Optik 126 (2015) 666–670

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

Growth and optical characterization of MoS_2 single crystals with different dopants

Mula Sigiro[a,b,*], Nasruddin MN[c]

[a] Department of Electronic and Computer Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan
[b] Department of Physics Education, Faculty of Teacher Training and Education, University of HKBP Nommensen, Medan 20234, Indonesia
[c] Department of Physics, Faculty of Mathematics and Natural Sciences, University of Sumatera Utara, Medan 20155, Indonesia

ARTICLE INFO

Article history:
Received 17 December 2013
Accepted 20 July 2014

Keywords:
Single crystals
Optical spectroscopy
Molybdenum disulfide
Doping effects

ABSTRACT

Single crystals MoS_2:X with different dopants X (X = Re, Nb, Fe, Co, Ni) were grown by the chemical vapor transport method using Br_2 as transport agent. By analyzing the X-ray diffraction patterns, the structure of the single crystals shows rhombohedral symmetry for Re and Nb-doped and hexagonal symmetry for Fe, Co, and Ni-doped. Piezoreflectance (PzR) measurements along ***c***-axis at 300 and 25 K were carried out to confirm the origin of the broad peak as observed in electrolyte electroreflectance (EER) measurements and check the optical quality of the samples. The energies and broadening parameters of the A and B excitons of the MoS_2:X single crystals have been determined accurately.

1. Introduction

Molybdenum disulfide (MoS_2), a two dimensional layered-structure materials which belong to the group VIA [1,2], have attracted much interest in recent years for their unique physical properties in thermal, optical and electronic devices. Recent demonstrations of MoS_2 devices such as field-effect transistors [3,4], logic circuits [5], phototransistors [6], chemical sensors and photonic detectors [7–9] are already promising. Early studies on the Hall and photoresponse measurements indicate that cobalt can be present only on the surface of MoS_2 and has not diffused appreciably into the bulk [12,13]. In catalyst, Co or Ni added to Mo increases the reactivity of catalysts, and because only a small fraction of Co or Ni relative to Mo is needed, they are considered promoters rather than catalysts in their own right [14] while in Fe-doped MoS_2, the charge carrier change from holes to electrons [15].

There are two known polytypes of MoS_2 [1,2,10]; two-layer hexagonal and three-layer rhombohedral termed 2H and 3R, respectively. Both have regular layered structures with six-fold trigonal prismatic coordination of the Mo atoms by the sulfur atoms within the layers; 2HMoS_2 has two layers per unit cell stacked in the hexagonal symmetry and belongs to the space group D^4_{6h}, while 3R-MoS_2 has three layers in the *c*-direction but has rhombohedral symmetry and belongs to the space group C^5_{3v}. Previous studies [11] suggest that natural rhombohedral MoS_2 is consistently rich in certain minor elements (e.g. Re, Nb, Ti, Zr, Fe), and that incorporation of such impurity elements has predetermined the adoption of the lower structural symmetry of MoS_2, i.e. 3R-MoS_2. The influence of dopant in transforming 2H-MoS_2 to 3R-MoS_2 had also been reported recently [16]. However, only few works concerning the effects of dopants in affecting the optical properties of MoS_2 have been reported [17].

In this study, we reported optical investigation of MoS_2:X single crystals with different dopants X (X = Re, Nb, Fe, Co, Ni) grown by the chemical vapor transport method using Br_2 as transport agent. The crystal structure was analyzed by X-ray diffraction (XRD) patterns. Room-temperature electrolyte electroreflectance (EER) measurements were carried out. Piezoreflectance (PzR) were also performed at 300 and 25 K. EER [18] and PzR [19,20] measurements have been used very extensively for semiconductor characterization. The derivative nature of EER and PzR spectrum suppresses uninteresting background effects and greatly enhances the precision in the determination of interband excitonic transition energies. The sharper line shapes as compared to the conventional optical techniques have enabled us to achieve a greater resolution and hence to detect weaker features. The EER and PzR spectra are fitted with a form of the Aspnes equation of the fist derivative Lorentzian lineshape [18,20]. From a detailed lineshape fit we are able to determine accurately the energies and broadening parameters of the excitonic transitions. The parameters which describe the behavior of excitonic transitions indicate that A–B, caused by interlayer interaction and spin-orbit splitting, correspond to excitonic

* Corresponding author. Tel.: +886 2 27376385; fax: +886 2 27376424.
E-mail address: mulasigiro@gmail.com (M. Sigiro).

http://dx.doi.org/10.1016/j.ijleo.2014.07.140
0030-4026/

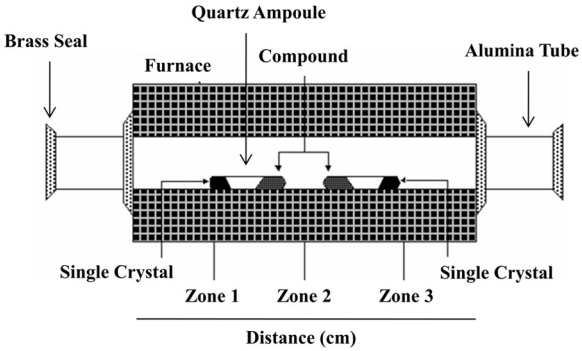

Fig. 1. Set up profile for the growth of MoS_2:X single crystals.

transitions with different origin. The origin of A, B excitons and the effects of dopant are discussed.

