High hydrogen sensitivity of vertically standing layered MoS₂/Si heterojunctions

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ABSTRACT

Molybdenum disulfide (MoS₂) thin films are deposited onto silicon (Si) substrates using magnetron sputtering technique. Raman spectra show that the out-of-plane vibration is preferentially excited for the film. X-ray diffraction patterns further illustrate that the deposited MoS₂ films have the preferential [100] orientation. These results demonstrate that the unit layers of S-Mo-S in the film are perpendicular to the substrate. This can supply high-speed paths for the transportation of the electron carriers along the out-of-plane orientation. Due to the unique vertically standing layered structure of the MoS₂ film, the fabricated MoS₂/Si sensor device exhibits excellent hydrogen (H₂) sensing properties. The device performance can be featured by a high sensitivity (687.3% under 100.0 ppm H₂), high detection resolution (a 1.0-ppm level), as well as fast response and recovery, and good reversibility. The sensing mechanisms were discussed based on the microstructural characteristics of the MoS₂ film and the energy-band alignment near the MoS₂/Si interface. The MoS₂/Si heterojunctions proposed in this work might open new avenues for the development of future high-performance sensor devices.

Keywords: MoS₂; thin films; heterojunctions; sensing; ppm levels

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1. Introduction

Hydrogen (H_2) has attracted significant attention as a clean energy source, particularly due to its use in fuel cells for civil transportation and in rockets for space vehicles. However, there is serious concern about its safe production, storage and usage since it has a low explosive limit of about 4.0 vol% in air [1]. As a consequence, it becomes an important issue to develop reliable sensors for the leakage detection in various kinds of H_2 applications [2]. Sensing materials based on noble metal or oxide thin films work in air as sensors allowing detection of H_2 gas [3-10]. In a relative higher H_2 concentration than several hundreds of parts per million (ppm), the reported sensors exhibits high sensitivity, fast response and recovery and stability. However, obvious sensing characteristics to H_2 at as extremely low concentrations as a ppm level have been reported seldom. Especially, the low detection resolution makes it impossible for these sensors to be applied in the area of the accurate real-time H_2 detection. Therefore, it possesses high scientific and practical significance to find novel sensitive materials to develop high-performance H_2 sensors.

Molybdenum disulfide (MoS_2) is one typical kind of the layered transition metal dichalcogenides [11]. Structurally, MoS_2 is a stack of planes where covalently bonded S-Mo-S atoms in layers are closely packed in a hexagonal arrangement. This results in a large surface area of MoS_2 , and gas molecules can be adsorbed easily on the surface. On the other hand, the adjacent planes of MoS_2 are held together by van der Waals interactions. The weak interaction allows gas atoms or electrons to infiltrate and transport freely in MoS_2 . Therefore, MoS_2 -based nanoscale materials, such as graphene-like monolayers and bulk-like thin films, have become good candidates to fabricate high-performance gas sensors, such as H_2 , NH_3 , NO, DNA molecules, and many kinds of chemical vapor [12-18].

Undoubtedly, monolayer MoS₂ has attracted considerable interest in the area of electronic devices due to its high mobility and large current on/off ratio at room temperature [19-23]. However, the synthesis of large-size MoS₂ thin layers is still a challenge and the lateral size of the monolayer MoS₂ synthesized by various kinds of methods is often on the order of several micrometers [24]. Especially, the saturation of the sensitivity of the monolayer sensors can be caused easily during the gas detection due to the absence of enough adsorption sites [25]. These issues limit seriously the development of monolayer MoS₂ in the area of gas sensor devices. Comparatively, bulk-like MoS₂ thin films are more competitive in developing high-performance gas sensors based on the followed three reasons. Firstly, large-area thin films can be grown readily using pulse laser deposition technique, magnetron sputtering technique and high-temperature sulfurization [26,27]. Secondly, the gas sensors using MoS₂ thin films as sensitive layers can exhibit excellent sensing performance, such as high sensitivity, high resolution and wide measurement range [28]. Importantly, MoS₂ thin films are fully compatible with conventional silicon (Si) fabrication technology and can lead to cheap and high-performance devices [29]. Intrinsic MoS₂ belongs to n-type semiconductors and its band gap is about 1.2-1.9 eV. When MoS₂ films are deposited on Si surface, heterojunctions can be formed due to the energy-band bending at the interface. Compared with the sensor devices composed of single MoS₂ material, the excellent properties of MoS₂ could be integrated onto Si semiconductors through the configuration of MoS₂/Si heterojunctions [30]. Furthermore, incorporating two or more semiconductors to form a heterojunction interface can enhance the gas sensor performance [31,32]. Especially, it is reported that novel vertically standing layered MoS₂ films can be formed on Si substrates [33]. This unique microstructure could supply

high-speed paths for the transportation of the electron carriers along the out-of-plane orientation and high-performance H₂ sensor devices would be realized.

