Journal of Alloys and Compounds 735 (2018) 88–97

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Giant lateral photovoltaic effect in $MoS_2/SiO_2/Si$ *p-i-n* junction

L.Z. Hao [a, b, *], Y.J. Liu [a], Z.D. Han [a], Z.J. Xu [a], J. Zhu [b]

[a] College of Science, China University of Petroleum, Qingdao, Shandong, 266580, People's Republic of China
[b] State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu, 610054, People's Republic of China

ARTICLE INFO

Article history:
Received 29 July 2017
Received in revised form
24 October 2017
Accepted 7 November 2017
Available online 8 November 2017

Keywords:
MoS_2
Film
Lateral photovoltage
Junction
Interface

ABSTRACT

Molybdenum disulfide (MoS_2) is investigated as one typical kind of two dimensional (2D) materials for developing various kinds of electronic devices. Here, we report a giant lateral photovoltaic effect (LPE) in a $MoS_2/SiO_2/Si$ *p-i-n* junction. MoS_2 films are deposited on Si substrates using magnetron sputtering technique and a SiO_2 layer is incorporated to perform the modification on the MoS_2/Si interface. After the first 5-nm-thickness horizontally lying layer on the SiO_2 layer, the atomic unit layers of S-Mo-S in the followed MoS_2 film are almost perpendicular to the substrate surface and the vertically standing layered structure is formed. Owing to the interface modification of the SiO_2 layer and the unique structure of the MoS_2 film, a giant LPE is observed in the fabricated junction. The LPE shows a linear dependence on the position of the laser illumination and the considerably large sensitivity of 355.4 mV/mm is obtained with the fast response of 16.2 μs. The mechanisms to the LPE are unveiled by building the correlation between microstructures, energy-band alignment and optoelectrical properties of the $MoS_2/SiO_2/Si$ junctions. The excellent LPE characteristics could make MoS_2 films combined with SiO_2/Si promising candidates for the application of high-performance position sensitive detectors.

1. Introduction

Since the first discovery by Wallmark [1], intensive research on lateral photovoltaic effect (LPE) have been conducted for a long time. Different from the ordinary longitudinal photovoltaic effect, the LPE originates from the lateral diffusion of the photogenerated carriers in the inversion layer induced by the built-in electrical field (E_{bi}) of the heterojunctions. In the LPE effect, a lateral photovoltage (LPV) can be obtained and it changes linearly with the laser spot position on the active region of the device surface. These characteristics make LPE very useful in developing high-performance position-sensitive detectors (PSDs). Thus, LPE has attracted much attention in the area of robotics, biomedical applications, process control, position information systems, and so on [2–4]. The LPE has been observed in many systems, such as metal-semiconductor Schottky devices and *p-n* junctions [5–8]. However, the reported sensitivities are mostly within the range of 0.2–50 mV/mm, which can't meet the requirement of high-resolution PSDs. In order to improve the device sensitivity, one ultra-thin TiO_2 layer is inserted into the interface of the Ti/Si devices by Yu et al. [9]. The results display that the LPE can be enhanced due to the modification of the TiO_2 layers on the Ti/Si interface and a large sensitivity of 113 mV mm^{-1} is obtained. However, high conduction nature of metals could lead to the danger of shorting and the instability of the metal-semiconductor device. Wang et al. further reports a device composed of SnSe semiconductor films and single-crystal Si [10]. The SnSe/Si devices shows a LPE with a sensitivity of 250 $mVmm^{-1}$. The high sensitivity of the SnSe/Si junction is attributed to the high resistivity of the SnSe film because it can increase the difference between the concentrations of the photoexcited carriers at the electrodes. At the same time, however, the high resistivity of the film increases the difficulties of the collection of the photoexcited carriers on the electrodes and the decrease of the LPE can be caused. These results demonstrate that the conduction of the active layer is crucial for PSDs to acquire high sensitivity. For ideal films applied on PSDs, low conduction along in-plane direction while high conduction along out-of-plane would be desired. This supplies ideas in the choice of active materials to achieve the LPE with a high sensitivity.

