Improving the Photoelectric Characteristics of MoS₂ Thin Films by Doping Rare Earth Element Erbium

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Abstract

We investigated the surface morphologies, crystal structures, and optical characteristics of rare earth element erbium (Er)-doped MoS₂ (Er: MoS₂) thin films fabricated on Si substrates via chemical vapor deposition (CVD). The surface morphology, crystalline structure, light absorption property, and the photoelectric characteristics of the Er: MoS₂ films were studied. The results indicate that doping makes the crystallinity of MoS₂ films better than that of the undoped film. Meanwhile, the electron mobility and conductivity of the Er-doped MoS₂ films increase about one order of magnitude, and the current-voltage (I-V) and the photoelectric response characteristics of the Er:MoS₂/Si heterojunction increase significantly. Moreover, Er-doped MoS₂ films exhibit strong light absorption and photoluminescence in the visible light range at room temperature; the intensity is enhanced by about twice that of the undoped film. The results indicate that the doping of MoS₂ with Er can significantly improve the photoelectric characteristics and can be used to fabricate highly efficient luminescence and optoelectronic devices.

Keywords: MoS₂ film, Er doping, Chemical vapor deposition, Photoelectric characteristics, Light absorption, Photoluminescence

Background

Layered quasi-two dimensional (2D) chalcogenide materials have attracted great interest due to their excellent optical, electrical, catalysis, and lubrication characteristics [1–3]. Especially, 2D molybdenum disulfide (MoS₂) has been widely studied and applied in field-effect transistors [4, 5] and energy harvesting [6, 7]. It has been found that a monolayer of MoS₂ has a direct bandgap of 1.8 eV when it is stripped from a bulk material that has an indirect bandgap of 1.29 eV [8, 9]. This large change in the energy band holds great potential for applications of MoS₂ in optoelectronic fields, such as red photodetectors and photodetectors [10, 11]. However, the efficiency of photoluminescence (PL) and photoelectric conversion of 2D MoS₂ [12] are relatively low. Researchers have explored many avenues to improve the PL intensity and the response rate of MoS₂ films. For example, Singha et al. found that gold nanoparticles may impose an obvious p-doping effect in single-layer and bi-layer MoS₂ samples, resulting in enhanced PL [13].

Rare earth elements (REE) are active elements that have been widely added in optoelectronic devices to improve PL and photoelectric conversion efficiency [14, 15]. So far, there have been few reports for REE-doped MoS₂. Herein, we report a study of the doping effects of rare earth element Er on the surface morphologies, crystal structures, and optical characteristics of MoS₂ thin films. Pure MoS₂ and Er: MoS₂ samples were fabricated on Si substrates by chemical vapor deposition (CVD). Additionally, we systematically analyzed the surface morphologies, structures, and optical absorption characteristics of the samples.

Methods

Er (NO₃)₃·5H₂O (99.9%) and MoS₂ powder (AR, 99%) reagents were used as the precursor materials. A mixed solution comprising 1-g analytical grade MoS₂ micro powder, 1-g analytical grade erbium nitrate penta hydrate (Er(NO₃)₃·5H₂O) crystals, and 200 mL of diluted sulfuric acid (H₂SO₄) was formed by mixing the above mentioned components for 5 min,
followed which the solution was maintained at 70°C via a water bath. The CVD system consisted of a horizontal quartz tube furnace, a vacuum system, an intake system, and a water bath. The Si substrates were placed in the center of the furnace, and subsequently, the pressure in the furnace was reduced to $10^{-2}$ Pa and the furnace was heated up to 650°C for 20 min. Ar gas was introduced into the mixed solution at a flow rate of 25 sccm, carrying Er$^{3+}$ and MoS$_2$ molecules into the furnace. Furthermore, to investigate the material properties of MoS$_2$ films, some pure MoS$_2$ samples were deposited on the Si substrates by the same method.

The surface morphologies and crystalline structures of the thin films were characterized using atomic force microscope (AFM) and X-ray diffraction (XRD). The electrical properties of the thin films were analyzed by a Hall Effect Measurement System (HMS-3000, Ecopia, Anyang, South Korea). The ultraviolet-visible (UV-vis) absorption spectra and photoluminescence properties of the samples were investigated by a UV-vis spectrophotometer (Shimadzu UV-3600) and fluorescence spectrophotometer at room temperature. Photocurrent current-voltage ($I$-$V$) curves of the doped and undoped MoS$_2$/Si heterojunction were investigated by a semiconductor analysis system (Keithley 4200).

Results and Discussion

The AFM images of the pure MoS$_2$ and Er: MoS$_2$ thin films on the Si substrates are shown in Fig. 1. The surface of the pure MoS$_2$ film in Fig. 1a is a continuous film with an average thickness about 25 nm, and some quantum dots around 20 nm are uniformly scattered on the Si substrate. The Er: MoS$_2$ film shown in Fig. 1b is a large fluctuation film composed of compact quantum dots with a uniform color, and the average thickness is about 50 nm. For the same deposition conditions and time, the density and size of the quantum dots in Er: MoS$_2$ film increase remarkably resulting from the catalytic action of Er$^{3+}$ on the deposition course. The crystal structures of the synthesized samples were characterized by using the X-ray diffraction (XRD) technique, as shown in Fig. 2. For the pure MoS$_2$ sample, there are four sharp diffraction peaks located at 14.7°, 47.8°, 54.6°, and 56.4°, corresponding to the (002), (105), (106), and (110) crystal planes of MoS$_2$, respectively, showing that the film is characterized by a polycrystal structure. In the Er: MoS$_2$ film, the position of the above four diffraction peaks is almost the same as that of pure MoS$_2$. Besides, there are two more peaks at 29.5° and 44.8°, corresponding to the (004) and (009) planes, respectively. No diffraction peaks from elemental Er is observed, indicating that the Er doping does not change the crystal structure of the MoS$_2$ film. Er atoms were doped in MoS$_2$ film in the way of substitution doping, and Mo atom was replaced by Er element. By doping, the diffraction peaks of MoS$_2$ crystal increased and the diffraction intensity was enhanced, showing that doping improved the crystallinity of the MoS$_2$ films.