In this work, gas sensor devices were fabricated through the integration of MoS₂ thin films onto Si. Due to the nature of the vertically standing layer structure of the MoS₂ film, the transportation of the electrons in the film along the out-of-plane could be facilitated. This could promise the device excellent gas sensing properties. According to the measurements, the device showed a high sensitivity, high detection resolution, fast response and recovery, and good reversibility. The sensing mechanisms were proposed by the determination of the energy-band structure of the MoS₂/Si heterojunction.

2. Materials and experiments

MoS₂ thin films were deposited on (100)-oriented Si substrates using dc magnetron sputtering technique. The MoS₂ powders (purity, 99.9%) were cold-pressed into a disk as the target during sputtering. The Si substrates used in this work are n-type semiconductors with the resistivity of 3.2-6.8 Ω cm. Before the deposition, the substrates were ultrasonically cleaned in sequence by alcohol, acetone, alcohol, and de-ionized water. Then, the substrates were dipped into HF solution (~5.0%) for 60.0 s to remove the natural oxide layer from the Si surface. After that, oxidation treatment of the substrates were performed in peroxide solution (~40.0%) at 100 °C for 20.0 min to form a ~3.0-nm-thickness SiO₂ passivation layer on the Si surface. Subsequently, MoS₂ thin films were deposited. During the deposition, the working pressure of argon gas and deposition temperature were 5.0 Pa and 400.0 °C, respectively. Finally, the top ~30-nm-thickness Pd electrode was fabricated on the MoS₂ film using dc magnetron sputtering technique. The whole top surface of the film was covered by the electrode layer. The back

~200-nm-thickness In electrode were fabricated on the whole backside of the Si substrate using thermal evaporation.

Samples were characterized using Raman spectroscopy (Renishaw, 514 nm laser). X-ray diffraction patterns (XRD) were performed on a Bede D1 X-ray diffractometer with Cu-K α radiation ($\lambda=0.15406$ nm). The cross-sectional image of the sample was characterized by field-emission scanning electron microscope (FESEM, JSM-7001F, JEOL). X-ray photoemission spectroscopy (XPS) was performed by a Kratos Axis ULTRA spectrometer using a monochromatic Al K α X-ray source (1486.6 eV). The transmission spectra were measured by Shimadzu UV-3150 spectrophotometer. Ultraviolet photoelectron spectroscopy (UPS) were performed using an unfiltered He-I (21.22 eV) gas discharge lamp to determine the work function of the films.

The sensor was mounted inside an enclosed home-made chamber with different concentration of H₂ by volume in dry synthetic air at room temperature (~300 K). Dry synthetic air mixed with the desired concentration of H₂ gas was introduced through the quartz tube at a constant flow rate of 150 ml/min using mass flow controllers. One sensing cycle consists of three consecutive steps that include exposure of the device to dry air condition to record a base value of the device currents, to H₂ to obtain a sensing signal, and to dry air for sensor recovery. The current-voltage (*I-V*) curves were measured using two-point measurement by a Keithley2400 source meter at room temperature (RT).

3. Results and discussion

Fig. 1 shows the Raman spectrum of the MoS₂ film. The left inset shows the image of the MoS₂ film on Si. From the figure, two characteristic MoS₂ Raman peaks can be seen, the E_{12g}¹ mode at ~379.8 cm⁻¹ and A_{1g} mode at ~407.8 cm⁻¹. The right two insets illustrate

the atomic vibration direction in MoS₂, respectively. The E_{2g}¹ mode corresponds to the sulfur and molybdenum atoms oscillating in antiphase parallel to the crystal plane and the A_{1g} mode corresponds to the sulfur atoms oscillating in antiphase out-of-plane. From the figure, we can see that the Raman peak corresponding to the A_{1g} mode is preferentially excited for the film due to the polarization dependence. According to our measurements, the intensity ratio of E_{2g}¹/A_{1g} is ~0.48. These Raman results are similar with other reported results about MoS₂ films and imply that the grown MoS₂ films might be vertically-aligned on the substrates [34-37].

