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Polarization sensitive behaviour of the band-edge transitions in ReS₂ and ReSe₂ layered semiconductors

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Abstract

The polarization sensitive behaviour of the band-edge transitions in ReS₂ and ReSe₂ layered compounds was studied using polarized-transmission and polarized-thermoreflectance (PTR) measurements with polarization angles from $\theta = 0^\circ$ ($E \parallel b$ -axis) to $\theta = 90^\circ$ ($E \perp b$ -axis) at 300 K. The polarization dependence of the polarized energy gaps of ReS₂ and ReSe₂ shows a sinusoidal-like variation with respect to the angular change of the linearly polarized light. The angular dependences of the polarized energy gaps of ReS₂ and ReSe₂ were evaluated. The polarization sensitive behaviour of the band-edge excitons in rhenium disulfide and diselenide was characterized using angular dependent PTR measurements from $\theta = 0^\circ$ to 90° . The polarized transition intensities of the band-edge excitons (E_1^{ex} and E_2^{ex}) of ReX₂ ($X = \text{S, Se}$) demonstrate a sinusoidal variation with respect to the angular change of the linearly polarized light. The angular dependence of the polarized transition probabilities of E_1^{ex} and E_2^{ex} is analysed. The polarization sensitive behaviours of ReX₂ ($X = \text{S, Se}$) layers are discussed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Layered crystals of ReX₂ ($X = \text{S, Se}$) are diamagnetic semiconductors that belong to the family of the transition-metal dichalcogenides (TMDCs) crystallizing in the distorted octahedral layer structure of triclinic symmetry [1, 2]. The lattice parameters of ReS₂ (ReSe₂) are $a = 6.450 \text{ \AA}$ (6.713 \AA), $b = 6.390 \text{ \AA}$ (6.623 \AA), $c = 6.403 \text{ \AA}$ (6.740 \AA), $\alpha = 105.49^\circ$ (104.59 $^\circ$), $\beta = 91.32^\circ$ (92.28 $^\circ$), and $\gamma = 119.03^\circ$ (118.79 $^\circ$), respectively [3]. Layered ReX₂ compounds are of considerable interest for various applications due to their optical, electrical

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and mechanical properties [1]. These applications include a sulfur-tolerant hydrogenation and hydrodesulfurization catalyst [4, 5] and as a promising solar-cell material in electrochemical cells [6, 7]. Unlike most of the layered TMDCs, ReX_2 crystallizes in a distorted CdCl_2 -type layer structure with triclinic symmetry. A clustering pattern of ‘diamond chains’ consisting of Re ions forms along the b -axis in the ReX_2 monolayer, resulting in the crystals being optically biaxial. The consequence of the in-plane anisotropy of ReX_2 is mostly probably attributed to the field-induced polarization of the lattice [8]. The mechanism leads to displacement of the lattice atoms, which may alter the electronic states of the solids. The lattice–field interaction is expected to be more pronounced for polarization parallel to the b -axis, which is along the direction of largest conductivity [9, 10]. The absorption-edge anisotropy in the layer plane of ReS_2 and ReSe_2 renders these crystals to possess the potential capability to fabricate a polarization sensitive photodetector applied in multi-channel optical communication for detecting the various orientations of linearly polarized light [11, 12].

ReX_2 ($X = \text{S}, \text{Se}$) are indirect semiconductors with energy gaps of 1.37 eV for ReS_2 and 1.19 eV for ReSe_2 , respectively [13]. Optically biaxial behaviour of ReX_2 is observed with linearly polarized light incident normal to the basal plane [$\mathbf{E} \parallel (001)$ and $\mathbf{k} \perp (001)$]. The in-plane optical anisotropy of ReX_2 ($X = \text{S}, \text{Se}$) with polarizations along and perpendicular to the b -axis has never been studied using polarization-dependent absorption and piezoreflectance (PzR) measurements [14–16]. The experimental results clearly indicated that the near-band-edge transitions (i.e. band gap and excitons) in ReS_2 and ReSe_2 are polarization dependent. The energy values of the polarized energy gaps (i.e. $E_{g\parallel}$ and $E_{g\perp}$) and band-edge excitons (E_1^{ex} and E_2^{ex}) were, respectively, determined from the analyses of absorption and PzR spectra [14, 15]. The polarized energy gaps ($E_{g\parallel}$ and $E_{g\perp}$) of ReX_2 provide a potential capability for the layered materials to be used as a polarized optical switch applied in polarized optical communication of the near-infra-red (NIR) region. Although various optoelectronic applications such as polarized optical switching and polarized optical detecting may be performable, the actual angular dependence of the polarized band-edge transitions in ReS_2 and ReSe_2 layered semiconductors has yet to be explored.

