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Temperature dependent study of the band edge excitons of ReS_2 and $ReSe_2$

Y.S. Huang[a,*], C.H. Ho[a], P.C. Liao[a], K.K. Tiong[b]

[a] *Department of Electronic Engineering, National Taiwan Institute of Technology, Taipei 106, Taiwan, P. R. of China*
[b] *Department of Electrical Engineering, National Taiwan Ocean University, Keelung 202, Taiwan, P. R. of China*

Abstract

ReS_2 and $ReSe_2$ are diamagnetic indirect semiconductors and belong to the family of transition-metal dichalcogenides crystallizing in the distorted octahedral layer structure of triclinic symmetry. We have measured the temperature dependence of the spectral features in the vicinity of the direct gaps E_g^d in the temperature range between 25 and 525 K using piezoreflectance (PzR). The polarization dependence of the PzR spectra provides conclusive evidence that the features are associated with the interband excitonic transitions from different origins. From a detailed lineshape fit to the PzR spectra, we have been able to determine accurately the temperature dependence of the energies and broadening parameters of the band-edge excitons. The parameters that describe the temperature variation of the transition energies and broadening function have been evaluated and discussed. © 1997 Elsevier Science S.A.

Keywords: Transition-metal dichalcogenides; Exciton; Piezoreflectance

1. Introduction

ReS_2 and $ReSe_2$ are diamagnetic indirect semiconductors and belong to the family of transition-metal dichalcogenides crystallizing in the distorted octahedral layer structure of triclinic symmetry [1,2]. In recent investigations, these compounds have been attractive as electrode or photoelectrode materials because of their catalytic properties and favorable stability [3,7]. In particular, considerable attention has been focused on ReS_2. It is of considerable interest as a catalytic material having potential application as a sulfur-tolerant hydrogenation and hydrodesulfurization catalyst [3,4], as a promising solar-cell material in electrochemical cells [5,6] and as a material for fabrication of polarization-sensitive photodetectors in the visible wavelength region [8]. Despite their various technological applications, the theoretical and experimental understanding of the solid-state properties of ReS_2 and $ReSe_2$ are still relatively incomplete.

In this paper we report a detailed study of the temperature dependence of the piezoreflectance (PzR) measurements in the spectral range near the direct fundamental band gap E_g^d of ReS_2 and $ReSe_2$ single crystals from 25 to 525 K. Piezoreflectance has been proven to be useful in the investigation and characterization of semiconductors [9,10]. The derivative nature of modulation spectra suppresses uninteresting background effects and greatly enhances the precision in the determination of 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 PzR spectra are fitted with a form of the Aspnes equation of the derivative Lorentzian line-

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[*] Corresponding author.

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shape [11]. From a detailed lineshape fit, we have been able to measure accurately the temperature dependence of the energies and broadening parameters of the excitonic transitions near band edge. We have analyzed the temperature variation of the transition energies by the Varshni equation [12] and an empirical expression proposed by O'Donnel and Chen [13]. The parameters that describe the temperature dependence of excitonic transition energies are evaluated and discussed. The temperature dependence of the broadening function also has been studied in terms of a Bose–Einstein equation that contains the exciton (electron)-longitudinal optical (LO) phonon coupling constant [14,15].

2. Experimental details

Single crystals of ReS_2 and $ReSe_2$ were grown by the chemical-vapor transport method, using Br_2 as a transport agent, leading to n-type conductivity. Prior to the crystal growth, quartz tubes containing Br_2 and the elements (Re, 99.95% pure; S, 99.999%; Se, 99.999%) were evacuated and sealed. The quartz tube was placed in a three-zone furnace and the charge prereacted for 24 h at 800°C with the growth zone at 1000°C, preventing 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 give the temperature gradient at which single-crystal growth took place. Best results were obtained with temperature gradients of approximately 1060 → 1010°C for ReS_2 and 1060 → 1010°C for $ReSe_2$. Both ReS_2 and $ReSe_2$ formed silver-colored, graphite-like, thin hexagonal platelets up to 2 cm^2 in area and 100 μm in thickness. X-ray diffraction patterns confirmed the triclinic symmetry of ReS_2 and $ReSe_2$ with all parameters consistent with those previously reported [2]. The weak van der Waals bonding between the layers of the material means that they display good cleavage properties parallel to the layers, which can be exploited to obtain thin single specimens. With a razor blade, thicker samples have been successfully thinned to a limiting thickness of ~ 10 μm. The PzR method has been reported in the literature [9,10]. The procedure for going to elevated temperatures is discussed in Huang et al. [16].