Fig. 2(a) shows the XRD pattern of the MoS₂ thin films. All the diffraction peaks can be indexed to MoS₂ with a hexagonal phase. Obvious diffraction peaks of the film at 33.9° and 69.1° corresponding to (100) and (200) can be observed from the figure. Combined the Raman characteristics, this further demonstrates that the deposited MoS₂ films on the Si substrate have the preferential [100] orientation. Thus, the S-Mo-S unite layers in the film are almost perpendicular to the substrate. This is similar with other studies about sputtered MoS₂ thin films on Si [38,39]. However, the MoS₂ layers are usually lying on the substrate with (001) planes parallel to the substrate surface in the recent reports about MoS₂ monolayer or multilayer [40-42]. The vertically standing layered structures of the as-deposited MoS₂ films would open up exciting opportunities for a variety of electronic devices [43], complementary to the MoS₂-based devices with horizontal atomic layers. Fig. 2(b) shows FESEM image of the MoS₂ thin films on Si. From the figure, column-like structures can be seen, which is complete different with the reported (001)-oriented MoS₂ films [44]. These results might be caused by the (100)-oriented lattice characteristics, where the film is vertically standing on the Si substrate [33,38,45]. Additionally, the

thickness of the film can be obtained from the FESEM image, about 88.0 nm and the deposition rate of ~5.9 nm/min for the film in our experiments can be determined.

Fig. 3(a) and (b) shows the XPS spectra of the MoS₂ film. The peaks at 229.3 and 232.5 eV are related to Mo 3d_{5/2} and Mo 3d_{3/2} orbitals, respectively, whereas S 2p_{3/2} and S 2p_{1/2} orbitals of divalent sulfide ions (S²⁻) are observed at 162.2 eV and 163.3 eV, respectively. The results are in good agreement with the reported values for the MoS₂ crystal [46].

Fig. 4(a) shows the schematic illustration of the electrical measurement of the fabricated sensor device. Forward voltages are defined as the positive voltages applied on the Pd top electrode. In the device, the thickness of the MoS₂ layer is ~15.0 nm determined by the sputtering time and deposition rate. Fig. 4(b) shows the *I-V* curves of the sensor device in air and 100.0 ppm H₂ at RT, respectively. The measurements were performed 30.0 min later after the device was put into air and H₂ condition, respectively. Under the air condition, the device exhibits good rectifying characteristics. This is similar with other junction-type devices [47,48]. The rectification ratio (I_+/I_-) at the voltage of ± 0.5 V reaches about 5.0×10^2 . In our studies [49], both the Pd/MoS₂ and In/Si contacts are ohmic. Thus, the rectifying characteristics in the device is mainly attributed to the MoS₂/Si junction. When the device is exposure upon 100.0 ppm H₂, obvious changes of the *I-V* curves happen, as shown in the figure. The current under a positive voltage increases largely. This demonstrates that the junction exhibits obvious H₂ sensing properties. Here, the sensitivity of the device to H₂ (*S*) is defined as

$$S = \left(\frac{I_{H_2}}{I_{Air}} - 1 \right) \times 100\% \quad (1)$$

where I_{H_2} and I_{Air} represent the current value of the device in H₂ and air conditions,

respectively. At +0.15 V, the current value increases from 1.4×10^{-2} mA to 1.1×10^{-1} mA and the S reached $\sim 685.7\%$. This sensitivity is much larger than other reported results [50-52]. The inset shows the semi-logarithm plot of measured I - V curves of the sensor devices with and without a MoS₂ sensitive layer under air and 100.0 ppm H₂ condition, respectively. From the figure, the sensing characteristics to H₂ can be also exhibited due to the interaction between H₂ and Pd layer. According to the calculated results, the sensitivity of the Pd/SiO₂/Si/In is only 33.5% which is much smaller than the Pd/MoS₂/SiO₂/Si/In sensor. Thus, the sensitivity to H₂ of the device can be enhanced greatly by the incorporation of the MoS₂ sensitive layer.

Fig. 5(a) shows the dynamic response of the Pd/MoS₂/SiO₂/Si/In sensor device upon varying H₂ levels from 1.0 ppm to 100.0 ppm at +0.15 V. The device shows significant response at each H₂ level, even at 1.0 ppm. When the conditions are changed alternately between air and H₂, two distinct current states for the device are shown, the “low” current state in air and the “high” current state in H₂, respectively. Both the “high” and “low” states are stable and well reversible. As shown in the figure, the background current exhibits a positive slope over the total duration of the exposure due to the charge accumulation. From the figure, strong dependence of the response on H₂ levels can be seen. Fig. 5(b) shows the dependence of the sensing response of the sensor device on H₂ levels. As can be seen, an almost linear correlation is obtained in the measured range of H₂ levels. When the junction is exposed to 1.0 ppm H₂, S is about 30.4%. With increasing the H₂ level, S increases gradually. Under 100.0 ppm H₂, S reaches 687.3%. Fig. 5(c) shows the dependence of the response time (t_{res}) and recovery time (t_{rec}) on H₂ levels, respectively. Here, t_{res} is defined as the time to rise from 10% to 90% of the total change and t_{rec} is