In this paper, the polarization sensitive behaviour of the band-edge transitions in ReS_2 and ReSe_2 layered semiconductors was characterized using polarized-transmission and polarized-thermoreflectance (PTR) measurements with polarization angles from $\theta = 0^\circ$ ($E \parallel b$ -axis) to $\theta = 90^\circ$ ($E \perp b$ -axis) at 300 K. The polarization dependence of the energy gaps for ReS_2 and ReSe_2 shows a sinusoidal-like variation with respect to the angular change of the linearly polarized light. The angular dependent relationships of the polarized energy gaps for ReS_2 and ReSe_2 are determined to be $E_g(\theta) = 1.367 - 0.023 \cos(2\theta)$ and $1.193 - 0.018 \cos(2\theta)$ eV, respectively. The polarization dependence of the band-edge excitons of ReX_2 layer compounds was also characterized by angular dependent PTR measurements from $E \parallel b$ ($\theta = 0^\circ$) to $E \perp b$ -axis ($\theta = 90^\circ$). The angular dependence of the PTR spectra clearly indicates that the exciton 1 (E_1^{ex}) transition is present only in the angular range from 0° to 45° , while the other transition, exciton 2 (E_2^{ex}), appears merely in the range 45° – 90° . For $\theta = 45^\circ$, E_1^{ex} and E_2^{ex} features simultaneously disappeared in the PTR spectra due to the forbidden transition by the selection rule. The angular dependence of the polarized transition intensities of E_1^{ex} and E_2^{ex} is analysed. The polarization sensitive behaviour for these triclinic layered materials is discussed.

2. Experimental procedure

Single crystals of ReS_2 and ReSe_2 were grown by the chemical vapour transport method using Br_2 as the transport agent. Prior to the crystal growth, quartz tubes containing bromine and

the elements (Re: 99.95% pure, S: 99.999%, Se: 99.999%) were evacuated and sealed. To improve the stoichiometry, sulfur or selenium with 2 mol% in excess was added with respect to rhenium. The quartz tube was placed in a three-zone furnace and the charge prereacted for 24 h at 800 °C while the temperature of the growth zone was set at 1000 °C to prevent the transport of the product. 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 takes place. Best results were obtained with temperature gradients of about 1060 → 1010 °C for ReS₂ and 1050 → 1000 °C for ReSe₂, respectively. Both ReS₂ and ReSe₂ formed thin, silver-coloured, graphite-like, hexagonal-shaped platelets up to 2 cm² in area and 100 μm in thickness. X-ray diffraction patterns of single crystals confirmed the triclinic symmetry of ReS₂ and ReSe₂ with all parameters consistent with those previously reported [2, 3, 17]. The weak van der Waals bonding between the layers of the materials means they display good cleavage property parallel to the layers; the thicker samples can be exploited to obtain thin specimens using a razor blade.

Measurements of the reflectance and transmittance at near-normal incidence were made on a scanning monochromatic measurement system with a resolution of 1 Å. A 150 W tungsten–halogen lamp filtered by a PTI 0.35 m monochromator provided the monochromatic light. The transmission intensity was closely monitored to obtain an incidence as close to 90° as possible. Single crystals with a thickness of about 100 μm were used in the transmission measurements. Plate-shaped crystals were selected and mounted on a copper sample holder fitted into a Dewar with optical windows. For the thermorefectance (TR) experiments, the same monochromatic system as used in the transmission measurement was used. The reflected light of the sample was detected by an EG&G type HUV-2000B silicon photodiode and the signal was recorded from an EG&G model 7265 dual phase lock-in amplifier. The experimental design of the heater structure and electronic circuits for the TR experiments were described in the previously published results [18]. The representative scheme of the arrangements of polarized-transmission and PTR measurements is demonstrated in figure 1. A pair of OPTOSIGMA near-infrared-dichroic-sheet polarizers with a measurement range of 760–2000 nm was employed in the polarization dependent measurements. The angular dependent polarization measurements were carried out with the polarization angles ranging from $E \parallel b$ ($\theta = 0^\circ$) to $E \perp b$ -axis ($\theta = 90^\circ$). The b -axis is parallel to the Re cluster chains, which corresponds to the longest edge of the platelet [11, 19].

