb in flowing or static air at room temperature in this paper. That is, V-MoS₂(few layers) sample has better self-desorption ability at room temperature than the metal oxide. (4) The most studied and used gas sensors are focused on the pump-suction technology at present. The sarin-containing gas is sucked into the sensor by a vacuum pump to achieve the purpose of quick detection. However, sarin molecules are sucked into the sensor only by the diffusion of sarin-containing flow in this study. Compared with pump-suction sensor, this type sensors have the advantages of low power consumption and easy operation.

4. Conclusions and outlook

 MoS_2 (few layers), V-MoS_2(few layers), MoS_2 (multilayer), and V-MoS_2(multilayer) thin films and corresponding gas sensors were successfully prepared by low pressure chemical vapor deposition (LPCVD) method. The gas-sensing properties of as-prepared sensors in sarin detection were investigated in detail. The results show that V-MoS_2(few layers) sample exhibits the highest response sensitivity and excellent recovery property, stability and repeatability to sarin detection. The low detection limit of V-MoS_2(5 layers) (< 0.02 mg/m³) meets the requirements of on-site identification and detection of sarin agent at trace level.

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