defined as the time to decay from 90% to 10% of the total change. According to the measured results, t_{res} and t_{rec} under 1.0 ppm H_2 are about 455.6 s and 389.3 s, respectively. As shown in the figure, both t_{res} and t_{rec} decrease continuously with increasing the H_2 levels. Under 100.0 ppm, t_{res} and t_{rec} are about 108.7 s and 101.9 s, respectively. From the figure, we can see that the recovery to H_2 of the device is always faster than the response. This demonstrates that a little difference between the processes of the adsorption and desorption of H_2 exists in the device.

Fig. 6 shows the transient H_2 response at varying H_2 levels from 1.0 ppm to 5.0 ppm with a 1.0-ppm interval. When the sensor device is exposure upon 1.0 ppm H_2 , the sensitivity increases gradually and then tend to reach a saturated vale. The similar characteristics of the sensitivity are shown in the period of each H_2 level. As shown in the figure, step-like increase of the sensitivity can be caused by a slight increase of 1.0 ppm of the H_2 level. This demonstrates that the detection resolution of the fabricated $Pd/MoS_2/SiO_2/Si/In$ sensor can reach the 1.0-ppm level. This resolution is comparable with the highest values among all the reported H_2 sensors [53]. All above sensing characteristics make it possible for the MoS_2/Si to act as high-performance H_2 sensors.

To clarify the sensing mechanisms, it is critical to construct the energy-band alignments near the interfaces of the sensor device. Using the data from the ultraviolet-visible (UV) spectra of the MoS_2 film, the $(\alpha h\nu)^2$ was plotted as a function of photon energy $h\nu$, as shown in Fig. 7(a), wherein h is the Planck constant and ν is photon frequency. The α is the absorption coefficient, calculated by $\alpha d = \ln(1/T)$, d and T are thickness and transmittance of films, respectively [54]. The band gap (E_{gl}) of the film can be obtained by intercept of the line on $h\nu$ axis. From the figure, $E_{gl}=1.29$ eV. The obtained

energy-band value for the film is much close to the value for MoS₂ bulk (~1.2 eV). Fig. 7(b) shows the UPS spectrum of the MoS₂ film on the Si substrate. The work function (W_1) of the film can be calculated from the difference between the cutoff of the highest binding energy and the photon energy of the exciting radiation. From the figure, W_1 of 4.33 eV can be obtained. Since the Fermi level (E_{FI}) of MoS₂ exists between the conduction band (E_{CI}) and the valence band (E_{VI}), the distance (ΔE_I) between E_{VI} and E_{FI} of MoS₂ film can be extracted from the onset energy, as shown in the inset. The ΔE_I is determined to be 0.93 eV. This further demonstrates the n-type behavior of the as-deposited MoS₂ film. The Fermi level (W_2) of n-type Si is 4.21 eV, and its electron affinity (χ_2) and band gap (E_{g2}) is respectively 4.05 eV and 1.12 eV [55]. Based on the above results, the energy-band diagram near the MoS₂/Si interface are constructed, as shown in Fig. 7(c). The isolated MoS₂ film has a larger work function than the Si substrate. Thus, there exists a barrier ($\Delta E_B = W_1 - W_2$) for electrons at the MoS₂/Si interface when the heterojunction are formed [56], as shown in the figure. Fig. 7(d) shows the schematic illustration of the sensing mechanism of the fabricated sensor device. When the device is exposure upon H₂, gas molecules quickly reacts with the top Pd electrode layer and forms palladium hydride (PdH_x), which is reversible [57,58]. This results that large quantities of electrons are released from the Pd layer and injected into MoS₂ film. These electrons can increase the concentration of the electron carriers in the MoS₂ film. This means that the Fermi level of the MoS₂ film is shifted toward the conduction band accordingly and the work function decreases. Consequently, the barrier height at the MoS₂/Si interface decreases and the junction currents increase after the device exposure to H₂, as shown in Fig. 4(b). Therefore, the fabricated device exhibits H₂ sensing characteristics. According to the obtain results