3. Results and discussion

Displayed in figure 2 are the polarized transmittance spectra of (a) ReS₂ and (b) ReSe₂ in the wavelength region of 820–1110 nm. The transmission measurements were carried out with polarization angles from $\theta = 0^\circ$ to 90° with an increment of 10° at room temperature. As shown in figure 2, the absorption edges of both ReS₂ and ReSe₂ simultaneously show an energy blue-shift behaviour with respect to the increase of the polarization angles from $\theta = 0^\circ$ to 90° . The absorption-edge anisotropy in rhenium disulfide and diselenide provides relevant evidence that the energy gaps of ReX₂ are polarization dependent. This property also lends a potential ability for ReS₂ and ReSe₂ to be used as a polarized optical switch suitable for the polarized optical communication of the NIR region. As is shown in figure 2(a), a polarized optical beam of ~880 nm with a polarization angle of $\theta = 0^\circ$ cannot pass through the ReS₂ layer when we set the transmission threshold at 0.1, while the layered compound can be regarded as ‘transparent’ when the linearly polarized light possesses a polarization angle of $\theta = 90^\circ$. By adding some electronic circuits for auxiliary, the ON and OFF states of the linearly polarized light can be clearly detected in polarized optical communications by using these layered compounds.

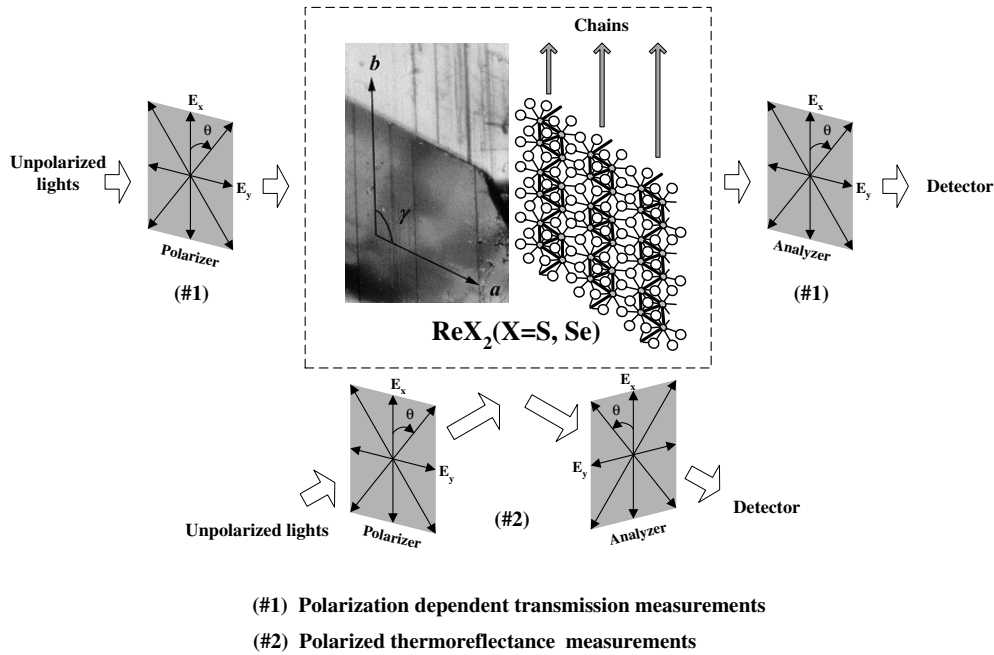


Figure 1. Representative scheme of the arrangements of polarized-transmission and PTR measurements for ReX_2 ($X = \text{S}, \text{Se}$). The polarization angle θ is defined as the angular difference between the orientation of the linearly polarized light and that of the crystal's b -axis.

