

Study of the near band-edge excitonic transition energies of the mixed layered compounds of $\text{Mo}_{1-x}\text{W}_x\text{Se}_2$ single crystals

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Abstract

The temperature dependence of the spectral features in the vicinity of the direct band edge of $\text{Mo}_{1-x}\text{W}_x\text{Se}_2$ single crystals was measured in the temperature range of 25–300 K using piezoreflectance (PzR). The near band-edge excitonic transition energies of the mixed layered compounds of $\text{Mo}_{1-x}\text{W}_x\text{Se}_2$ single crystals determined accurately from a detailed line-shape fit of the PzR spectra. From a detailed line-shape fit of the PzR spectra, the temperature dependence of the energies of the band-edge excitons are determined accurately.

1. Introduction

Layered-structure transition metal dichalcogenides have the formula MX_2 , where $\text{M} = \text{Mo}$, W and $\text{X} = \text{S}$, Se that exhibit many physical properties with a pronounced two-dimensional character.¹⁻³ The peculiar properties of these materials result from their layered structure, consisting of mostly covalently bonded X-M-X sheets linked by weak Van der Waals (VdW) forces. The layered transition metal dichalcogenides MX_2 semiconductors have been extensively investigated due to the potential application of the materials as solid lubricants, catalysts and photovoltaic solar cell materials.⁴⁻⁷ Agarwal *et al.* have successfully described the growth and some of the key properties of $\text{Mo}_{1-x}\text{W}_x\text{Se}_2$, $\text{Mo}_{0.5}\text{W}_{0.5}\text{Se}_2$ and $\text{W}_x\text{Se}_{2-x}$ single crystals.⁸⁻¹¹ Similar mixed-layered crystals of compounds such as $\text{Mo}_x\text{W}_{1-x}\text{Se}_2$, $\text{Mo}_{0.5}\text{W}_{0.5}\text{Se}_2$ and $\text{Mo}_{0.02}\text{W}_{0.98}\text{Se}_2$ by using various methods have been published.¹²⁻¹⁴ Our previously work, $\text{Mo}_{1-x}\text{W}_x\text{S}_2$ single crystals have been experimentally realized to vary their bandgap values and temperature dependence of energies and broadening parameters of the band-edge excitons.^{15,16}

In this paper we report a detailed study of the temperature dependence of the piezoreflectance (PzR) measurements in the spectral range near the direct band gap of $\text{Mo}_{1-x}\text{W}_x\text{Se}_2$ single crystals in the temperature range 25–300 K. The PzR spectra are fitted with a form of the Aspnes equation of the first-derivative Lorentzian line shape.¹⁷ From a detailed lineshape fit we are able to determine accurately the energies and broadening parameters of the excitonic transitions.

2. Experiment

Single crystals of $\text{Mo}_{1-x}\text{W}_x\text{Se}_2$ solid solutions were grown by chemical-vapour transport method. The chemical transport was achieved with Br_2 as transport agent in the amount of about 10 mg/cm³. Prior to the crystal growth the powdered compounds of the series were prepared from the elements (Mo: 99.99%; W: 99.99%; and Se:99.99%) by reaction at 1000 °C for 10 days in evacuated quartz ampoules. To improve the stoichiometry, sulphur 2 mol% in excess was added with respect to the stoichiometry mixture of the constituent elements. The mixture was slowly heated to 1000 °C. This slow heating is necessary to avoid any explosions due to the strongly exothermic reaction between the elements. The growth temperature was



about 1050 °C in a temperature gradient of about 3 °C/cm and the growth time was about 20 days. The crystals had the shape of thin layer plates with a thickness of 20–100 μm and a surface area of 5–200 mm². X-ray analysis confirmed that the samples were single-phase materials of two hexagonal structure over the entire range of the W composition x . The lattice constants determined for the crystals were practically identical to those of the stoichiometric polycrystalline starting materials.

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_{rms} sinusoidal wave at 200 Hz. The alternating expansion and contraction of the transducer subject the sample to an alternating strain with a typical rms $\Delta l/l$ value of $\sim 10^{-5}$. A 150 W tungsten-halogen lamp filtered by a 0.25 m monochromator provided the monochromatic light. The reflected light was detected by a silicon detector. 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 $\Delta R/R$. A close-cycle cryogenic refrigerator equipped with a 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 discussion

