Piezoreflectance study of Nb-doped MoS$_2$ single crystals

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Abstract. We have measured the temperature dependence of the spectral features in the vicinity of direct band-edge excitonic transition of the Nb-doped MoS$_2$ single crystals from 25 to 300 K using piezoreflectance (PzR). The energies and broadening parameters of the A and B excitons of the Nb-doped MoS$_2$ samples have been determined accurately via a detailed line shape fit of the PzR spectra. we can infer that the Nb ions are most likely intercalated between the van der Waals gap and stabilize the rhombohedral 3R phase of the MoS$_2$ crystal.

1. Introduction

Molybdenum disulphide MoS$_2$ belongs to the group IVA layer type transition metal dichalcogenides having C$_7$ type crystal structure which is formed of unit layers consisting of transition metal (Mo) atoms sandwiched by chalcogen (S) atoms [1]. The MoS$_2$ compound has been extensively investigated because of the possible practical application as a solid state lubricant and a catalyst for hydrosulfurization (HDS) and hydrogen evolution reaction (HER) [2-4], photoelectrochemical solar cells [5-6], and can also be synthesized in large scale by chemical vapor deposition [7-11]. The monolayer MoS$_2$ single crystal exhibits high luminous energy photoconversion efficiencies [12-13], excellent electrical [14-16] and optical performance [17, 18] compared to its bulky counterpart. The successful application of this semiconductor compound originates largely from the sandwich interlayer structure, loosely bound by the weak van der Waals forces, as evidenced by easy cleavage in the c-direction along which the S-Mo-S layers are stacked to form the crystal [1, 19]. There are two known polytypes of MoS$_2$ [1, 19]: 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; 2H-MoS$_2$ has two layers per unit cell stacked in the hexagonal symmetry and belongs to the space group D$_6^3$ while 3R-MoS$_2$ has three layers in the c-direction but has rhombohedral symmetry and belongs to the space group C$_3^5$. Naturally occurring 3R-MoS$_2$ has been found to be consistently rich in certain minor elements such as Re, Nb etc [20]. The incorporation of the impurity will essentially influence the structure symmetry of MoS$_2$, this is the adoption of the polytype 3R-MoS$_2$. For Nb-doped MoS$_2$, the niobium substitutions improve the photocurrent gain much more slowly than in the case of rhenium [21]. Niobium dopants seems to serve more than just as an impurity donor, it is most likely that niobium transition ions can either substitute for the Mo metal ions interstitially or intercalate between the Vander Waals gap resulting in a distortion of crystal structure [20, 21]. The sandwich Nb ions create stronger bonds than the original van der Waals forces and transform the two-layer hexagonal MoS$_2$ (2H-MoS$_2$) into three-layer rhombohedral MoS$_2$ (3R-MoS$_2$). The transformation of 2H-MoS$_2$ into 3R-MoS$_2$ by doping with niobium is perhaps not too surprising as it has been found that naturally...
occurring 3R-MoS\textsubscript{2} is consistently rich in certain minor elements such as Nb, Re etc [21]. Despite the potentially attractive fundamental research offered by Nb-doped MoS\textsubscript{2}, very few studies concerning the influence of niobium dopant on the electrical and optical properties of the material have been reported.

In this study, we present piezoreflectance (PzR) measurements which has been proven to be useful in the characterization of semiconductors [22, 23] of Nb-doped MoS\textsubscript{2} which grown by chemical vapor transport method with I\textsubscript{2} as transport agent. An elaborate temperature dependence of the spectral features near the direct band-edge excitonic transitions of the Nb-doped MoS\textsubscript{2} in the range 25 to 300 K has been obtained. The derivative nature of modulation spectra suppresses uninteresting background effects and greatly enhances the precision in the determination of inter band excitonic transition energies. The sharper line shape as compared to the conventional optical techniques has enabled us to achieve a greater resolution and hence to detect weaker features. The PzR spectra are fitted with a form of the Aspnes equation of the first derivative Lorenzian lineshape [23, 24]. 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 temperature behaviour of excitonic transitions indicate that A-B, caused by interlayer interaction and spin-orbit splitting, correspond to excitonic transitions with different origin. The origin of A, B excitons and the effects of dopant are discussed. The temperature variation of the transition energies has been analyses by the Varshni equation [25] and an expression containing the Bose-Einstein occupation factor for phonons [26,27]. The temperature dependence of the broadening function also has been studied in term of a Bose-Einstein equation that contains the electron (exciton)-longitudinal optical (LO) phonon coupling constant [26,27]. The addition of dopant impurities to a semiconductor is what enables the fabrication of a multitude of interesting devices. The physical role of niobium in influencing the electronic states of the MoS\textsubscript{2} crystal will also be discussed.

