

Electrical and optical properties of Co-doped and undoped MoS₂ crystals

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Abstract

Co-doped and undoped MoS₂ layered crystals were grown by chemical vapor transport (CVT) method using iodine as the transport agent. Optical properties were studied by reflectance (R) and piezoreflectance (PzR) measurements, while electrical properties were investigated by Hall effect measurements and photoconductivity (PC) measurements. Two direct band edge transitions of excitons around 1.9 and 2.1 eV are observed by R and PzR measurements. Hall effect measurements were carried out to consider the electrical effects of Co dopants on MoS₂, which indicate that the Co-doped MoS₂ sample has a low carrier concentration and lowered mobility. Furthermore, using PC measurements we find that Co-doped MoS₂ has a better spectral responsivity than undoped MoS₂.

1. Introduction

MoS₂ is a layered semiconductor and belongs to the family of transition-metal dichalcogenides (TMDCs) [1]. A unit layer structure consists of two hexagonal plans of sulfur atoms and an intermediate hexagonal plan of molybdenum atoms, which are prismatically coordinated to the sulfur atoms. It is crystallized in a lattice with strong covalent bonds within a unit layer and weak interactions, usually of the van der Waals type, between the individual layers. Owing to the unique optical and electrical properties, the layered semiconductors have attracted considerable interest in basic studies and applications, such as photodetectors [1], solar cells [2-5], hydrogen fuel generation [6], hydrodesulfurization, water splitting [7], biosensors [8,9]. Moreover, MoS₂ has a direct band gap about 1.8 eV and high spectral responsivity for becoming phototransistors or photodetectors with good device mobility. The existence of band gap makes the devices much easier to being switch, which is an essential characteristic of phototransistors [10].

In this study, we studied the electrical and optical properties of Co-doped and undoped MoS₂ crystals grown by CVT method using the reflectance and piezoreflectance measurements for optical properties, Hall effect measurement and photoconductivity measurements for electric properties. From the results we found the optical characteristics do not have significant changes due to the doping of cobalt atoms, which means the crystal structure did not be distorted, but the electric properties change a lot. Doping cobalt atoms into MoS₂ can form bound states of electrons

and holes to increase the resistance. As a result, the light ON/OFF current ratio is considerably increased and the spectral responsivity has been increased a lot.

2. Results and discussions

Figures 1 and 2 show the R and PzR spectra of the Co-doped and undoped MoS₂ crystals at different temperatures between 20 and 300 K. In the spectra two main resonance features are observed and assigned to be A and B features, respectively. The photon energy values of features A and B are a little lower than that observed in the absorption peaks and PL peaks of atomically thin MoS₂ samples [11]. In Fig. 3 the fitted transition energies of features A and B are indicated by solid squares and hollow triangles, respectively. Their temperature dependences are fit to Varshni equation and the empirical expression proposed by O'Donnell and Chen.

Their carrier concentrations and mobilities are measured at room temperature by Hall effect measurements and listed in Table I. Co-doped MoS₂ has a high resistance due to low carrier concentration and the mobility decreases from 79 to 10 cm²/Vs. The Doping of cobalt atoms introduce some lattice imperfections and impurity states to form bound states of electrons and holes. As a result of high resistance, the light ON/OFF current ratio is considerably increased and the spectral responsivity has been increased as well.

The PC spectra were measured at different temperatures between 20 and 300 K. The results are shown in Fig. 4. The absorption edge of indirect band gap and its temperature dependence are clearly observed and well determined [12,13]. The frequency dependence is studied by the PC spectra measured at 20 K at different frequencies between 7 to 200 Hz as shown in Fig. 5. The results show that the doping of cobalt atoms increase the responsivity a lot as shown in Fig. 6 and the frequency dependence show that from 200 to 7 Hz the responsivity of Co-doped MoS₂ increases about three times.

