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Effects of Zinc doping on the optical and electrical properties of SnS_2

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Abstract

Beyond the graphene, two-dimensional (2D) materials attract much interest because of their unique physical properties and potential uses of new electronic and optical devices in daily life. In this study we used chemical vapor transport (CVT) method to grow undoped and zinc doped tin disulfide (SnS_2) single crystals. We investigated the surface morphology and elemental composition of SnS_2 and Zn-doped SnS_2 crystals by scanning electron microscope (SEM) and electron probe microanalysis (EPMA). The analysis shows that the composition of the SnS_2 is close to the ideal ratio, but the doping composition of Zn only 0.8%. X-ray diffraction, TEM and Raman scattering have been carried out to confirm the crystal structure of SnS_2. We measured the energy gap and light responsivity by photoconductivity (PC), frequency dependent photoconductivity and persistent photoconductivity (PPC) measurements. We observed a blue shift of ban gap energy due to the doping of Zn atoms. The photoresponsivity has been increased from 2.34 to 8.04 mA/W at bias voltage of 20 V. Furthermore, the rise time and fall time have been decreased from 0.83 to 0.22 ms and 0.98 to 0.21 ms, respectively, after using Zn-doping. We also measure the current-voltage (IV) curves at different temperatures to understand the activation energy.

1. Introduction

SnS_2 which is one of the layered metal dichalcogenides (LMDC) has a layered two-dimensional structure and crystalizes in the hexagonal CdI_2-type lattice structure. Each unit layer consists of three layers of S-Sn-S and has been bounded by a weak Van der Waals force. From the side view, one can see that the intermediate layer is a metal tin atom layer, while the upper and lower layers are sulfur atoms. From the top view, a hexagonal structure stacking by three sulfur and three tin atoms has been observed. SnS_2 is a yellow colored crystal with a band gap energy around 2.3 eV, which also has good flexibility and high chemical and thermal stability. In this study we used CVT method for single crystal growth. High purity elements such as Sn (99.99%, 3.246 g) and S (99.99%, 1.753 g) were weighted to match the molar ratio of 1:2 for the growth of SnS_2, while Sn (99.99%, 3.2 g) and S (99.99%, 1.763 g) and Zn (99.99%, 0.035 g) were prepared for the growth of Zn-doped SnS_2 crystals. These materials have been put into a quartz tube with I_2 (99.99%, 0.3 g) as transporting agent. A vacuum system was used to evacuate the air from the tube, which was sealed when the pressure down to 2×10^{-5} torr. The source materials were placed at the high-temperature zone (700 °C) and the crystals were grown at the low-temperature zone (600 °C). We switched alternately the settings of high and low temperature zones every 24 hours and the total growth duration was about 360 hours.

2. Results and discussions

To understand whether the structure of the sample is consistent with the structure of SnS_2. Figure 1 (a) shows the results of the X-ray diffraction experiment. The vertical axis is the X-ray diffraction intensity, and the horizontal axis is the scanning angles 2θ range : 10 ° ~ 70 °. The diffraction peaks of SnS_2 have been observed as following: the 15 degree-peak presents the (001) plane signal, the 30.28 degree-peak is the (002) plane signal, the 46.2 and 63 degree-peaks are the (003) and (004) plane signals, respectively. The Bragg's law is used to calculate the lattice constant c = 5.8992 Å. Figure 1 (b) shows the Raman spectra and it can be seen that after the doping of Zn atoms, the position of Raman peak is still obvious and does move. This result indicates the whole crystal structure did not change. But from the TEM and SAED images as shown in Figure 2, we can see the samples are hexagonal lattice structures and also can calculate the lattice constants of a are 3.51 and 3.25 Å for SnS_2 and Zn-doped SnS_2, respectively. The results are summarized in Table 1. Here we can observe that the lattice constant *a* becomes smaller due to the doping of Zn atoms. Because the radius of Zn atoms is smaller than that of Sn atoms, the substitution of Zn atoms may result in a small deformation in lattice.