Displayed by the dashed curves in Figs. 1(a) and 1(b) are the PzR spectra in the vicinity of direct band edge for several mixed crystals of Mo_{1-x}W_xSe₂ at 25 and 300 K. The nature of the line shape indicates the presence of two oscillators on the high-energy side of the spectra. The oscillations on the lower-energy side are caused by the interference effects. The experimental curves have been fitted to a functional form appropriate for excitonic transitions that can be expressed as a Lorentzian line-shape function of the form.¹⁷

$$\frac{\Delta R}{R} = \text{Re} \left[\sum_{i=1}^n A_i^{ex} e^{j\varphi_i^{ex}} (E - E_i^{ex} + j\Gamma_i^{ex})^{-2} \right], \quad (1)$$

where A_i^{ex} and φ_i^{ex} are the amplitude and phase of the line shape, E_i^{ex} and Γ_i^{ex} are the energy and broadening parameters of the interband excitonic transitions, respectively. Shown by the solid curves in Fig. 1 are the least-squares fits using Eq. (1). The fits yield the parameters A_i^{ex} , E_i^{ex} and Γ_i^{ex} . The obtained values of E_i^{ex} are indicated by arrows and denoted as A₁, A₂ and B in the figures. However, at 300 K (see Fig. 1(b)), only A₁ and B features are clearly visible over most of the x values except that of $x = 0$, $x = 0.2$, $x = 0.3$ and $x = 0.4$ where a weak shoulder on the higher-energy side of A₁ excitonic transitions is visible. The weak shoulder corresponds to the A₂ peak. The energies and their splitting of the A, B excitons of Mo_{1-x}W_xSe₂ are listed in Table II. For comparison purposes, we have also listed numbers for MoS₂,^{18,19} MoSe₂,¹⁹ MoTe₂,¹⁹ WS₂,^{20,21} WSe₂²¹ and our previous work of Mo_{1-x}W_xS₂.²²

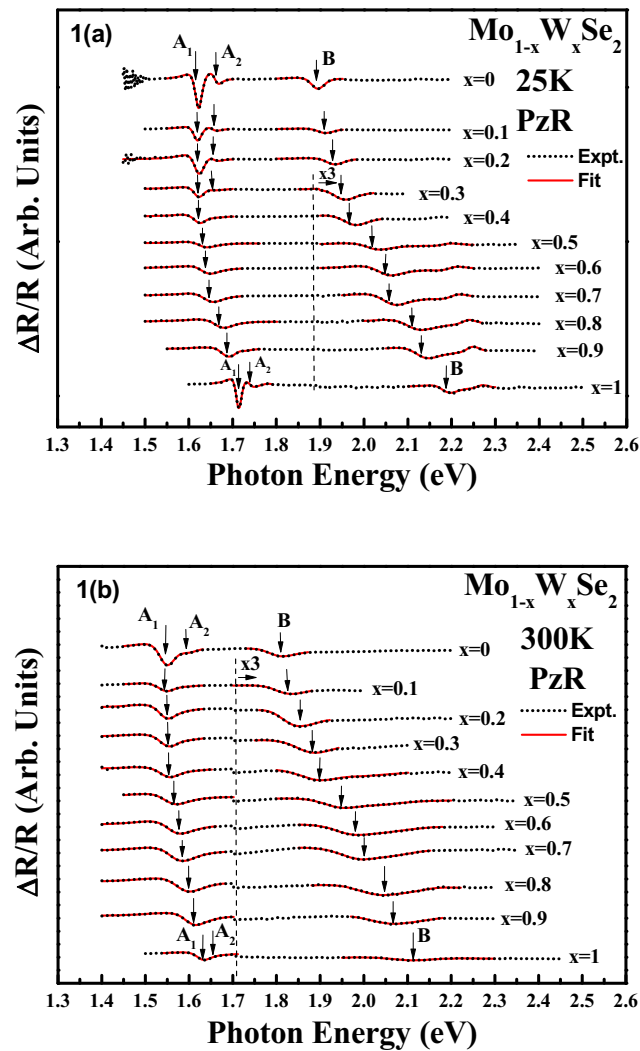


Figure. 1 The experimental PzR spectra (dashed curves) of $\text{Mo}_{1-x}\text{W}_x\text{Se}_2$ at (a) 25 K and (b) 300 K. The solid curves are least-squares fits to Eq. (1) which yields the excitonic transition energies indicated by the arrows.

Table.1 Energy of A, B excitons and their splittings in $\text{Mo}_{1-x}\text{W}_x\text{Se}_2$, $\text{Mo}_{1-x}\text{W}_x\text{S}_2$, MoSe_2 , MoTe_2 and WSe_2 .