The absorption coefficient α for these layered materials can be determined from the transmittance T_r by taking into account the spectral dependence of the reflectance R using the relation [20]

$$T_r = \frac{(1 - R)^2 e^{-\alpha d}}{1 - R^2 e^{-2\alpha d}}, \quad (1)$$

where d is the sample thickness. Equation (1) assumes that there are multiple reflections within the sample, but that they add incoherently due to sample inhomogeneity or a sufficiently large spread of the incident angles. Because αd is large for the sample crystals, the second term in the denominator of the T_r relation can be neglected. The absorption coefficients of ReX_2 as a function of photon energy from $\theta = 0^\circ$ to 90° can be obtained from the calculations of the transmittance spectra displayed in figures 2(a) and (b). Spectral analyses of the absorption curves indicate that the absorption coefficient α of ReX_2 is proportional to $(h\nu - E_g)^n$ with $n = 2.0 \pm 0.1$. This suggests an indirect allowed transition for the layered crystals. A more complete analysis taking into account both absorption and emission phonons such as that in the previously used approach [14] can be utilized to determine the band-gap energies and the average phonon temperatures from the polarized absorption spectra. Shown in figure 3 by solid diamonds are the values of polarized energy gaps of (a) ReS_2 and (b) ReSe_2 from $\theta = 0^\circ$ to 90° with representative error bars. The average phonon energies for indirect ReS_2 and ReSe_2 at 300 K are determined to be 25 ± 5 and 20 ± 5 meV, respectively. As shown in figure 3, the angular dependence of the polarized energy gaps of ReX_2 shows a sinusoidal-like variation of energies ranging from 1.344 ± 0.003 eV ($\theta = 0^\circ$) to 1.390 ± 0.003 eV ($\theta = 90^\circ$) for ReS_2 , and 1.175 ± 0.003 eV ($\theta = 0^\circ$) to 1.211 ± 0.003 eV ($\theta = 90^\circ$) for ReSe_2 , respectively. The angular dependence of the polarized gaps of ReS_2 and ReSe_2 can be analysed by fitting the

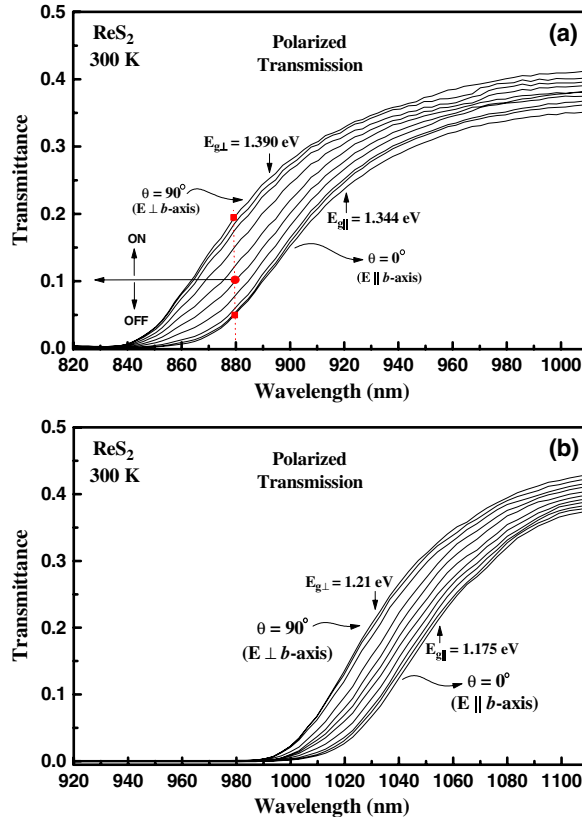


Figure 2. Angular dependent polarized-transmission spectra of (a) ReS_2 and (b) ReSe_2 at 300 K. The measurements were carried out with polarization angles ranging from $\theta = 0^\circ$ ($E \parallel b$ -axis) to $\theta = 90^\circ$ ($E \perp b$ -axis) with an angular increment of 10° .

experimental data to a sinusoidal functional form of

$$E_g(\theta) = E_0 - \Delta \cos[2\theta], \quad (2)$$

where E_0 is closely related to the energy gap measured with unpolarized light, and Δ is the amplitude of the sinusoidal energy change. The energy-variation relation of equation (2) is similar to the generalized Malus law [21] that describes the dependence of the linearly polarized light. The solid curves displayed in figures 3(a) and (b) are the results of fitting the polarized energy gaps to equation (2). Also shown in figures 3(a) and (b) are two polar-coordination plots which depict the angular dependence of the fitting data from $\theta = 0^\circ$ to 180° for ReS_2 and ReSe_2 , which are included for comparison. From the least-square fits, the energy values of E_0 and Δ are determined to be 1.367 and 0.023 eV for ReS_2 , and 1.193 and 0.018 eV for ReSe_2 , respectively. The values of E_0 are in good agreement with the band gaps of ReS_2 and ReSe_2 that have been determined from unpolarized transmission measurements [13].