We used piezoelectric modulation reflection spectroscopy and absorption spectroscopy to analyze the band gap energies of these two samples. From Figure 3, we can observe the PzR signal has been shifted from 2.28 to 2.37 eV due to the doping of Zn toms. From the absorption measurements we also see the shift of absorption edge from 2.3 to 2.36 eV. This result provides an evidence of the lattice distortion. When the Sn atoms were substituted by small Zn atoms, the lattice distance decreases and therefore the band gap energy was increased. This phenomenon is a little bit like the thermal expansion and contraction effect on the band gap energy of semiconductors. Through the

light response analysis shown in Figure 4 (a), we can find that the light responsivity at different laser power has been enhanced several times (about 6.5 times max.) for Zn doped SnS_2. From Figure 4 (b) the PPC measurements reveal the rise time and fall time at 500 Hz. We observed that the response times also reduced several times. The term of activation energy is often used in the semiconductor field to describe the energy required to activate bound carriers into free carriers in doped semiconductors. In the paper, as shown in Figure 4(d), it can be found that the activation energy of undoped SnS2 is 256 meV while two activation energies are found after doping Zn atoms. The deep one is 381 meV and the shallow one is only 62 meV. We believe that the shallow trapping level is attributed to doping Zn atoms and can enhance the optical response and reduce the response time. It can be verified in this paper that the greater the activation energy, the slower the reaction rate; the smaller the activation energy, the faster the reaction rate.

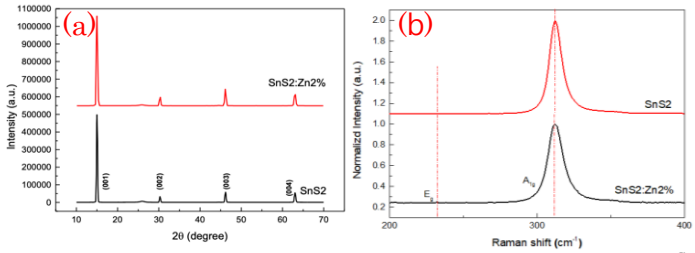

Figure 1 (a) shows the Zn-doped $SnS_2$and SnS_2 XRD lattice constant, and (b) SnS_2, Zn-doped SnS2 Raman scattering line

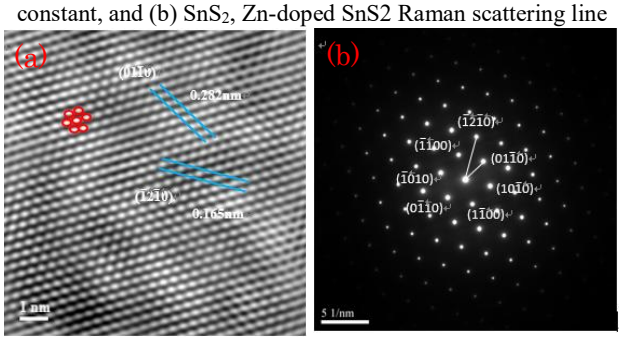

Figure 2 (a) shows the TEM of the Zn -doped SnS_2 and(b) shows the SAED images of the Zn -doped SnS_2

