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Thermal Evaporation Deposition of Few-layer MoS_2 Films

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Abstract: We present a study of the fabrication of monolayer MoS_2 on n-Si (111) substrates by modified thermal evaporation deposition and the optoelectrical properties of the resulting film. The as-grown MoS_2 ultrathin film is about 10 nm thick, or about a few atomic layers of MoS_2. The film has a large optical absorption range of 300-700 nm and strong luminescence emission at 682 nm. The optical absorption range covered almost the entire ultraviolet to visible light range, which is very useful for making high-efficiency solar cells. Moreover, the MoS_2/Si heterojunction exhibited good rectification characteristics and excellent photovoltaic effects. The power conversion efficiency of the heterojunction device is about 1.79% under white light illumination of 10 mW/cm^2. The results show that the monolayer MoS_2 film will find many applications in high-efficiency optoelectronic devices.

Keywords: Monolayer MoS_2; Thermal evaporation deposition; Absorption spectrum; I-V behavior

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Introduction

Two-dimensional materials have attracted much interest for their interesting physics and possible use in electronic devices [1,2]. Molybdenum disulfide (MoS_2) is a sandwich-like compound in which a metal atom is bonded to six sulfur atoms, and each layer is linked by a weak Van der Waals force [3]. Analogous to graphene, MoS is easily split into a layered structure. A monolayer MoS_2 sheet undergoes a large transformation of the energy band gap from an indirect to a direct one [4,5]. With a large direct energy band of 1.8 eV [3], high electron mobility [6], reduced dimensionality, and favorable mechanical properties [7], single- or few-layer MoS_2 has attracted interest for novel nanoscale electronic and optical applications [6,8]. Transistors fabricated with MoS_2 atomic thin layers exhibit an excellent on/off current ratio and high carrier mobility, which make them suitable as next-generation transistors [6]. The optical and electronic properties of MoS_2 also make it a potential candidate for efficient solar energy cells [9,10] and for use as a cathode in high-density lithium batteries [11,12]. In these devices, the fabrication of a thin MoS_2 film and investigation of the electrical properties of the MoS_2 heterojunction system are the most commonly encountered processes. Monolayer MoS_2 films have been prepared by a variety of techniques such as an adhesive-tape-based micromechanical cleavage technique commonly associated with the production of graphene [6], lithium-based intercalation [13,14], chemical vapor transport [15,16], and metalorganic chemical vapor deposition [17]. The preparation process or equipment used in these approaches is very complex. In this work, the objective of our research was to find a simple method of fabricating a MoS_2 film of atomic thickness and study its optical and electronic properties. Thin MoS_2 films were prepared by modified thermal evaporation deposition. Then we investigated their morphology and optical and electrical characteristics.

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Experimental

The MoS_2 films were fabricated on n-Si (111) surfaces by a modified thermal evaporation vapor deposition process. The growth system consists of a large horizontal quartz tube furnace, a vacuum system, a gas meter, and an automatic temperature controller. The n-Si substrates 15×15 mm^2 in size were cleaned ultrasonically with a sequence of acetone, ethanol, and deionized water, and then they were blown dry with N_2 and placed at the center of the furnace. Before deposition, the furnace was pumped to 10^{-2} Pa and heated to 300℃ for 10 min to remove any water moisture. In the traditional evaporation technique, the source material is put in an open pot and evaporated by heating. It is hard to control the growth speed and thickness of the deposited film. In our experiment, the source material, analytically pure MoS_2 powder, was first pressed into tablets and sintered for 20 min at 300℃. One tablet was placed in a closed cubic iron box with many pinholes on one side, which was positioned at the front end of the quartz furnace. In the MoS_2 film deposition process, MoS_2 molecules evaporated from the tablet and became MoS_2 molecular beams by passing through the pinholes of the closed box; this technique can enable the deposition of a MoS_2 film at a very low speed. To obtain uniform growth, Ar gas with a volume ratio of 10~30 sccm was introduced into the reactive chamber at 500℃, and the working pressure was kept at 50 Pa. After MoS_2 molecules were absorbed and condensed on the Si substrates, thin MoS_2 films were formed by varying the evaporation time between 2 and 10 min. Finally, the samples were removed after the system cooled to room temperature. Al contact electrodes (2×2 mm^2, 300 nm) were formed by thermal evaporation through a shadow mask at the corner of the MoS_2 and the back side of the Si substrates.

