Extended Abstracts of the 2014 International Conference on Solid State Devices and Materials, Tsukuba, 2014, pp784-785

# Influence of Rhenium on the Structural and Optical Properties of Molybdenum Disulfide

Mula Sigiro[1], Ying-Sheng Huang[1], Ching-Hwa Ho[2], Yung-Chang Lin[3], Kazu Suenaga[3] and Kwong-Kau Tiong[4]

[1]Department of Electronic and Computer Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan. Phone: +886 2 27376385; Fax: +886 2 27376424
E-mail: mulasigiro@gmail.com and ysh@mail.ntust.edu.tw
[2]Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taipei 106, Taiwan.
[3]National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305-8565, Japan.
[4]Department of Electrical Engineering, National Taiwan Ocean University, Keelung 202, Taiwan

**Abstract**

**We report on extensive structural and optical studies of Re-doped molybdenum disulfide ($MoS_2$) grown by chemical vapor transport (CVT) method using $Br_2$ as a transport agent. In order to perform the influence of Re on the structural properties of crystals we conducted X-ray diffraction (XRD) and transmission electron microscopy (TEM). For optical characterization we used piezoreflectance (PzR) and electrolyte electroreflectance (EER).**

## 1. Introduction

Dopant in solid generally governs the physical and chemical properties of any kind of materials and is of great technological importance. In the case of bulk system, a prominent example is seen in semiconductor industry where doping is used to adjust carrier densities and to tailor the electronic characteristics of the devices [1]. Moreover, the effect of doping is very significant in two dimensional systems. Recently, transition-metal dichalcogenide compounds (TMDs), particularly molybdenum disulfide ($MoS_2$), have been extensively investigated because of the possible practical application as catalysts, lubricants, lithium batteries, and phototransistors as well as in nanoelectronics [2]. How dopant atoms influence and interact with the host TMD lattices are important knowledge of both in fundamental science and future device technology. This paper deals with the influence of rhenium mainly on the structural and optical properties of $MoS_2$ single crystals grown by chemical vapor transport method using $Br_2$ as a transport agent.

## 2. Experimens, results and discussion

*Experimental methods*

Single crystals of the system Re-doped $MoS_2$ were grown using the chemical vapor transport method using $Br_2$ as a transport agent. The total charge used in each growth experiment was about 10 g. The stoichiometrically determined weight of doping material was added in the hope that it will be transported at a rate similar to that of Mo. Before the crystal growth, the powdered compounds were prepared from the elements by reaction at $1{,}000^0$C for 10 days in an evacuated quartz ampoule. Prior to the crystal growth, a quartz ampoule (22 mm OD, 17 mm ID, 20 cm length) containing $Br_2$ (~5 mg/cm$^3$) and the elements (Mo, 99.99% pure; Re, 99.99%; S, 99.999%) was evacuated to $10^{-6}$ Torr and sealed. It was shaken well for uniform mixing of the powder. The ampoule was placed in a three-zone furnace and the charge prereacted for 24 h at $800^0$C with the growth zone at $950^0$C, preventing the transport of the product. The temperature of the furnace was increased slowly. The slow heating was necessary to avoid any possibility of explosion due to the exothermic reaction between the elements. The furnace was then equilibrated to give a constant temperature across the reaction tube, and was programmed over 24 h to produce the temperature gradient at which single crystal growth took place. Optimal results were obtained with temperature gradient of approximately $960^0$C $\rightarrow$ $930^0$C. After 240 h, the furnace was allowed to cool down slowly ($40^0$C/h) to about $200^0$C. The ampoule was then removed and wet tissues applied rapidly to the end away from the crystals to condense the $Br_2$ vapor. When the ampoule reached room temperature, it was opened and the crystals removed. The crystals were then rinsed with acetone and deionized water. Single crystalline platelets up to 10 x 10 mm$^2$ surface area and 2 mm in thickness were obtained. In order to characterize our samples we used different experimental methods like X-ray diffraction (XRD), transmission electron microscopy (TEM), piezoreflectance (PzR) and electrolyte electroreflectance (EER). They are described in detail in our previous work [3-5].