Table 1 Compositions SnS_2, Zn-doped SnS2, lattice constants a and c table

Material	a（Å）	c（Å）	c/a
SnS_2 (010)	3.51	5.90	1.681
SnS_2:Zn(010)	3.25	5.90	1.815

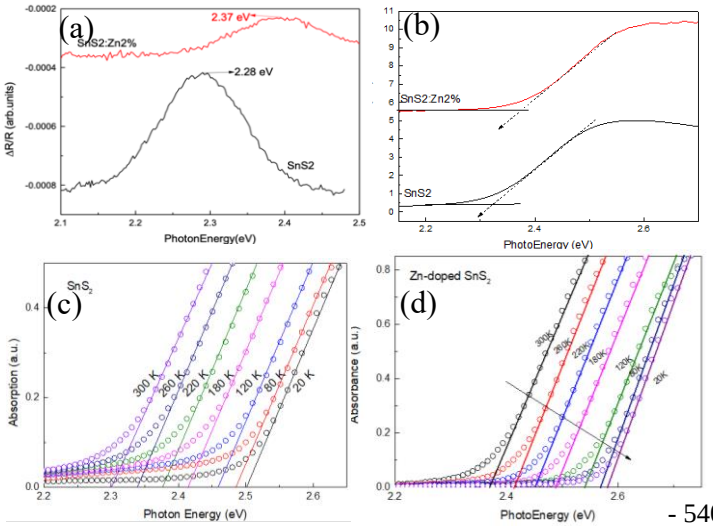

Figure 3 (a) Piezoelectric modulation spectrum of SnS_2 and SnS_2 doped Zn (b) Absorption spectra of SnS_2 and SnS_2 doped Zn (C)and (D) Shows the blue shift phenomenon as the temperature decreases of SnS_2 and Zn-doped SnS_2

Table 2 Compositions, band-gaps and lattice parameter of SnS_2

Sample	Absorption	PzR
	Eg（eV）	Eg（eV）
SnS_2	2.3	2.28
Zn-doped SnS_2	2.36	2.37

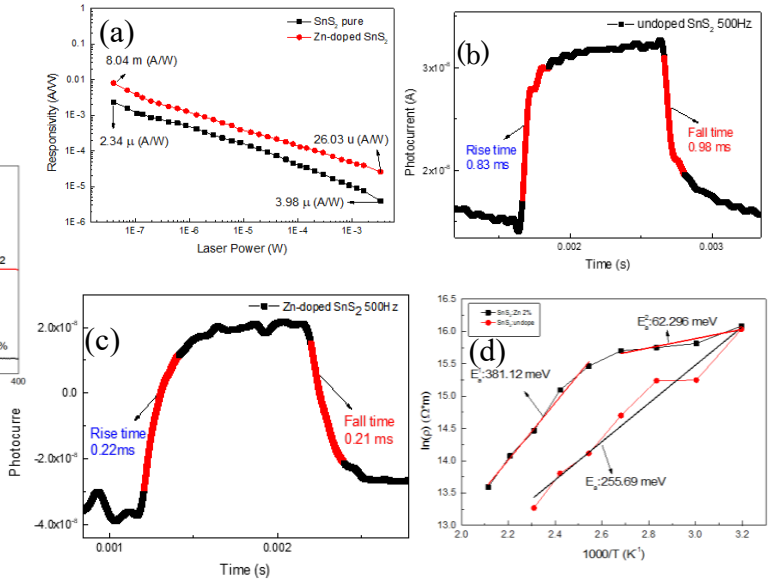

Figure 4 (a) Spectra of shows the Zn-doped SnS_2 response-optical power graph. (b) and (c) shows the Optical response diagram of Laser 520 nm Zn-doped SnS_2 and SnS_2 variable frequency PPC,and(d) Comparison of activation energy of Zn-doped SnS_2 and undoped SnS_2 activation energy of Zn-doped SnS_2 and undope-SnS_2

3. Conclusions

In Conclusion, we have grown the SnS_2 and Zn doped SnS_2 crystals by using CVT. The results of XRD, HR-TEM and Raman spectroscopy indicate that the samples' quality is very good. The doping of Zn atoms introduced a very small deformation in lattice constant of a, but no change in the lattice constant of c. We conducted a series of optical studies using PzR and absorption measurements. Calculated from the PzR spectrum and absorption spectrum, the band gap energy has a small blue shift, which gives an evidence of small crystal deformation. Knowing that SnS_2 has adjustable optical properties and electronic structure, the change in activation energy can improve the electrical properties after doping. We have demonstrated that the doping Zn atoms can effectively increase the photoresponsivity and reduce the response time for several times.