The morphology and structure of the samples were characterized by atomic force microscopy (AFM). The structure was analyzed by X-ray diffraction (XRD) using a RINT2000 vertical goniometer with Cu Kα radiation ($\lambda = 0.1541$ nm). The optical absorption spectrum of the MoS_2 films was investigated by ultraviolet-visible (UV-vis) spectroscopy (Shimadzu UV-3600). Finally, the photovoltaic characteristics of the MoS_2/Si heterojunction solar cells were evaluated by a Keithley 4200 SCS instrument under white light illumination.

Results and discussion

Figure 1(a) shows an AFM image of the deposited MoS_2 film on the n-Si substrate. Many MoS_2 slices or islands are scattered uniformly at the top of the picture. From the scales of bottom and right of Fig. 1(a), we can estimate the slices are about 50-200 nm in length and 5-6 nm thick, which is about ten layers of MoS_2 (a mono layer about 0.65 nm). In the sublayers of the slices, we can see that there is a large, uniform, continuous MoS_2 film with a deep yellow color. We confirmed that the MoS_2 film grows in layer-island mode. That is, MoS_2 islands form on the substrate initially; then the islands gradually combine with each other and become a continuous film, on which new islands are formed continuously with time. This growth mode corresponds to the characteristics of the layered structure of MoS_2. Figure 1(b) shows the XRD pattern of the as-grown MoS_2 sample. Four strong diffraction peaks are located at 13.4°, 28.3°, 33°, and 36.7°, corresponding to the (002), (004), (100), and (101) crystal planes of MoS_2, respectively.

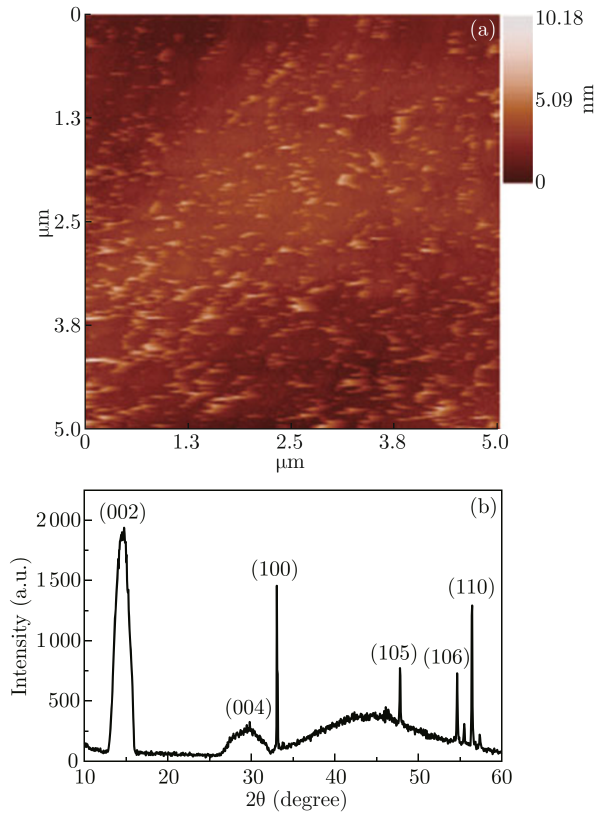

Fig. 1 (a) AFM image of MoS_2 film deposited on n-Si substrate. MoS_2 islands are about 50-200 nm in length and 5-10 nm thick, equaling ten layers of MoS_2. (b) XRD pattern of MoS_2 film.

The optical absorption properties of the MoS_2 film samples were measured at room temperature, as shown in Fig. 2. The deposited MoS_2 thin film has strong optical absorption at wavelengths 627 nm and 690 nm, that is, the strong absorption is just in visible light range of 400-700 nm. According to A. Splendiani [3], these two resonances have been well established to be the direct excitonic transitions at the Brillouin zone K point. The observed absorption peaks at 1.79 eV (690 nm) and 1.98 eV (627 nm) correspond to the A1 and B1 direct excitonic transitions with the energy split from valence band spin-orbital coupling. Above 700 nm, the absorption intensity drops abruptly, and no other absorption peaks are appeared. This can be defined as the absorption edge of MoS_2, corresponding to intrinsic absorption by the direct energy band gap of MoS_2. For intrinsic semiconductor absorption, the electrons in the valence band absorb optical energy and transmit it to the conduction band. The absorbed optical energy is given by $h\nu = E_c - E_v = E_g$, where E_c is the energy of the conduction band, E_v is that of the valence band, and E_g is the band energy gap. From the absorption edge, we can estimate the energy band gap of MoS_2 to be about 1.79 eV, very close to the energy band of 1.8 eV [6], showing that the MoS_2 thin film we deposited had a large direct energy band gap. Moreover, the optical absorption covered almost the entire UV-vis wavelength range of 300-700 nm, which is very useful for making high-efficiency solar cells.