3. Results and discussion

Fig. 1 shows the polarization dependence of the PzR spectra of ReS_2 and $ReSe_2$ in the vicinity of E_g^d at 25 K. The results indicate that feature 1 is present in E‖[010] polarization while feature 2 only appears in E ⊥ [010] polarization. We believe this provides conclusive evidence that both features 1 and 2 are associated with the interband excitonic transitions from different origins. Detailed theoretical study of the anisotropic optical properties in the van der Waals plane of ReS_2 and $ReSe_2$ is needed and is at present beyond the scope of this work. Displayed in Fig. 2a,b are the PzR spectra with two different polarizations in the vicinity of E_g^d of ReS_2 and $ReSe_2$ for several temperatures between 25 and 525 K. We have fitted the PzR spectra to a functional form appropriate for excitonic transitions that can be expressed as a Lorentzian lineshape function of the form [11]

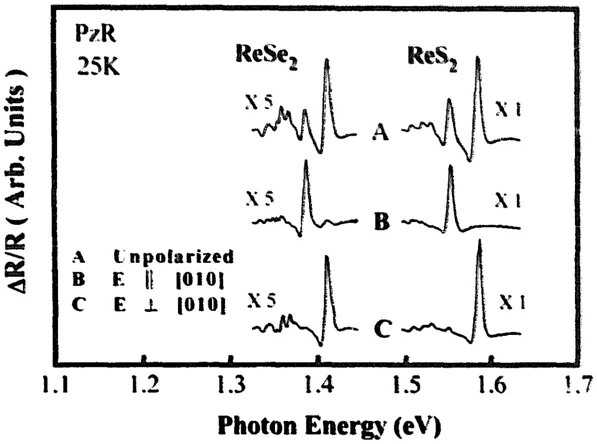

Fig. 1. Polarization dependence of the PzR spectra for ReS_2 and $ReSe_2$ at 25 K.

$$\frac{\Delta R}{R} = \mathrm{Re}\left[A_i^{ex} e^{j\phi_i^{ex}} (E - E_i^{ex} + j\Gamma_i^{ex}) \right] \tag{1}$$

where $i = 1$ or 2, A_i^{ex} and ϕ_i^{ex} are the amplitude and phase of the lineshape, and E_i^{ex} and Γ^{ex} are the energy and broadening parameter of the interband excitonic transitions. The solid curves in Fig. 2a,b are the least-squares fits using Eq. (1). The fits yield the parameters E_i^{ex} and Γ_i^{ex}. The obtained values of E_1^{ex} and E_2^{ex} are indicated by arrows in the figures.

Plotted in Fig. 3 are the experimental values of the temperature dependence of $E_1^{ex}(T)$ and $E_2^{ex}(T)$ for ReS_2 and $ReSe_2$ with representative error bars. The full curves in Fig. 3 are the least-squares fits to the Varshni empirical relationship [12]

$$E_i^{ex}(T) = E_i(0) - \frac{a_i T^2}{(b_i + T)} \tag{2}$$

where $i = 1$ or 2, $E_i(0)$ is the excitonic transition energy at 0 K, and a_i and b_i are constants referred to as Varshni coefficients. The constant a_i is related to the electron (exciton)-phonon interaction and b_i is closely related to the Debye temperature. The obtained values of $E_i(0)$, a_i and b_i corresponding to the excitonic transitions for ReS_2 and $ReSe_2$ are listed in Table 1. For comparison purposes, we have also listed numbers for the indirect band gap of ReS_2 and $ReSe_2$