Molybdenum disulfide (MoS_2), a typical 2D metal dichalcogenide, has become one of the hottest research topics due to its good electrical, mechanical, optical and electrochemical properties

* Corresponding author. College of Science, China University of Petroleum, Qingdao, Shandong, 266580, People's Republic of China.
E-mail address: haolanzhong@upc.edu.cn (L.Z. Hao).

https://doi.org/10.1016/j.jallcom.2017.11.094
0925-8388/

[11–15]. Especially, MoS_2 can absorb up to 5–10% incident sunlight even in a thickness of less than 1 nm, showing one order of magnitude higher sunlight absorption than the most commonly used sunlight absorbers Si and GaAs [16]. Thus, MoS_2 would open up exciting opportunities for developing high-performance optoelectronic devices, such as photodetectors and solar cells [17–30]. Structurally, MoS_2 has a crystal structure consisting of sandwich atomic unit layers of S-Mo-S, where a Mo-atom layer is enclosed within two S-atom layers and the atoms in layers are hexagonally packed. These layers are held together by van der Waals interaction. The weak van der Waals interaction makes it easy for MoS_2-based materials to be exfoliated into monolayers. In the previous reports about MoS_2 monolayer [31–33], the MoS_2 layers are always lying on the SiO_2/Si substrates with the S-Mo-S unit layers parallel to the Si surface. Recently, MoS_2 thin films with the vertically standing layered structure are also synthesized successfully [34–40]. Different with the horizontal atomic layers, the S-Mo-S unit layers in the films are perpendicular to the substrate surface. Due to its unique microstructural characteristics, the vertically standing layered MoS_2 films exhibit many excellent properties, such as the enhanced catalytic activity [34], superior sensing performance [35], ultrafast photoresponse [36] and etc. In the vertically standing layered MoS_2 films, the out-of-plane conduction can be enhanced because each vertical standing atomic layer supplies high-speed transporting path for the carriers, while the in-plane conduction is suppressed due to the large gaps between the unit layers. Thus, the MoS_2 films with the vertically standing layered structure show anisotropic conduction and the ratio of out-of-plane and in-plane conductivity can reach 10^3 [41]. Based on these characteristics, large LPE would be realized if the vertically standing layered MoS_2 films with the anisotropic conduction were combined with other semiconductors. Qiao et al. reported an ITO/MoS_2/*p*-Si heterojunction with an obvious LPE of 42.27 mV/mm, which could be caused by the poor MoS_2/Si interface [42]. Hu et al. further fabricated PSD devices through the deposition of the amorphous MoS_2 films onto the *n*/*p*-Si substrates [43]. From the results, we can see that the sensitivity of the fabricated devices is only 183 mV mm^{-1} due to the weak transporting ability of the carriers in the amorphous layer along the out-of-plan orientation. As well known, there is a large lattice difference between MoS_2 and Si, which would result in large quantities of lattice defects at the interface when MoS_2 films were deposited straight on Si surface. Additionally, serious element diffusion and inherent reactivity at the interface are unavoidable during the film growth. These interfacial characteristics can degrade largely the performance of the MoS_2/Si devices. Thus, it is necessary to conduct interface modification before making viable functional devices on Si. The results show that the power conversion efficiency of the MoS_2/Si solar cells can be enhanced significantly by the insertion of buffer layers into the interface, such as SiO_2, Al_2O_3, BN, etc [44–46]. However, the studies about the influence of the interface modification on the LPE of the MoS_2 devices are absent.

In this work, MoS_2 films were deposited on *n*-Si substrate using magnetron sputtering technique. The modification on the MoS_2/Si interface was performed by the incorporation of a SiO_2 layer at the interface. A giant LPE was observed in the fabricated MoS_2/SiO_2/Si heterojunction and the sensitivity reached 355.4 mVmm^{-1}. Through the characterization of the microstructure and electrical properties, the energy-band alignment at the interface was constructed and the mechanisms to the LPE in the devices were proposed.