3. Conclusions

In this study, we presented the Co-doped and undoped MoS₂ layered crystals grown by CVT method and investigated the effect of Co dopants on the electrical and optoelectronic properties of MoS₂ by using Hall effect, R, PzR and PC measurements. Two direct transitions and one indirect band gap absorption were observed. The doping of cobalt atoms lowers the carrier density and mobility. But the spectral responsivity has been increased a lot.

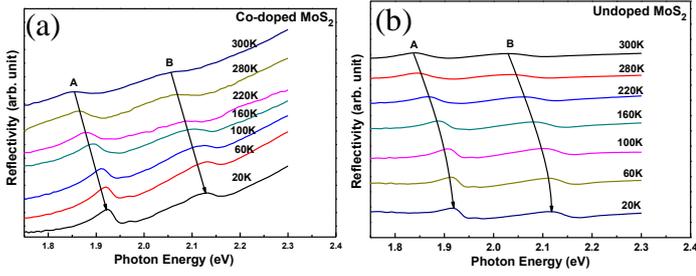


Fig. 1 Reflectance spectra of (a) Co-doped MoS₂ and (b) undoped MoS₂ at different temperatures.

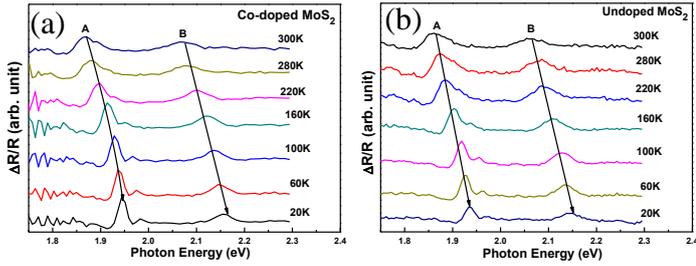


Fig. 2 Piezoreflectance (PzR) spectra of (a) Co-doped MoS₂ and (b) undoped MoS₂ at different temperatures.

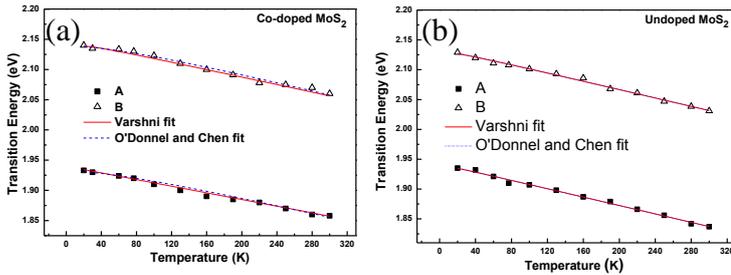


Fig. 3 Temperature dependence of excitonic transition energies of (a) Co-doped MoS₂ and (b) undoped MoS₂.

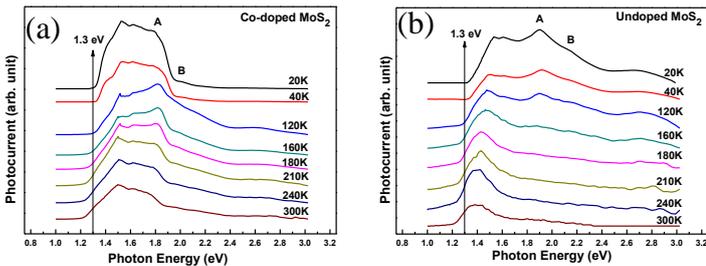


Fig. 4 Photocurrent spectra of (a) Co-doped MoS₂ and (b) undoped MoS₂ at different temperatures.

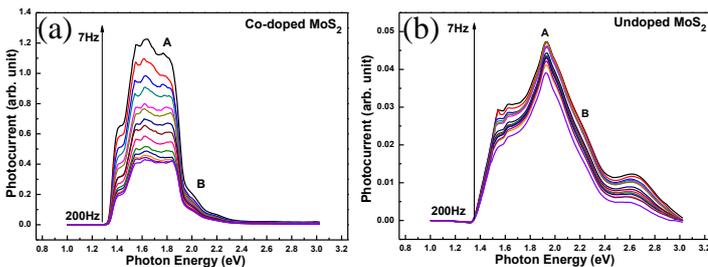


Fig. 5 PC spectra of (a) Co-doped MoS₂ and (b) undoped MoS₂ measured at 20 K in the frequency range of 7 to 200 Hz.