The polarized nature of the band-edge excitons in ReS_2 and ReSe_2 were characterized using angular dependent PTR measurements at room temperature. The PTR spectra of (a) ReS_2 and (b) ReSe_2 with polarization angles ranging from $\theta = 0^\circ$ to 90° are shown in figure 4. There are two oscillators (E_1^{ex} and E_2^{ex}) simultaneously detected in the unpolarized TR spectra of ReX_2 . The angular dependent PTR spectra in ReX_2 clearly indicate that the exciton 1 (E_1^{ex}) transition is only present in the angular range from 0° to 45° , while the other transition,

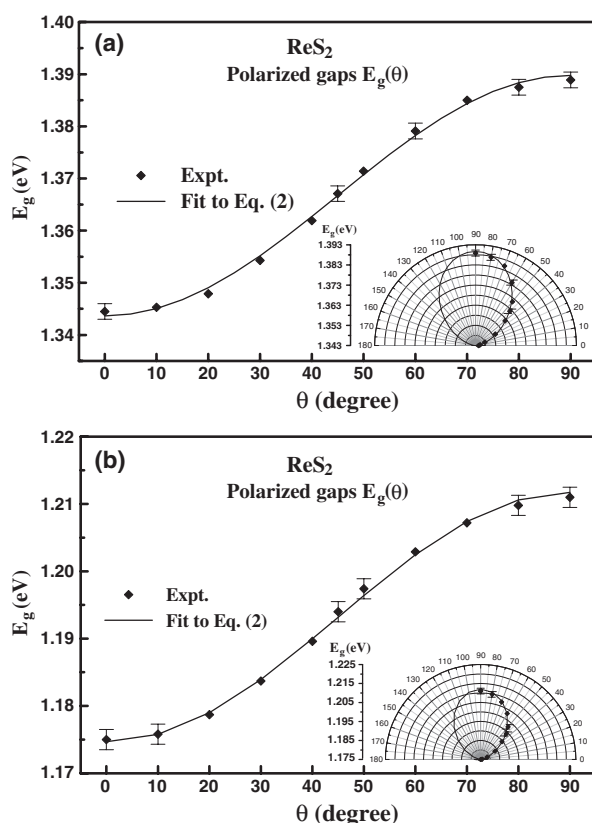


Figure 3. Angular dependence of the polarized energy gaps of (a) ReS_2 and (b) ReSe_2 with representative error bars. The solid diamonds are the experimental data, and the solid curves are least-square fits to equation (2).

exciton 2 (E_2^{ex}), appears merely in the range 45° – 90° . For $\theta = 45^\circ$, both E_1^{ex} and E_2^{ex} features simultaneously disappeared in the PTR spectra due to the forbidden transition by the selection rule. These observations provide conclusive evidence that E_1^{ex} and E_2^{ex} arise from different origins. A previous study showed that E_1^{ex} and E_2^{ex} are closely related to the transitions of the nonbonding Re 5d t_{2g} (d_{xy} , $d_{x^2-y^2}$) to 5d t_{2g}^* band [22].

The excitonic transitions of E_1^{ex} and E_2^{ex} in the PTR spectra of ReS_2 and ReSe_2 can be analysed via a derivative Lorentzian line-shape function [15]. The solid-diamond curves in figure 4 are the fitting results, and the obtained values of the transition energies are indicated with arrows. As shown in figures 4(a) and (b) the signal intensities of E_1^{ex} decreased as the polarization angles increased from $\theta = 0^\circ$ to 45° , while the amplitudes of E_2^{ex} gradually enlarged when the angle of the linearly polarized light increased from $\theta = 45^\circ$ to 90° . The angular dependence of the normalized transition intensities of E_1^{ex} and E_2^{ex} is shown in figure 5 by hollow diamonds (ReS_2) and solid diamonds (ReSe_2). The transition intensities of E_1^{ex} with an angular range of $\theta < 45^\circ$ are normalized to the signal intensities at $\theta = 0^\circ$ ($E \parallel \mathbf{b}$), whereas the transition intensities of E_2^{ex} with an angular range of $\theta > 45^\circ$ are normalized to that of the $\theta = 90^\circ$ ($E \perp \mathbf{b}$) spectrum. As shown in figure 5, the angular dependence of the normalized transition intensities of E_1^{ex} and E_2^{ex} for both ReS_2 and ReSe_2 shows a sinusoidal variation of transition probabilities with respect to the angular change of linearly polarized