2. Materials and experiments

MoS_2 thin films were deposited on (100)-oriented Si substrates using dc magnetron sputtering technique. The Si substrates used in this work are n-type and the resistivity is about 3.2–6.8 Ω cm. Before the deposition, the substrates were ultrasonically cleaned in sequence by alcohol, acetone, and de-ionized water. Then, the substrates were dipped into HF solution (~5%) 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 SiO_2 passivation layer on the Si surface. Subsequently, MoS_2 thin films with different thickness (5 nm, 15 nm, 40 nm, 60 nm, 100 nm, 150 nm and 350 nm) were grown on the SiO_2 covered Si substrates at the temperature of 400 °C, respectively. During the deposition, the working pressure and power were kept at 1.0 Pa and 10.0 W, respectively. As a reference, the samples without SiO_2 layers at the interface were also fabricated under the same condition. Finally, about 300-μm In pads with a diameters of 0.5 mm as electrodes were pressed on the MoS_2 film.

MoS_2 films were characterized using Raman spectroscopy (HORIBA, HR800) with the excitation wavelength of 488 nm. *X*-ray photoemission spectroscopy (XPS) was performed by a Kratos Axis ULTRA spectrometer using a monochromatic Al Kα X-ray source (1486.6 eV). The cross-sectional images of the samples were characterized by field-emission scanning electron microscope (SEM) (JSM-7001F, JEOL). Transmission electron microscope (TEM) was performed on a JEOL JEM-2100F and selected area electron diffraction (SAED) technique were done to characterize the crystallization. The transmission spectra were measured by Shimadzu UV-3150 spectrophotometer. Ultraviolet photoelectron spectroscopy (UPS) was performed using an unfiltered He-I (21.22 eV) gas discharge lamp.

LPVs were measured using a Keithley 2000 voltmeter and three dimensional electric motorized stage with a laser of 650-nm wavelength as the illumination source. The current-voltage (*I-V*) curves were measured with a Keithley 2400 SourceMeter. The response and recovery speeds of the device were evaluated by combining a digital oscilloscope (Keysight DSOX 2012A) with a light chopper (SR540, Stanford Research System).

3. Results and discussion

Fig. 1(a)-(b) show the XPS spectra of the as-deposited MoS_2 film on the SiO_2/Si substrate. The peaks at 232.9 eV and 230.1 eV are related to Mo $3d_{3/2}$ and Mo $3d_{5/2}$ orbitals, respectively, whereas S $2p_{3/2}$ and S $2p_{1/2}$ orbitals of divalent S^{2-} can be observed at 162.3 eV and 163.6 eV, respectively. The results are in good agreement with the reported values for MoS_2 crystals [47]. Fig. 1(c) shows the Raman spectrum of the MoS_2 film. Two characteristic MoS_2 Raman peaks can be seen, the E^1_{2g} mode at ~379.8 cm^{-1} and A_{1g} mode at ~407.8 cm^{-1}. The insets illustrate the atomic vibration direction in MoS_2. The E^1_{2g} mode corresponds to the S and Mo atoms oscillating in antiphase parallel to the crystal plane and the A_{1g} mode corresponds to the S atoms oscillating in antiphase along the out-of-plane direction. As shown in the figure, the Raman peak corresponding to the A_{1g} mode is preferentially excited for the film. According to our measurements, the intensity ratio of E^1_{2g}/A_{1g} is about 0.42. This can be attributed to the pronounced out-of-plane vibration A_{1g} over in-plane vibration E^1_{2g}, implying the vertically standing structure of the MoS_2 film on the surface of the SiO_2/Si substrate [48].

Fig. 2 shows the SEM images of the 60-nm-thickness MoS_2/SiO_2/Si and 350-nm-thickness MoS_2/SiO_2/Si heterostructures. According to the film thickness and the deposition time, the growth rate of the MoS_2 films in our experiments is determined, about 6.5 nm/min. As shown in Fig. 2(a)-(b), the as-deposited MoS_2 films are composed of large quantities of nanosheets and the distinct vertically standing