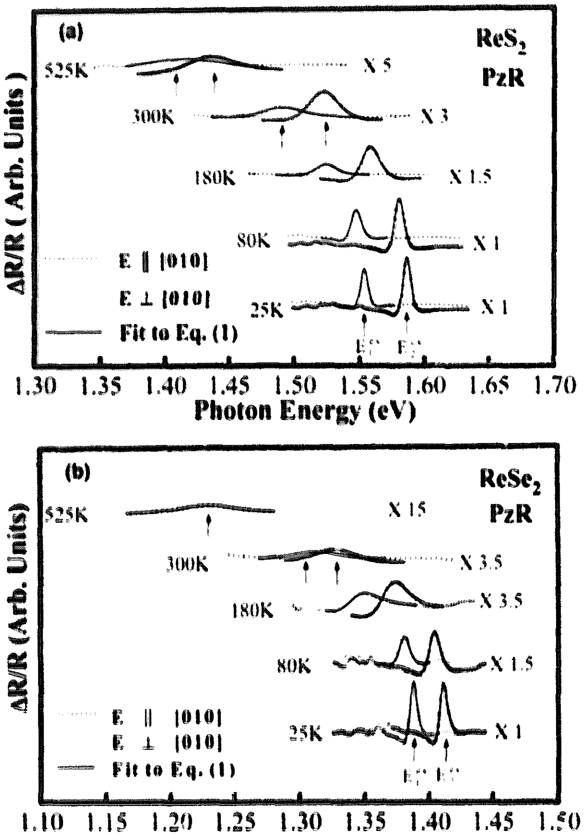

Fig. 2. The polarization dependent PzR spectra of ReS$_2$ and ReSe$_2$ at several temperatures between 25 and 525 K. The full curves are least-squares fits to Eq. (1) which yields the excitonic transition energies indicated by the arrows.

[17]. The Debye temperature was estimated to be approximately 196 K for ReS$_2$ and 181 K for ReSe$_2$. Our values of b_i equal 175 ± 75 K for E_1^{ex} and 170 ± 75 K for E_2^{ex} for both ReS$_2$ and ReSe$_2$ are in reasonable agreement with the theoretical estimation. It is noted that the values of a_i are much smaller than those obtained from the indirect gap [17]. We will discuss the differences in a later section.

The temperature dependence of the interband transition energies have also been fitted (dotted curves in Fig. 3) by an empirical expression proposed recently by O'Donnel and Chen [13],

$$E_i^{ex}(T) = E_i(0) - S_i\langle\hbar\Omega_i\rangle[(\coth <\hbar\Omega_i>/2kT) - 1] \tag{3}$$

where $i = 1$ or 2, $E_i(0)$ is the excitonic transition energy at 0 K, S_i is a dimensionless coupling constant related to the strength of electron-phonon interaction, and $\langle\hbar\Omega_i\rangle$ is an average phonon energy. The obtained values of the various parameters are also listed in Table 1. For comparison purposes, the numbers from previous reports on the direct gap of n-type and p-type ReS$_2$ [18], and the indirect gap of ReS$_2$ and ReSe$_2$ [17] are also included in Table 1. The value of S_i is much smaller than that for the indirect gap of ReS$_2$ and ReSe$_2$ [17]. The results, in which the electron (exciton)-phonon coupling constants a_i in Eq. (2) and S_i in Eq. (3) describe the temperature dependence of the excitonic transition energies for ReS$_2$ and ReSe$_2$ smaller than those for the indirect band gaps, are similar to those of the previous report on 2H-MoS$_2$ and 2H-MoSe$_2$ layer crystals [19]. Goldberg et al. [19] reported a detailed study of the low-energy absorption in layer crystals of MoS$_2$ and MoSe$_2$. The experimental results showed that the temperature shift of the exciton is smaller than that of the absorption tail. The phenomena can be interpreted as follows: as the temperature is lowered, the reduction in the thermal broadening of the exciton causes a faster shift of the absorption tail. From Eq. (3), with kT much larger than $\langle\hbar\Omega\rangle$, $dE_2^{ex}(T)/dT = -2kS_2$ (at higher temperature, the signal strength of E_1^{ex} is negligible). The calculated values of dE_2^{ex}/dT equal −0.34 (ReS$_2$) and −0.48 (ReSe$_2$) meV K^{-1} are in good agreement with the values of −0.33 ± 0.01 (ReS$_2$) and −0.46 ± 0.01 (ReSe$_2$) meV K^{-1} as ob-

Table 1
Values of the fitting parameters of the expressions proposed by Varshni [12] and O'Donnel and Chen [13] which describe the temperature dependence of the excitonic transition energies, and the direct [18] and indirect [17] band gaps of ReS$_2$ and ReSe$_2$