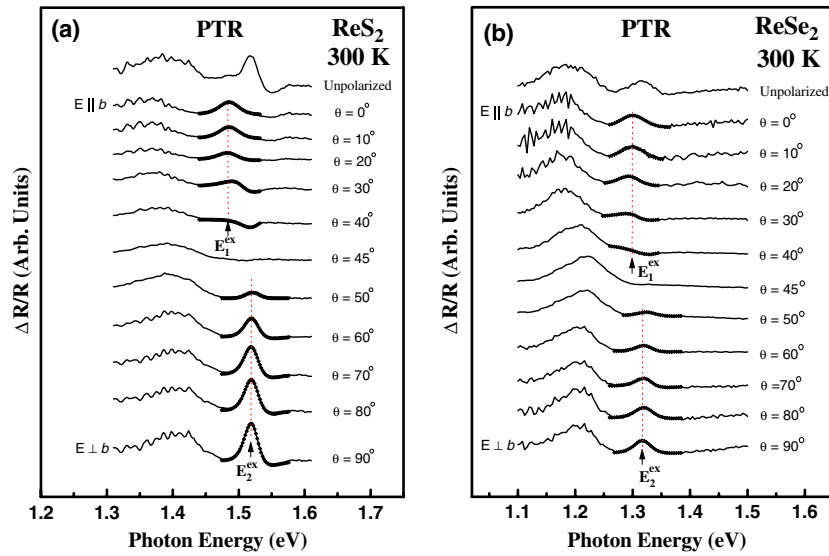


Figure 4. Polarized-thermoreflectance spectra of (a) ReS_2 and (b) ReSe_2 with polarization angles ranging from $\theta = 0^\circ$ to 90° . The solid curves are the experimental results and the solid-diamond curves are fitted to a derivative Lorentzian line-shape function.

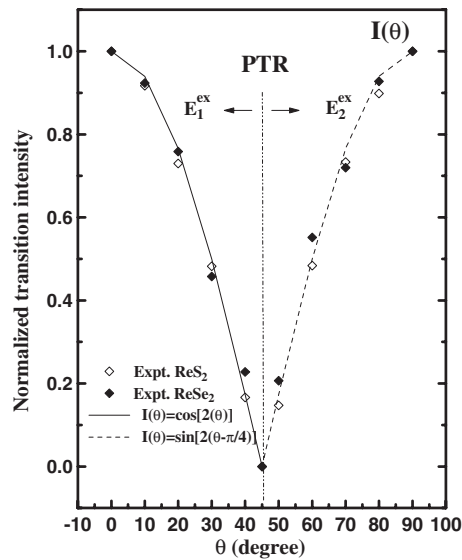


Figure 5. Angular dependence of the normalized transition intensities of E_1^{ex} and E_2^{ex} for ReX_2 ($X = \text{S}, \text{Se}$). The solid curve corresponds to the functional curve of $I(\theta) = \cos[2\theta]$ ($\theta \leq 45^\circ$) and the dashed curve is that of $I(\theta) = \sin[2(\theta - \pi/4)]$ ($\theta \geq 45^\circ$).

light. The variation of the normalized transition intensities of E_1^{ex} with an angular range of $\theta \leq 45^\circ$ matches well with the function $I(\theta) = \cos[2\theta]$, while the variation in E_2^{ex} with an angular range of $\theta \geq 45^\circ$ is in accordance with $I(\theta) = \sin[2(\theta - \pi/4)]$. The polarization sensitive behaviour of E_1^{ex} and E_2^{ex} provides potential usage for ReX_2 ($X = \text{S}, \text{Se}$) to fabricate a polarization sensitive photodetector applied in multi-channel optical communications for detecting the various orientations of linearly polarized light.