from XRD patterns in Fig. 2(b), the deposited MoS₂ films on the Si substrate are vertically standing layered structure, as illustrated in Fig. 7(d). From the figure, we can see that the injected electrons can pass the MoS₂ film by two kinds of paths: The first one is the unit layers of S-Mo-S. High-speed movement for electrons in the layers could be realized along this path. This can be well demonstrated by the nature of a high in-plane conductivity and mobility of MoS₂ monolayers [19,21]. Another path is the gaps between S-Mo-S unit layers. Due to the large distance (~0.64 nm) and the weak van der Waals interactions between the nearest neighbor layers [59], electrons could pass the layer gaps freely. As a result, the transportation of the electrons in the MoS₂ film could be greatly facilitated along the out-of-plane orientation. Compared to other nanoscale materials [7-9,60,61], it is much easier for the injected electrons to reach the interface area in the vertically-standing layered MoS₂ film and larger effects on interface barrier could be caused after the device exposure to H₂. Thus, a slight change of surrounding H₂ condition, even at a 1.0-ppm level, can be detected by the fabricated MoS₂/Si sensor and excellent sensing performance can be exhibited, such as high sensitivity, high detection resolution and fast response. When the device is exposed to air again, H₂ molecules are desorbed from the Pd layer resulting in the electrons being released from the MoS₂ film, so that the sensor device is recovered. Additionally, the thin SiO₂ layer at the MoS₂/Si interface can serve as a passivation layer to reduce the interface defects [62], thus improving the sensing properties of the device.

4. Conclusions

In summary, (100)-oriented MoS₂ thin films were deposited on n-Si substrates using magnetron sputtering technique and the Pd/MoS₂/Si sensor devices were fabricated. Due to the vertically standing layered structure of the film, the sensor device exhibited

excellent sensing properties to H₂. The device performance was featured by a high sensitivity (687.3% under 100.0 ppm H₂), high detection resolution (a 1.0-ppm level), as well as fast response and recovery, and good reversibility. Thus, the present device architectures can be envisaged as valuable candidates for high-performance H₂ sensors.

Acknowledgments

The authors would like to acknowledge the financial support by the National Science Foundation of China (Grant No. 51502348 and 21476262) and the Fundamental Research Funds for the Central Universities (14CX05038A and 15CX08009A).

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Caption

Fig. 1. Raman spectrum of the deposited MoS₂ films. The left inset shows the image of the MoS₂ film on Si. The right insets show the schematic illustrations of the oscillating mode of E_{12g}¹ and A_{1g}, respectively. Atom color code: light blue-green, Mo; yellow, S.

Fig. 2. (a) X-ray diffraction pattern of the MoS₂ thin films. (b) FESEM image of the MoS₂ thin film on Si.

Fig. 3. (a) and (b) Binding energies of Mo and S for the MoS₂ film, respectively.

Fig. 4. (a) Schematic illustration of the electrical measurement of the Pd/MoS₂/SiO₂/Si/In sensor device. (b) *I-V* curves of the sensor device in air and 100.0 ppm H₂ at RT, respectively. The inset shows the semi-logarithm plot of measured *I-V* curves of different kinds of sensor devices under different gas conditions: numbers of 1-4 represent the *I-V* curves for Pd/SiO₂/Si/In and Pd/MoS₂/SiO₂/Si/In sensors in air and 100.0 ppm H₂, respectively.

Fig. 5. (a) Dynamic responses of the Pd/MoS₂/SiO₂/Si/In sensor upon consequent H₂ at varying H₂ levels from 1.0 ppm to 100.0 ppm at +0.15 V. (b) Dependence of the sensitivity of the junction on H₂ levels. (c) Dependence of the response time and recovery time on H₂ levels, respectively.

Fig. 6. Transient H₂ response at varying H₂ levels from 1.0 ppm to 5.0 ppm with a 1.0-ppm interval.

Fig. 7. (a) Plot of $(\alpha h\nu)^2$ versus $h\nu$ for the MoS₂ film. (b) UPS spectra of the MoS₂ film on Si, showing its Fermi level and the gap between the Fermi level and the conduction band, respectively. (c) Schematic illustration of the energy-band structure of the device. E_0 is vacuum-energy level, W is work function, E_g is energy band gap, E_F is Fermi-energy level, E_C is the bottom of conduction band, and E_V is the top of valence band, respectively. (d) Schematic illustration of the sensing mechanism of the MoS₂/Si sensor device.

Novel H₂ sensors were fabricated through the integration of vertically standing layered MoS₂ thin films onto silicon. The sensing performance was featured by a high sensitivity, a ppm-level detection resolution, as well as fast response and recovery, and good reversibility.