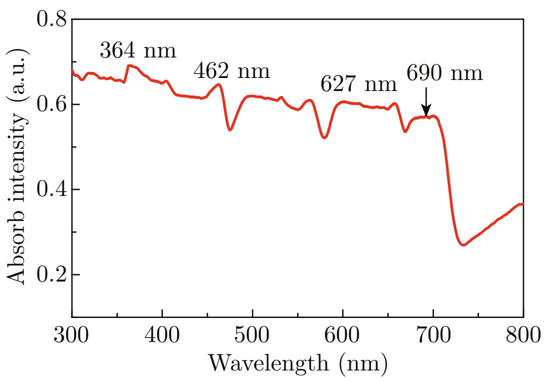

Fig. 2 Optical absorption spectrum of MoS_2 film samples. Strong absorption covered almost the entire UV-vis wavelength range of 300-700 nm.

Figure 3 shows the photoluminescence (PL) spectrum of the MoS_2 thin film measured at room temperature. It exhibits strong red emission peaking at 690 nm, which originates from the band-to-band emission of MoS_2 [18], where the excited electrons undergo transitions from the conduction band to the valence band. The emission peak of 690 nm corresponds to energy of 1.79 eV, which is quite consistent with the absorption edge of 690 nm in Fig. 2. The position of the PL emission offers more precise measurement of the energy band gap than that of the absorption edge. In addition to the absorption spectrum Fig. 3, no other absorption bands from indirect band gap (1.2 eV) appeared, we can drive that the deposition MoS_2 thin film exhibits the characteristics of this direct energy band. Moreover, as-grown MoS_2 films prepared using conventional deposition methods usually require additional treatment, such as surface modification and annealing, to obtain prominent PL emission. In our experiment, the MoS_2 sample achieved very strong red PL emission through simple thermal evaporation deposition with no additional treatment, showing that the as-grown MoS_2 films are of high quality [3].

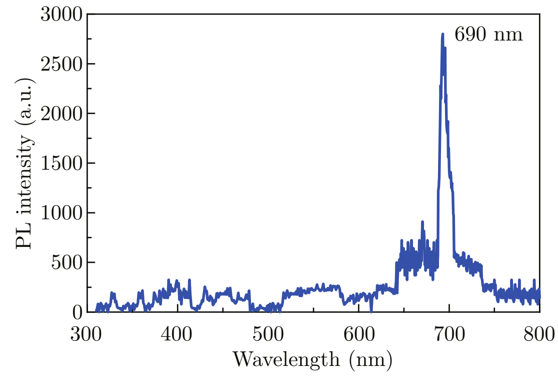

Fig. 3 Photoluminescence (PL) spectrum of pure MoS_2 thin film measured at room temperature. It exhibits strong red emission peaking at 690 nm.

The surface carrier concentration and electron mobility of the MoS_2 film were determined by Hall effect measurement. The surface current-voltage (I-V) plot of the MoS_2 film is shown in Fig. 4(a). It shows four perfectly linear I-V lines corresponding to four typical measurement points. From the measurement, we determined that the surface carrier concentration of the samples is about 10^9 cm^{-2}. The electron mobility is 5.1×10^2 cm^2/V·s, which is much greater than that of the monolayer MoS_2(3.06×10^2 cm^2/V·s) [6]. The current behavior of the MoS_2/Si heterojunction is shown in Fig. 4(b), the insert is the structure of the heterojunction. The heterojunction is conducted by on and down Al electrodes. Remarkably, the device shows good rectification characteristics. The current increases exponentially with the applied positive voltage, whereas it is almost zero when a reversed voltage is applied. Figure 4(c) shows the devices' pronounced photovoltaic effects when they are illuminated by white light with an intensity of 10 mW/cm^2. The current density is plotted versus bias voltage for the MoS_2/Si heterojunction device. The device shows a much improved open circuit voltage V_{oc} of 0.39 V, and the short-circuit current density (J_{sc}) is 0.46 mA/cm. The power conversion efficiency of the MoS_2/Si heterojunction device is about 1.79%.

