Optical characterization of $Mo_{1-x}W_xS_2$ single crystals

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Abstract — **A systematic optical study of $Mo_{1-x}W_xS_2$ single crystals grown by the chemical vapor transport method in a wide range composition ($0 \leq x \leq 1$) is presented. The optical characterization was carried out using piezoreflectance (PzR) and photoluminescence (PL) measurements at room temperature. The origin and composition x dependence of A and B excitons are evaluated from PzR, indicating that the nature of the direct band edges is similar to the $Mo_{1-x}W_xS_2$ compounds. Radiative recombination processes near indirect band gap in $Mo_{1-x}W_xS_2$ single crystals are investigated by PL. The strong sharp lines attributed to recombination of excitons bound on electron-attractive neutral centers are observed in PL of $2H-MoS_2$ and $2H-WS_2$ but they are not visible in PL spectra of $Mo_{1-x}W_xS_2$ single crystals. The broad-bands emission observed in PL spectra of $Mo_{1-x}W_xS_2$ compounds are ascribed to recombination via deep centers due to the intrinsic defects of the layered crystals.**

Index Terms — **exciton, layered crystal, photoluminescence, piezoreflectance.**

I. INTRODUCTION

Layered-structure transition metal dichalcogenides TX_2 (T = Mo or W; X = S or Se) have been extensively investigated because of their interesting fundamental properties including the strong anisotropy of physical properties, the role of the d orbitals of the transition metal atom in the electronic band structure and the sharp excitonic structures in the visible region [1-3]. Besides applications in such important areas as photovoltaic solar cells, catalysts, solid lubricants or intercalation batteries [4-6], the TX_2 compounds could be of interest as efficient luminescent materials in the near IR spectral region [7, 8]. Last decade, several papers concerning to preparation and characterization of $Mo_{1-x}W_xS_2$ compounds by various methods have been published [9-13]. In addition, only a few works on the study of the excitonic transitions have been reported [10].

In this article a detailed study of the piezoreflectance (PzR) measurements in the spectral range of the A, B excitonic structures near direct band edge as well as the photoluminescence (PL) of $Mo_{1-x}W_xS_2$ single crystals at 300 K are presented.

II. EXPERIMENT

Single crystals of $Mo_{1-x}W_xS_2$ solid solutions were grown by the chemical-vapour transport method from the instant elements (Mo: 99.99%; W: 99.95% and S: 99.999%). To improve the stoichiometry, sulphur 2 mol% in excess was added with respect to the stoichiometric mixture of the constituent elements. The chemical transport was achieved with Br_2 as a transport agent in the amount of about 8 mg/cm³. The growth temperature was about 1030 °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 to 500 μm and a surface area of 20 to 100 mm². For simplicity, the value of x henceforth is defined by the nominal composition of the starting material. The weak van der Waals bonding between the layers of the crystals means that they display good cleavage property parallel to the layers.

The PzR measurements were achieved by gluing the thin single crystal specimens on a 0.15 cm thick lead–zirconate–titanate piezoelectric transducer driven by a 200 V_{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 $\Delta l=l$ value of ~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 an EG&G type HUV-2000B silicon photodiode, and the signal was recorded from an NF model 5610B lock-in amplifier.

The steady-state PL measurements were performed with a variable temperature optical cryostat, a 325.5 L/mm grating monochromator coupled to a cooled InGaAs-detector, and standard lock-in detection techniques. The luminescence excitation was provided by a He-Ne laser (λ=633 nm). All spectra were corrected for the wavelength dependent response of the optical system.
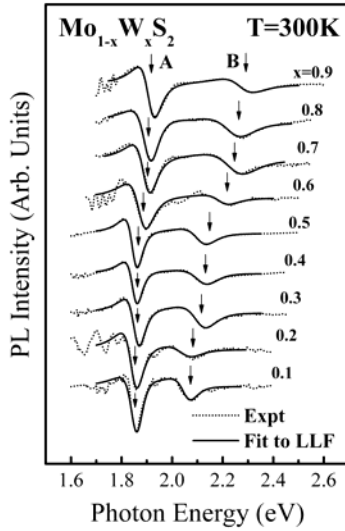
Fig. 1. The experimental PzR spectra (dotted curves) of $Mo_{1-x}W_xS_2$ at 300 K. The solid curves are least-squares fits to LLF which yields the excitonic transition energies indicated by the arrows.