2. Experimental

Niobium-doped MoS\textsubscript{2} single crystals have been grown by the chemical vapour transport method with I\textsubscript{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 containing Br\textsubscript{2} (~5 mg cm\textsuperscript{-3}) and uniformly mixed elements (99.99% pure Mo, Nb and S) was sealed at 10\textsuperscript{-6} Torr. The ampoule was then placed in a three-zone 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 were obtained with a temperature gradient of approximately 960 → 930 °C. Single crystalline platelets up to 10 x 10 mm\textsuperscript{2} surface area and 2 mm in thickness were obtained. After 24 h, the furnace was allowed to cool down slowly (40\textdegree 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 I$_2$ 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 niobium-doped MoS$_2$ single crystal is shown in Fig.1. MoS$_2$ crystallizes with 2H or 3R structure, while NbS$_2$ crystallizes in a distorted C6 structure, so that only a small solubility range is to be expected. 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.

The PzR measurements were achieved by gluing the thin single crystal specimens on a 0.15 cm thick lead-zirconate-titanate (PZT) piezoelectric transducer driven by a 200 V$_{\text{rms}}$ sinusoidal wave at 200 Hz. The alternating expansion and contraction of the transducer subjects the sample to an alternating strain with a typical rms $l/l$ value of $\sim 10^{-5}$. A 150 W tungsten-halogen lamp filtered by a model 270 McPherson 0.35 m monochromator provided the monochromatic light. The reflected light was detected by EG&G type HUV-2000B silicon photodiode. The DC output of the silicon photodiode was maintained constant by a servo mechanism of a variable neutral density filter. A dual-phase lock-in amplifier was used to measure the detected signal. Modulated spectra were normalized to the reflectance to obtain $\Delta R/R$. An RMC model 22 close-cycle cryogenic refrigerator equipped with a model 4075 digital thermometer controller was used to control the measurement temperature between 25 and 300 K with a temperature stability of 0.5 K or better.

3. Results and Discussions

Displayed by the dashed curve in Fig. 2 are the PzR spectra near the direct band edge over the range 1.7-2.25 eV for the Au-doped MoS$_2$ single crystals. The spectra are characterized by two prominent excitonic transitions, A and B excitons. In order to determine the position of the transitions accurately, we performed a theoretical line shape fitting. The energies of both excitonic transitions show the general trend of up-shifting as the temperature is lowered. The linewidths also become narrower in the process. The functional form used in the fitting procedure corresponds to a first derivative Lorenzian line shape function of the form [23, 24].
\[
\frac{\Delta R}{R} = \text{Re} \left[ \sum_{i=1}^{n} A_{i}^{*} e^{i\phi_{i}} \left( E - E_{i}^{ex} + j\Gamma_{i}^{ex}\right)^{-n_{i}} \right]
\]  