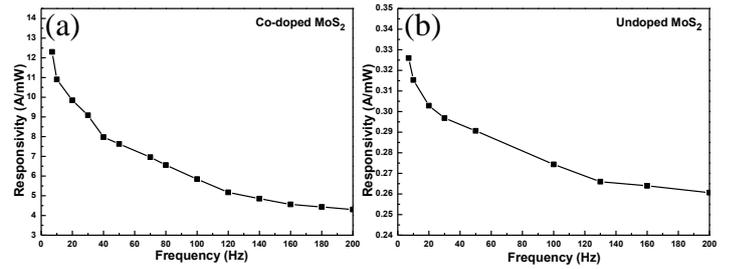


Fig. 6 Frequency dependence of responsivity at 20K for (a) Co-doped MoS₂ and (b) undoped MoS₂.

Table I Hall effect parameters of MoS ₂ and Co-doped MoS ₂ .		
Sample	Undoped- MoS ₂	Co-doped- MoS ₂
Type	n	n
Resistance (Ω)	6.7×10^3	8.9×10^6
Carrier density (cm ⁻²)	$1.1E13$	$9.8E10$
Mobility (cm ² / V * s)	79	10

References

- [1] W. Zhang, C. P. Chuu, J. K. Huang, C. H. Chen, M. L. Tsai, Y. H. Chang, J. H. He, Scientific reports, **4** (2014).
- [2] J. Zhang, S. Najmaei, H. Lin, and J. Lou, Nanoscale, **6** (2014) 5279.
- [3] M. L. Tsai, S. H. Su, J. K. Chang, D. S. Tsai, C. H. Chen, C. I. Wu, L. J. Lin, L. J. Chen, and J. H. He, ACS nano, **8** (2014) 8317.
- [4] R. Raja, P. Sudhagar, A. Devadoss, C. Terashima, L. K. Shrestha, K. Nakata, R. Jayavel, K. Ariga, and A. Fujishima, Chem. Commun, **51** (2015) 522.
- [5] M. Wu, Y. Wang, X. Lin, N. Yu, L. Wang, L. Wang, A. Hagfeldt, and T. Ma, PCCP, **13** (2011) 19298.
- [6] J. V. Lauritsen, M. Nyberg, J. K. Nørskov, B. S. Clausen, H. Topsøe, E. Lægsgaard, and F. Besenbacher, J. Catal., **224** (2004) 94.
- [7] J. Liao, B. Sa, J. Zhou, R. Ahuja, and Z. Sun, The Journal of Physical Chemistry C, **118** (2014) 17594.
- [8] D. Sarkar, W. Liu, X. Xie, A. C. Anselmo, S. Mitragotri, and K. Banerjee, ACS nano, **8** (2014) 3992.
- [9] W. Yang, K. R. Ratinac, S. P. Ringer, P. Thordarson, J. J. Gooding, F. Braet, Angew. Chem., Int. **49** (2010) 2114.
- [10] H. S. Lee, S.W. Min, Y.G. Chang, M. K. Park, T. Nam, H. Kim, J. H. Kim, S. Ryu, and S. Im, Nano Lett. **12** (2012) 3695.
- [11] K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, Phys. Rev. Lett. **105** (2010) 136805.
- [12] R. S. Sundaram, M. Engel, A. Lombardo, R. Krupke, A. C. Ferrari, P, Nano Lett., **13** (2013) 1416.
- [13] S. Y. Wang, T. S. Kso, D. Y. Lin, C. C. Huang, and Y. S. Huang, Jpn. J. Appl. Phys., **53** (2014) 04 EH07.