III. RESULTS AND DISCUSSION

Displayed by the dashed curves in Fig. 1 are the PzR spectra near the direct band edge for several mixed crystals of $Mo_{1-x}W_xS_2$ at 300 K. The nature of the lineshape indicates the presence of two oscillators, corresponding to the first two levels of exciton A, on the lower-energy side of the spectra. The features on the higher-energy side belong to exciton B. The experimental curves have been fitted to a functional form appropriate for excitonic transitions that can be expressed as a Lorentzian lineshape function (LLF) [14] shown by the solid curves. The obtained values of excitonic energy are indicated by arrows and denoted as A and B (Fig. 1).

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 [1]. The nature of the direct gaps has been investigated by studying these exciton pairs. The results show that the valence band maximum is located at the sixfold-degenerate K point of the Brillouin zone. Adopting the experimental results [15] and detailed band structure calculations [16, 17], it leads to conclusion that the A and B excitons correspond to the smallest direct gap at the K point and the A–B exciton splitting is due to interlayer interactions and spin–orbit splitting. So A-B excitonic separation is due to spin–orbit splitting at the top of the valence band at the K point. Spin–orbit splitting is expected to play an important role in the band structure of MoS_2 and its molybdenum and tungsten isomorphs because of the high atomic numbers of Mo and W. The splitting energies of the A and B excitons of $Mo_{1-x}W_xS_2$ are located between the splitting energies of MoS_2 and WS_2 (see Fig. 1). The separation energy for dichalcogenides such as MoS_2, $MoSe_2$, $MoTe_2$, WS_2 and WSe_2 differs varying from the smallest value of 0.18 eV for MoS_2 to the biggest 0.59 eV for WSe_2 [3, 18, 19]. For the sulphides of both Mo and W the lattice parameters are almost identical. Overlap between the outer orbitals of nearest-neighbour metal atoms will therefore be greater for

TABLE I. RESULTS OF THE EXCITONIC TRANSITIONS OF $Mo_{1-x}W_xS_2$ TERNARY COMPOUNDS AT 300 K WHICH ARE FITTED BY EQ. (1)

Feature	$E^{ex}(0)$(eV)	b	c
A	1.83 ± 0.01	0.04 ± 0.02	0.07 ± 0.02
B	2.06 ± 0.01	0.14 ± 0.03	0.14 ± 0.03

the larger W atoms. This will tend to increase the spin–orbit splitting on the top of the valence band at the K point. Consistent with this view, the increase in the splitting with increasing W composition x for the $Mo_{1-x}W_xS_2$ compounds is observed (Fig. 1).

Figure 2 shows the dependence on the tungsten composition x of the excitonic transition energies with error bars at 300 K. The excitonic transition energies and the splitting between A and B transitions vary smoothly with W composition x. The smooth variation of the transition energies and their splittings with tungsten composition x indicates that the nature of the direct band edge remains unchanged for $0 \leq x \leq 1$. The composition dependences of the excitonic transition energies A and B are fitted by the expression [20]

$$E_i^{ex}(x) = E_i^{ex}(0) + b_i x + c_i x^2, \qquad (1)$$

where i = A and B. This relation is customarily used to express the composition-dependent gap energy for the direct band gaps in mixed III–V semiconducting compounds where c_i is the bowing parameter [20]. The theoretical situation concerning bowing of the band gap in alloys is still somewhat unclear, but seems to agree in the existence of a contribution to energy gap bowing as a result of the nonlinear dependence of the crystal potential on the properties of the component ions, independent of local potential fluctuations. The results are summarized in Table I.

Figure 3 illustrates PL spectra of $Mo_{1-x}W_xS_2$ solid solutions at 9 K as well as the spectra of 2H-MoS_2 and 2H-WS_2 synthetic crystals at 6 K [7, 8], for comparison reason.