where \(A_{i}^{*}\) and \(\phi_{i}^{ex}\) are the amplitude and phase of the line shape, \(E_{i}^{ex}\) and \(\Gamma_{i}^{ex}\) are the energy and broadening parameters of the inter band excitonic transitions and the value of \(n_{i}\) depend on the origin of the transition. For the first derivative functional form, \(n = 2.0\) is appropriate for the bounded states, such as excitons or impurity transition, while \(n = 0.5\) is applicable for three dimensional critical point inter band transitions [28]. The least-squares fits using equation (1) with \(n = 2\) can be achieved and the fits are shown as solid curve in figure 1. The fits yield the parameters \(A_{i}\), \(E_{i}\) and \(\Gamma_{i}\). The obtained values of \(E_{i}\) are indicated as arrows and denoted as A and B. The nomenclature used here follows closely that of Wilson and Yoffe [1] and Beal et al [29]. The value of \(E_{i}\) obtained here show a general agreement with slight deviation from the corresponding low temperature transmission data of Beal et al [29]. We believed the derivative nature of the PzR spectra should offer better accuracy. The fitted values of \(E_{i}\) are displaced in table 1 together with the relevant works of [29-33] for comparison. The prominent A and B excitons are observed to be red-shifted. The energy position of A and B excitons are measured accurately with the PzR experiment. The splittings of excitons A and B (\(\Delta_{BA} = E_{B} - E_{A}\)) are determined to be 0.16 ± 0.013 eV. These number agreed well with the corresponding previously work [31,32], transmission data of Beal et all [29], Reflectance [33], Wavelength modulated reflectance (WMR) spectra of Fortin and Raga and Photoconductivity [30]. In the case of the WMR data of Fortin and Raga, their observed signature, \(B^{*}\) is almost certain to be due to the presence of 3R-MoS\(_{2}\) in their 2H-MoS\(_{2}\) sample. From the more recent theoretical and experimental studies [34-36], the A and B excitons are attributed to the smallest direct transitions at the K point of the Brillouin zone split by interlayer interaction and spin-orbit splitting [34, 35]. The A exciton belongs to \(K_{4}\) to \(K_{5}\) while the B exciton corresponds to \(K_{1}\) to \(K_{3}\) optical transitions. The K states have been shown by Coehoorn et al [34, 35] to be predominantly metal \(d\) states with a small contribution from the non-metal \(p\) states. According to the figure 2, during growth of Nb-doped MoS\(_{2}\), the niobium transition ion can interfere between two layer, according to the weak van der Waals forces which link them together. This well known process involves a reduction in stoichiometry, distortion of the crystal structure and/or a variation in the position of the Fermi level. The sandwich Nb ions creates stronger bonds than the original van der Waals forces and converts the two-dimensional structure MoS\(_{2}\) (2H-MoS\(_{2}\)) of the compound into a three-dimension structure MoS\(_{2}\) (3R-MoS\(_{2}\)). It is very likely that Nb ions stabilize the 3R polytype of MoS\(_{2}\). The resulting van der Waals forces of 3R-MoS\(_{2}\) should be weaker than the 2H polytype and this is reflected by the measured reduction in \(\Delta_{BA}\).
Figure 2. Piezoreflectance spectra of Nb-doped MoS$_2$ at several temperatures between 25 and 300 K. The dashed curves are the experimental results and the solid curves are least squares fits of Eq. (1).

Table 1. Energies of the excitons A, B and their splitting in MoS$_2$, MoS$_2$:Au using equation (1). Relevant values for previously works are included for comparison.

| Material      | A (eV)    | B (eV)    | $E_{A-B}$ (eV) | Temperature (K) |
|---------------|-----------|-----------|----------------|-----------------|
| MoS$_2$:Nb$^a$| 1.928 ± 0.005 | 2.167 ± 0.008 | 0.157 ± 0.013 | 25              |
|               | 1.920 ± 0.005 | 2.160 ± 0.008 | 0.159 ± 0.005 | 77              |
|               | 1.852 ± 0.008 | 2.086 ± 0.01  | 0.160 ± 0.018 | 300             |
| MoS$_2$:Re$^b$| 1.915      | 2.066      | 0.151          | 15              |
| Undoped       | 1.928      | 2.136      | 0.208          | 15              |
| MoS$_2$$^c$   | 1.88       | 2.06       | 0.18           | 300             |
| MoS$_2$$^d$   | 1.9255     | 2.137      | 0.2115         | 4.2             |
| MoS$_2$$^e$   | 1.92       | 2.124      | 0.204          | 4.2             |
| MoS$_2$$^f$   | 1.929 ± 0.005 | 2.136 ± 0.008 | 0.207 ± 0.013 | 25              |
|               | 1.845 ± 0.008 | 2.053 ± 0.01 | 0.208 ± 0.018 | 300             |
| 2H-MoS$_2$$^g$| 1.910      | 2.112      | 0.202          | 5               |
| 3R-MoS$_2$$^g$| 1.908      | 2.057      | 0.149          | 5               |

$^a$Present work. $^b$PzR [31]. $^c$Reflectance [33]. $^d$WMR [33]. $^e$Photoconductivity [30]. $^f$PzR [32]. $^g$Transmission [29].

4. Summary
In summary we have measured the temperature dependence of the energies and broadening parameters of the direct band-edge excitonic transitions of Nb-doped MoS$_2$ using PzR in the temperature range 25 to 300 K. From the experimental observations and detailed analysis of
the broadening parameters and energies of the excitonic features A and B, we can infer that the Nb ions are most likely intercalated between the van der Waals gap and stabilize the rhombohedral 3R phase of the MoS\(_2\) crystal instead of forming the ternary Mo\(_{1-x}\)Nb\(_x\)S\(_2\) system. As a result the electronic states of the MoS\(_2\) crystals are modified with a reduction of energy splitting of A and B excitons.

Acknowledgements
The authors would like to acknowledge Professor Ying-Sheng Huang and Professor Ching-Hwa Ho for advising and providing materials and experimental equipment at Semiconductor Characterization Laboratory, National Taiwan University of Science and Technology (NTUST).

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