4. Summary

In summary, the polarization dependence of band-edge transitions in rhenium disulfide and diselenide is studied using polarized-transmission and polarized-thermoreflectance (PTR) measurements with polarization angles from $\theta = 0^\circ$ ($E \parallel \mathbf{b}$ -axis) to $\theta = 90^\circ$ ($E \perp \mathbf{b}$ -axis). The angular dependence of the polarized energy gaps shows a sinusoidal variation of energy values ranging from ~ 1.344 eV ($E \parallel \mathbf{b}$) to ~ 1.390 eV ($E \perp \mathbf{b}$) for ReS_2 and ~ 1.175 eV ($E \parallel \mathbf{b}$) to ~ 1.211 eV ($E \perp \mathbf{b}$) for ReSe_2 , respectively. The angular dependent relationships of the polarized energy gaps of ReS_2 and ReSe_2 are determined to be $E_g(\theta) = 1.367 - 0.023 \cos(2\theta)$ and $1.193 - 0.018 \cos(2\theta)$ eV, respectively. The polarization dependence of the band-edge excitons of rhenium disulfide and diselenide is characterized using angular dependent PTR measurements at 300 K. The angular dependence of the PTR spectra clearly indicates that the exciton 1 (E_1^{ex}) transition is only present in the angular range from 0° to 45° , while the other transition, exciton 2 (E_2^{ex}), appears merely in the range 45° – 90° . For $\theta = 45^\circ$, E_1^{ex} and E_2^{ex} features simultaneously disappeared in the PTR spectra due to the forbidden transition by the selection rule. The angular dependence of the normalized transition intensities of E_1^{ex} and E_2^{ex} for ReX_2 shows a sinusoidal variation of transition probabilities with respect to the angular change of linearly polarized light. The variation in normalized transition intensities of E_1^{ex} with an angular range of $\theta \leq 45^\circ$ matches well with the function $I(\theta) = \cos[2\theta]$. The variation of E_2^{ex} with an angular range of $\theta \geq 45^\circ$ is in good agreement with the form $I(\theta) = \sin[2(\theta - \pi/4)]$.

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References

- [1] Wilson J A and Yoffe A D 1969 *Adv. Phys.* **18** 193
- [2] Wildervanck J C and Jellinek F 1971 *J. Less-Common Met.* **24** 73
- [3] Ho C H, Huang Y S, Liao P C and Tiong K K 1999 *J. Phys. Chem. Solids* **60** 1797
- [4] Broadbent H S, Slangh L H and Jarvis N L 1954 *J. Am. Chem. Soc.* **76** 1519
- [5] Harris S and Chianelli R R 1984 *J. Catal.* **86** 400
- [6] Koffyberg F P, Dwight K and Wold A 1979 *Solid State Commun.* **30** 433
- [7] Wheeler B L, Leland J K and Bard A J 1986 *J. Electrochem. Soc.* **133** 358
- [8] Weiser G 1973 *Surf. Sci.* **37** 175
- [9] Ho C H, Huang Y S, Tiong K K and Liao P C 1999 *J. Phys.: Condens. Matter* **11** 5367
- [10] Tiong K K, Ho C H and Huang Y S 1999 *Solid State Commun.* **111** 635
- [11] Friemelt K, Lux-Steiner M-Ch and Bucher E 1993 *J. Appl. Phys.* **74** 5266
- [12] Ho C H, Yen P C, Huang Y S and Tiong K K 2002 *Phys. Rev. B* **66** 245207
- [13] Ho C H, Liao P C, Huang Y S, Yang T R and Tiong K K 1997 *J. Appl. Phys.* **81** 6380
- [14] Ho C H, Huang Y S, Tiong K K and Liao P C 1998 *Phys. Rev. B* **58** 16130
- [15] Ho C H, Liao P C, Huang Y S and Tiong K K 1997 *Phys. Rev. B* **55** 15608
- [16] Ho C H, Huang Y S and Tiong K K 2001 *J. Alloys Compounds* **317/318** 222
- [17] Alcock N W and Kjekshus A 1965 *Acta Chem. Scand.* **19** 79
- [18] Ho C H, Lee H W and Cheng Z H 2004 *Rev. Sci. Instrum.* **75** 1098
- [19] Parkinson B A, Ren J and Whangbo M-H 1991 *J. Am. Chem. Soc.* **113** 7833
- [20] Pankove J I 1975 *Optical Processes in Semiconductors* (New York: Dover)
- [21] Medvedkin G A, Rud Yu V and Tairov M A 1989 *Phys. Status Solidi a* **115** 11
- [22] Ho C H, Huang Y S, Chen J L, Dann T E and Tiong K K 1999 *Phys. Rev. B* **60** 15766