*Results and discussions*

Fig. 1 reveals the XRD pattern of doped and undoped $MoS_2$ single crystals. The relative intensity and resolution of observed peaks change for Re-doped one. For Re-doped crystals observed peaks correspond to rhombohedral structure (3R) having cell dimension $a$ = 3.164 Å and $c$ = 18.371 Å, whereas for the undoped one the patterns correspond to hexagonal structure (2H). The lines were identified with a 3R in which, by referring to the 2H, the $a$ parameter of the unit cell is similar to that of the 3R ($a$ = 3.160 Å) but the $c$ parameter was about 1.5 times larger than that of that 2H ($c$ = 12.295 Å). We noticed that $a$ parameter remains unchanged for the Re-doped and undoped samples, whereas the $c$-parameter shows appreciable increase in consistent agreement with the increase in the $d$-spacing.

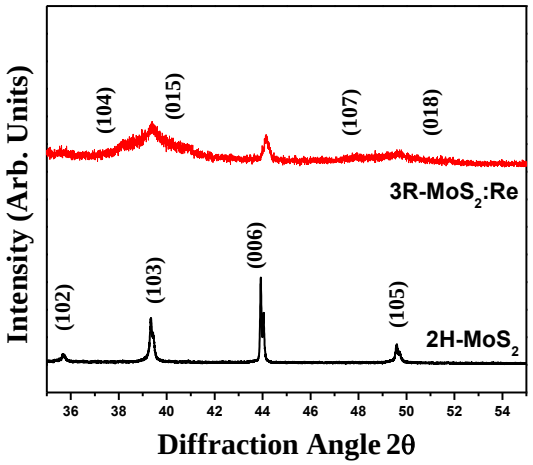


Fig.1 XRD spectra of the Re-doped and undoped $MoS_2$

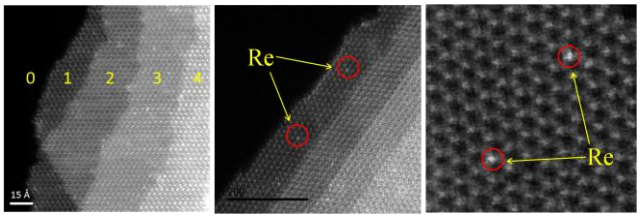


Fig.2 TEM images of the Re-doped $MoS_2$

In Fig. 2 the TEM images of Re-doped $MoS_2$ crystals are presented. It is clearly seen that Re atoms tend to occupy or substitute Mo atoms in host $MoS_2$ lattice. The PzR spectra (Fig.3 for comparison between 2H and 3R) have recorded in the range 25 to 300 K to determine the energies, broadening parameters, and temperature dependence of the line-width of the A dan B excitons accurately by equations 1, 2, 3, and 4 respectively in the reference [5]. The splitting of A and B excitons of 3R calculated around 150 meV, whereas around 200 meV for 2H. Re-doped effect shows up in a slight reduction in the splitting of the excitonic features as shown in Fig.4. The Re impurity is also observed to affect the symmetry selection rules of the excitonic transitions as shown in Fig.5.