2. Crystals growth

The crystal growth of set up profile is shown in Fig. 1. MoS_2:X with different dopants X (X = Re, Nb, Fe, Co, Ni) single crystals have been grown by the chemical vapor transport method with Br_2 as a transport agent. The total charge used in each growth experiment was about 10 g. The stoichiometrically determined weight of the doping material was added in the hope that it would be transported at a rate similar to that of Mo. The quartz ampoule (40 mm in diameter) containing Br_2 ($\sim$5 mg cm^{-3}) and uniformly mixed elements (99.99% pure Mo, Re, Nb, Fe, Co, Ni and S) was sealed at 10^{-6} Torr. The ampoule was then placed in a Linberg model 54529 three-zone tube furnace and the charge prereacted for 24 h at 800 °C with the growth zone at 950 °C, preventing the transport of the product. The temperature of the furnace was increased slowly 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 programmed over 24 h to produce the temperature gradient at which single-crystal growth took place. Optimal result was obtained with a temperature gradient of approximately 960 → 930 °C. After 24 h, the furnace was allowed to cool down slowly (40 °C/h) to about 200 °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 10×10 mm^2 surface area and 2 mm in thickness were obtained. The as-grown MoS_2:X single crystal is shown in Fig. 2. We do not expect the two solid solutions to be miscible. It was found that a 5% nominal doping of MoS_2 prevented the growth of single crystals.

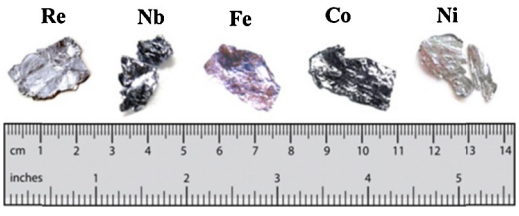

Fig. 2. Photograph of the as-grown MoS_2:X with different dopants X (X = Re, Nb, Fe, Co, and Ni) single crystal with the surface normal to ***c***-axis.

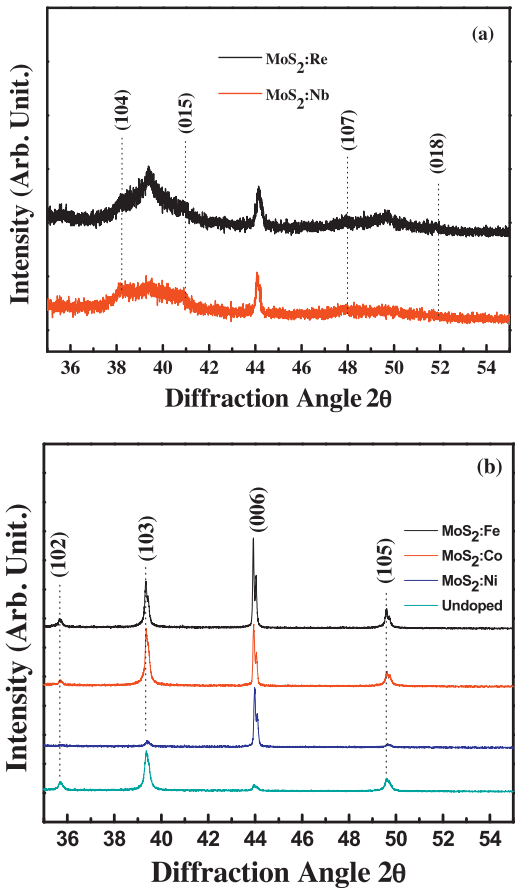

Fig. 3. X-ray diffraction patterns of the MoS_2:X with different dopants X (X = Re, Neb, Fe, Co, and Ni) single crystal.

3. Characterization

3.1. X-ray diffraction

XRD patterns of single crystals were obtained by using a Rigaku RTP300RC X-ray with Ni-filtered Cu K_α radiation (λ = 1.5418 Å) and a silicon standard was used to calibrate the diffractometer. For the studies, several small crystals from batches of as-grown MoS_2:X with different dopants X (X = Re, Nb, Fe, Co, Ni) were finely ground with a mixture of glass powder and the X-ray powder patterns were taken and recorded by means of a slow-moving radiation detector. Lattice parameters were calculated with the aid of computer using a least-squares refinement program.

From the evaluation of the X-ray powder diffraction patterns in Fig. 3, we may conclude that Re and Nb-doped MoS_2 samples are of 3R polytype and Fe, Co, and Ni-doped MoS_2 samples are 2H-polytype. The X-ray pattern of of Re and Nb-doped MoS_2 crystals differed from that of the crystals of Fe, Co, and Ni-doped MoS_2 in that the relative intensities of the lines were different and additional lines were present. The change in relative line intensities could not be explained but the additional lines were determined to be due to the presence of the rhombohedral polytype having cell dimension ***a*** = 3.164 Å and ***c*** = 18.371 Å, these numbers are quite similar with JCPDS no. 77-0744 for comparison. The lines were identified with a rhombohedral structure in which, by referring to the hexagonal lattice, the ***a*** parameter of the unit cell was similar to that of the hexagonal polytype (***a*** = 3.160 Å) but the ***c*** parameter was about 1.5 times larger than that of the hexagonal polytype (***c*** = 12.295 Å), these number agreed well with the JCPDS no. 37-1492 for comparison. We notice that the ***a***-parameter