Conclusions

We fabricated a MoS_2/n-Si heterojunction and studied its optical and electrical properties. The as-grown MoS_2 thin film is about 10 nm thick, which equals ten layers of MoS_2. The optical absorption covered almost the entire UV-vis wavelength range, which is very useful for making high-efficiency solar cells. Further, the MoS_2 thin film produced strong optical luminescence emission at 690 nm. Moreover, the heterojunction exhibited good rectification characteristics and excellent photovoltaic effects. The power conversion efficiency of the MoS_2/Si heterojunction device is about 1.79% under white light illumination of 10 mW/cm^2.

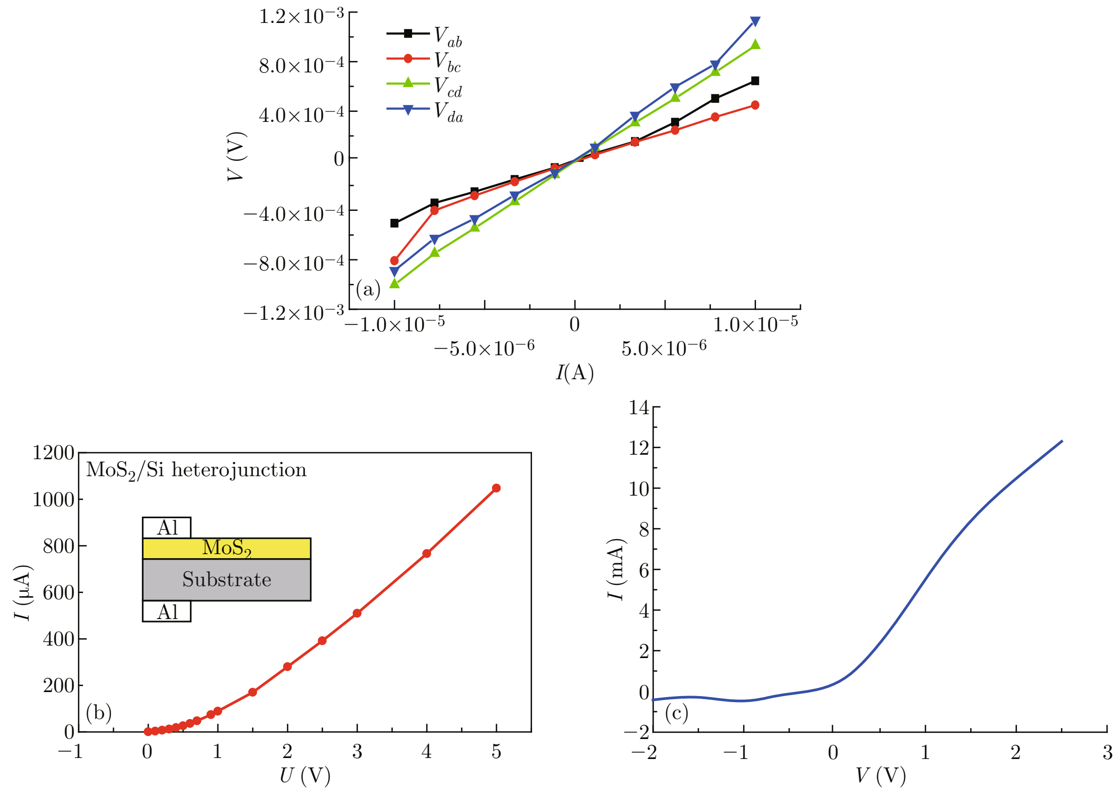

Fig. 4 (a) Surface $I-V$ behavior of MoS_2 film obtained by Hall effect measurement; (b) I-V characteristics of the MoS_2/Si heterojunction, which exhibits good rectification characteristics; (c) Pronounced photovoltaic effects of the MoS_2/Si heterojunction illuminated by white light with an intensity of 10 mW/cm^2.

Acknowledgements

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