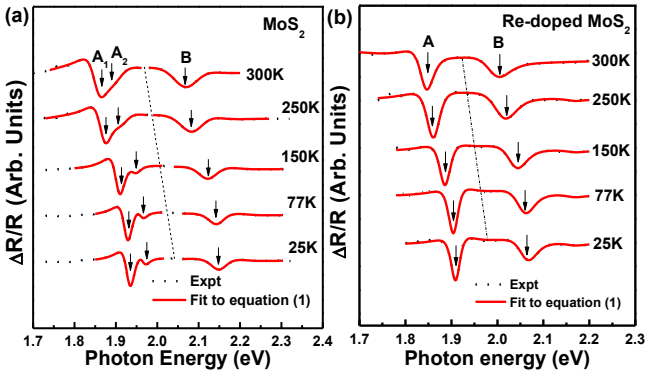


Fig.3 PzR spectra at between 25 K and 300 K

## 3. Conclusions

We have demonstrated the synthesis of single crystals of Re-doped $MoS_2$ by CVT method using $Br_2$ as a transport agent. XRD revealed 3R structure for Re-doped compound and 2H for undoped one. Re atoms tend to occupy or substitute Mo atoms in host $MoS_2$ lattice and stabilize the formation of 3R-$MoS_2$. Optical spectra were recorded to unravel the spectral features near the direct band-edge excitonic transitions and showed a splitting of around 150 meV between the A and B excitons for 3R compound. The corresponding splitting is measured to be 200 meV for the 2H compound. As a result of doping, the electronic states of the $MoS_2$ crystals are modified with a reduction of the energy splitting of A and B excitons, and affect the symmetry selection rules of the excitonic transitions. In addition, the A and B excitons of Re-doped $MoS_2$ also shows a slight red-shift with respect to the undoped sample.

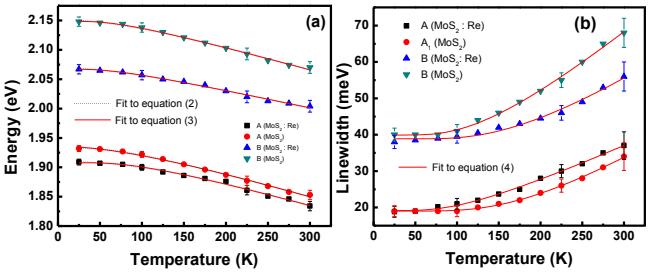


Fig.4. Temperature variation of the energies and the linewidths of the A and B excitons.

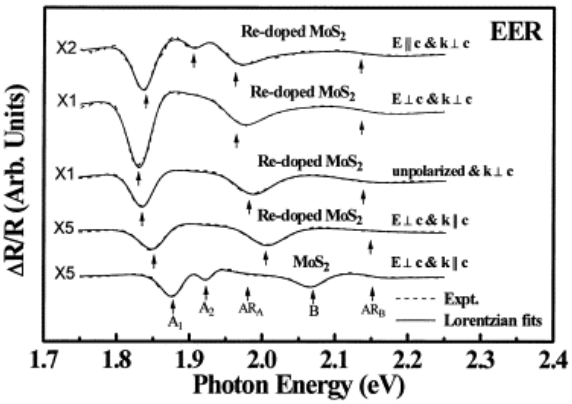


Fig.5. Polarization dependent EER spectra of Re-doped and undoped $MoS_2$ over the range 1.75 eV to 2.25 eV.


## Acknowledgements

The authors would like to acknowledge the financial supports by the National Science Council of Taiwan under Grant No NSC 100-2112-M-011-001-MY3.


## References


[1] P. M. Voyles, D. A. Muller, J. L. Grazul, P. H. Citrin and H. J. L. Gossmann, Nature **416** (2002) 826.

[2] Z. Huang, X. Peng, H. Yang, C. He, L. Xue, G. Hao, C. Zhang, W. Liu, X. Qia and J. Zhong, RSC Adv. **3** (2013) 12939.

[3] C. C. Huang, C. C. Kao, D. Y. Lin, C. M. Lin, F. L. Wu, R. H. Horng and Y. S. Huang, Jpn. J. Appl. Phys. **52** (2013) 04CH11.

[4] D. O. Dumcenco, H. Kobayashi, Z. Liu, Y.S. Huang and K. Sueenaga, Nat. Commun. **4** (2013) 1351.

[5] D. O. Dumcenco, H. P. Hsu, Y. S. Huang, C. H. Liang, K. K. Tiong and C.H. Du, Mater. Chem. Phys. **111** (2008) 475.