The surface $I$-$V$ properties, carrier mobilities, and Hall coefficients of the MoS$_2$ and Er: MoS$_2$ samples were
measured using a Hall Effect measurement system via the four measured points on the samples at dark condition, as shown in Fig. 3. The currents of the samples show a linear dependency on the applied voltage, revealing that the films have a good conductivity. The slopes of the \( J-V \) curves show the resistivity of the MoS\(_2\) samples. The curve of the Er: MoS\(_2\) film has good linearity and a small slope, with the films showing a significant reduction in resistivity when Er ions are doped. According to the equation for calculation of mobility: \( \sigma = nqe \mu \) (\( \sigma \) is conductivity, \( n \) is electron concentration, \( q \) is electron charge, \( \mu \) is mobility), the electron motilities in the MoS\(_2\) and Er: MoS\(_2\) films are \( 3.996 \times 10^3 \) cm\(^2\)/Vs and \( 5.547 \times 10^3 \) cm\(^2\)/Vs, respectively. Note that the mobility value for the MoS\(_2\) film is obviously improved by doping Er\(^{3+}\). Furthermore, According to the equation for the Hall coefficients: \( \epsilon_y = R_H J_x B_z \) (\( \epsilon_y \) is electric field intensity, \( R_H \) is Hall coefficients, \( J_x \) is current density, \( B_z \) is magnetic induction intensity), the Hall coefficients of the MoS\(_2\) and Er: MoS\(_2\) films are \( 1.905 \times 10^7 \) cm\(^3\)/C and \( 4.581 \times 10^8 \) cm\(^3\)/C, respectively, showing that the films are \( p \)-type semiconductors. The \( J-V \) curves in the MoS\(_2\) film show a significant decrease in resistivity after Er doping. Good conductive properties can reduce the surface heat loss in the photodetector, thereby increasing the lifetime and frequency response of the MoS\(_2\) photovoltaic device.

Figure 4 shows the absorption spectra of the pure MoS\(_2\) and Er: MoS\(_2\) films in the visible light range. Clearly, the absorption of the Er: MoS\(_2\) film is enhanced significantly by doping Er, attributing to the absorptions of Er ions and the impurity energy level in the bandgap of MoS\(_2\) by doping Er. Additionally, a few maximum values emerge at 475, 578, 670, and 735 nm in the absorption spectra, showing that the film has strong light absorption in these wavebands. The absorption peak at 670 nm corresponds to a bandgap width of 1.85 eV in the MoS\(_2\) film, close to the energy gap of a monolayer of MoS\(_2\), 1.80 eV. MoS\(_2\) films have strong absorption at 735 nm, which can be considered as the optical absorption edge, corresponding to a bandgap width of 1.69 eV. Therefore, the doping of Er significantly improves the light absorption and does not change the position of the absorption peak. The increase of the light absorption of Er\(^{3+}\)-doped MoS\(_2\) film can be improved by the photovoltaic effect of MoS\(_2\) semiconductor devices.

Figure 5 shows the photoluminescence spectra of the MoS\(_2\) and Er: MoS\(_2\) film excited by 360 nm light at room temperature. In the pure MoS\(_2\) film, an obvious PL peak is centered at 693 nm, coinciding with the intrinsic radiative transition photoluminescence of the single-layer MoS\(_2\). In the Er: MoS\(_2\) film, two significantly enhanced PL peaks are located at 394 and 693 nm each. The peak at 394 nm is due to the transitions from the \( ^4H_{11/2} \) energy level to the ground state \( ^4I_{15/2} \) [16–18].
The intense peak at 693 nm is largely enhanced result from the direct-gap luminescence of MoS2. It is important to note that the PL intensity of the Er: MoS2 film is almost twice as strong as that of the undoped film, i.e., the doping of Er in MoS2 can largely improve the absorption and photoluminescence efficiency of MoS2, which in turn acts as an exciting active center in the film.

The photocurrent $I-V$ behavior of the MoS2-Si heterojunction was obtained while irradiating the surface of the films by a standard white light with a power of 100 mW/cm², as shown in Fig. 6. For two samples, the current increases exponentially with an increase in the voltage. The short-circuit currents ($I_{SC}$) of the MoS2 and Er: MoS2 film samples are 0.392 and 4.35 mA, respectively, and the open-circuit voltage ($U_{OC}$) is 49.98 and 90.02 mV, respectively. Obviously, after Er doping the short-circuit current and open-circuit voltage both increase significantly. This is because the doped Er ions will increase light absorption, resulting in an increase in the number of photogenerated carriers and finally enhancing the photocurrent response.

Conclusions

We have studied the effects of Er doping on the surface morphologies, crystalline, optical absorption, PL, and photoelectrical properties of MoS2 films. We found that the Er$^{3+}$ ions do not change the crystal structure of MoS2 films but make the crystallinity better. At the same time, Er$^{3+}$ doping improves the carrier mobility and enhances the current-voltage ($I-V$) characteristics of the MoS2 thin films. Additionally, Er$^{3+}$-doped MoS2 films exhibit stronger light absorption and photoluminescence in the visible light range at room temperature. The results show that Er$^{3+}$-doped MoS2 film can be used to fabricate highly efficient luminescence and optoelectronic devices.

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