Materials	E_A (eV)	E_B (eV)	E_{A-B} (eV)	Temperature (K)
MoSe_2^a	1.622 ± 0.005	1.892 ± 0.008	0.270 ± 0.013	25
	1.546 ± 0.008	1.799 ± 0.01	0.253 ± 0.018	300
MoSe_2^b	1.57	1.82	0.25	300
$\text{Mo}_{0.9}\text{W}_{0.1}\text{Se}_2^a$	1.619 ± 0.005	1.909 ± 0.008	0.290 ± 0.013	25
	1.544 ± 0.008	1.816 ± 0.01	0.272 ± 0.018	300

Mo _{0.8} W _{0.2} Se ₂ ^a	1.620 ± 0.005	1.929 ± 0.008	0.309 ± 0.013	25
	1.550 ± 0.008	1.834 ± 0.01	0.284 ± 0.018	300
Mo _{0.7} W _{0.3} Se ₂ ^a	1.621 ± 0.005	1.947 ± 0.008	0.326 ± 0.013	25
	1.552 ± 0.008	1.871 ± 0.01	0.319 ± 0.018	300
Mo _{0.6} W _{0.4} Se ₂ ^a	1.622 ± 0.005	1.966 ± 0.008	0.344 ± 0.013	25
	1.553 ± 0.008	1.903 ± 0.01	0.350 ± 0.018	300
Mo _{0.5} W _{0.5} Se ₂ ^a	1.631 ± 0.005	2.018 ± 0.008	0.387 ± 0.013	25
	1.555 ± 0.008	1.942 ± 0.01	0.387 ± 0.018	300
Mo _{0.4} W _{0.6} Se ₂ ^a	1.638 ± 0.005	2.044 ± 0.008	0.406 ± 0.013	25
	1.561 ± 0.008	1.960 ± 0.01	0.399 ± 0.018	300
Mo _{0.3} W _{0.7} Se ₂ ^a	1.645 ± 0.005	2.057 ± 0.008	0.421 ± 0.013	25
	1.569 ± 0.008	1.980 ± 0.01	0.411 ± 0.018	300
Mo _{0.2} W _{0.8} Se ₂ ^a	1.668 ± 0.005	2.110 ± 0.008	0.442 ± 0.013	25
	1.583 ± 0.008	2.001 ± 0.01	0.418 ± 0.018	300
Mo _{0.1} W _{0.9} Se ₂ ^a	1.687 ± 0.005	2.130 ± 0.008	0.443 ± 0.013	25
	1.600 ± 0.008	2.043 ± 0.01	0.443 ± 0.018	300
WSe ₂ ^a	1.714 ± 0.005	2.187 ± 0.008	0.473 ± 0.013	25
	1.629 ± 0.008	2.113 ± 0.01	0.484 ± 0.018	300
2H-WSe ₂ ^c	1.71	2.30	0.59	77
Mo _{0.7} W _{0.3} S ₂ ^d	1.932 ± 0.005	2.223 ± 0.008	0.291 ± 0.013	25
	1.858 ± 0.008	2.168 ± 0.01	0.290 ± 0.018	300
Mo _{0.5} W _{0.5} S ₂ ^d	1.943 ± 0.005	2.252 ± 0.008	0.309 ± 0.013	25
	1.860 ± 0.008	2.170 ± 0.01	0.310 ± 0.018	300
Mo _{0.3} W _{0.7} S ₂ ^d	1.976 ± 0.005	2.333 ± 0.008	0.357 ± 0.013	25
	1.902 ± 0.008	2.253 ± 0.01	0.351 ± 0.018	300
MoS ₂ ^d	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
WS ₂ ^d	2.064 ± 0.005	2.489 ± 0.008	0.425 ± 0.013	25
	1.981 ± 0.008	2.401 ± 0.01	0.420 ± 0.018	300
WS ₂ ^e	2.06	2.47	0.41	77
	2.0	2.386	0.386	300
3R-WS ₂ ^f	2.06	2.50	0.44	77
MoTe ₂ ^g	1.71	2.30	0.59	77
MoS ₂ ^h	1.9255	2.137	0.2115	4.2
MoS ₂ ⁱ	1.92	2.124	0.204	4.2

^athis work^dReference 22.^gReference 19.^bReference 19.^eReference 21.^hReference 18.^cReference 20.^fReference 20.ⁱReference 18.

The A and B exciton peaks near the optical absorption edge are characteristic features of the optical spectra of all layered molybdenum and tungsten dichalcogenides.²² The nature of the direct gaps has been investigated by studying these exciton pairs. Following Wilson and Yoffe²² many authors have attributed the A–B exciton pair to transitions at the Γ point, split by spin–orbit splitting, as suggested by the dependence of the splittings on the masses of the constituent elements.

4. Conclusions

In conclusions we have measured the temperature dependence of the energies and broadening parameters of the direct band-edge excitonic transitions of $\text{Mo}_{1-x}\text{W}_x\text{Se}_2$ using PzR in the temperature range between 25 and 300 K. The transition energies of A, B excitons and their separation at various temperatures change smoothly with W composition x , indicating that the nature of the direct band edges of $\text{Mo}_{1-x}\text{W}_x\text{Se}_2$ are similar, even for $\text{Mo}_{1-x}\text{W}_x\text{S}_2$. The splitting of excitons A and B for $\text{Mo}_{1-x}\text{W}_x\text{Se}_2$ is larger than $\text{Mo}_{1-x}\text{W}_x\text{S}_2$ at various temperatures.

Acknowledgements

The author 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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