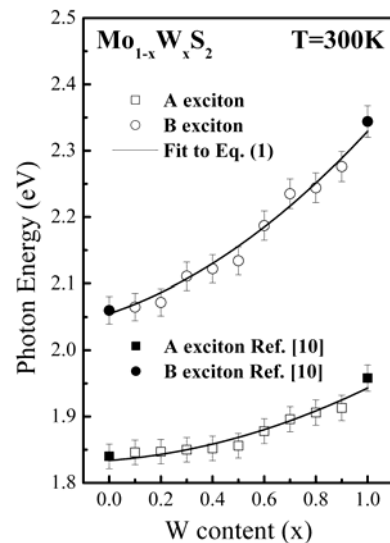Fig. 2. The composition dependence of the excitonic transition energies for A and B features of $Mo_{1-x}W_xS_2$ at 300K. The solid curves are least-squares fits to Eq. (1) with fitting parameters given in Table I.

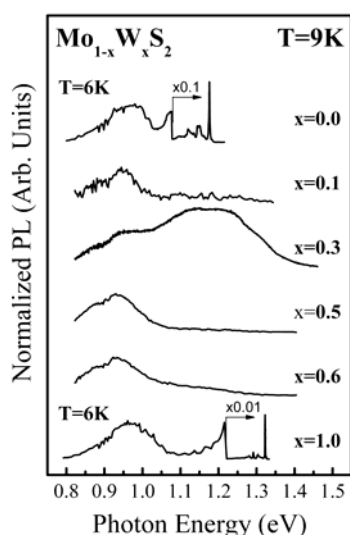Fig. 3. PL spectra of $Mo_{1-x}W_xS_2$ at 9 K. Two distinct regions are present for 2H-MoS$_2$ and 2H-WS$_2$ synthetic crystals at 6 K [7, 8]: a broadband region and an excitonic region. The excitonic region contains a zero-phonon lines and phonon replicas.

For non-mixed crystals, all spectra consist of two characteristic parts: a short-wavelength region with several intense, sharp lines located at about 0.1 eV below the energy of the indirect band gap [21, 22] and a broad spectral band centered at ~ 0.97 eV with a half-width of about 0.15 eV. The excitonic region, prominent in the 6 K spectrum, is usually composed of zero-phonon lines followed by phonon replicas. As for $Mo_{1-x}W_xS_2$ solid solutions, in the higher-energy side, the several sharp intense lines are not observed. While for the broad-band region, its intensity and spectral shape remain largely similar. Besides, the PL spectra of the natural MoS$_2$ samples do not reveal any excitonic region and only the IR broad-band emission with the same spectral shape- and temperature-dependent behavior as that of the synthetic crystals was detected.

The spectral shape of the broad-band observed for $Mo_{1-x}W_xS_2$ samples suggest that this emission occurs as a result of radiative transitions between a deep donor center and the valence band in the conditions of a strong electron-phonon coupling [23, 24]. The intensity of the broadband emission for 2H-MoS$_2$ and 2H-WS$_2$ does not depend on the excitonic recombination efficiency - the quenching of the band takes place only when the sharp lines have totally vanished [7, 8]. This indicates that the recombination rate via the broadband channel is much higher than that via the excitonic one. Therefore, the radiative recombination caused by the deep level can be treated as a shunt channel for the excitonic luminescence.

IV. CONCLUSION

In summary we have measured the energies and broadening parameters of the direct band-edge excitonic transitions of $Mo_{1-x}W_xS_2$ using PzR at 300 K. The transition energies of A and B excitons and their separation change smoothly with W composition *x*, indicating that the nature of the direct band edges of $Mo_{1-x}W_xS_2$ are similar. The existence of compositional fluctuations and alloy scattering effects causes the broader linewidth of the mixed ternary compounds. In addition, the radiative recombination processes near indirect band gap in $Mo_{1-x}W_xS_2$ single crystals investigated by PL show the strong sharp lines attributed to recombination of excitons bound on electron-attractive neutral centers for 2H-MoS$_2$ and 2H-WS$_2$ but they are not visible in PL spectra of $Mo_{1-x}W_xS_2$ single crystals. The broad-bands emission observed in PL spectra of $Mo_{1-x}W_xS_2$ as well for 2H-MoS$_2$ and 2H-WS$_2$ compounds are ascribed to recombination via deep centers due to the intrinsic defects of the layered crystals.

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