		$E(0)$ (eV)	a (meV K^{-1})	b (K)	S	$\langle\hbar\Omega\rangle$ (meV)
E_1^{ex}	ReS$_2$	1.554 ± 0.005	0.37 ± 0.05	175 ± 75	2.0 ± 0.1	19 ± 3
E_2^{ex}	ReS$_2$	1.588 ± 0.005	0.39 ± 0.05	180 ± 75	2.0 ± 0.1	20 ± 3
E_1^{ex}	ReSe$_2$	1.387 ± 0.005	0.45 ± 0.05	175 ± 75	2.8 ± 0.1	25 ± 3
E_2^{ex}	ReSe$_2$	1.415 ± 0.005	0.51 ± 0.05	170 ± 75	2.8 ± 0.1	20 ± 3
E_g^d [18]	p-ReS$_2$ n-ReS$_2$				2.56 2.24	19 16
E_{ind} [17]	ReS$_2$ ReSe$_2$	1.52 ± 0.02 1.36 ± 0.02	0.62 ± 0.05 0.75 ± 0.05	115 ± 50 135 ± 50	4.05 ± 0.5 4.35 ± 0.5	20 ± 2 18 ± 2

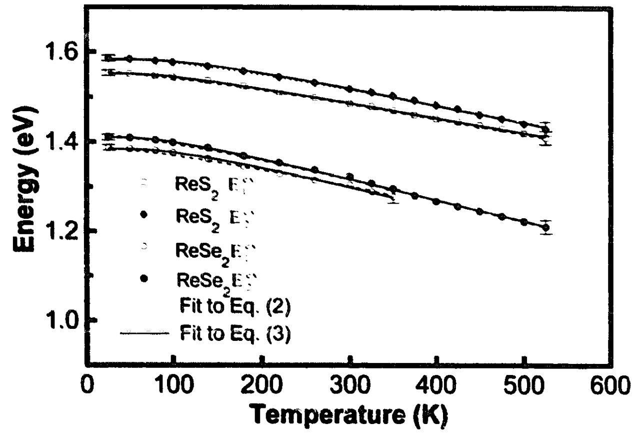

Fig. 3. The temperature dependence of the excitonic transition energies of ReS$_2$ and ReSe$_2$ with representative error bars. The dashed curves are least-squares fits to Eq. (2) and the full curves are least-squares fits to Eq. (3).

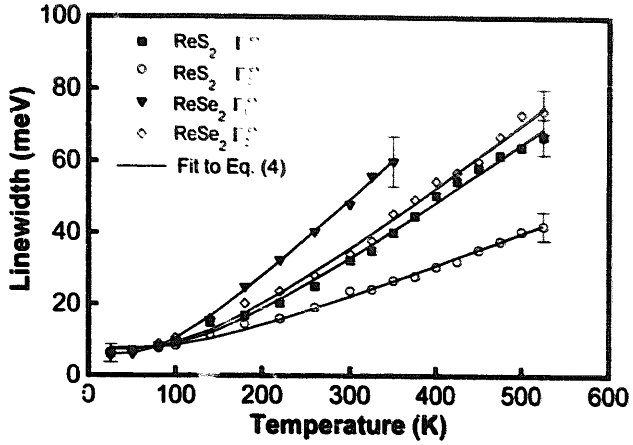

Fig. 4. The temperature dependent linewidths of the E_1^{ex} and E_2^{ex} transitions of ReS$_2$ and ReSe$_2$ with representative error bars are shown. The full curves are least-squares fits to Eq. (4).

tained from the linear extrapolation of our $E_2^{ex}(T)$ data.

The experimental values of [half width at half maximum (HWHM)] of the E^{ex} and E_2^{ex} transitions as obtained from the lineshape fit for ReS$_2$ and ReSe$_2$ with representative error bars are displayed in Fig. 4. The temperature dependence of the broadening parameters of semiconductors can be expressed as [14,15]

$$\Gamma_i(T) = \Gamma_{i0} + \frac{\Gamma_{iLO}}{[\exp(\Theta_{iLO}/T) - 1]} \qquad (4)$$

where $i = 1$ or 2, the first term of Eq. (4) represents the broadening invoked from temperature-independent mechanisms, such as electron-interactions, impurity or dislocation, whereas the second term is caused by the electron (exciton)-LO phonon (Fröhlich) interaction. The quantity Γ_{iLO} represents the strength of the electron (exciton)-LO phonon coupling while Θ_{iLO} is the LO phonon temperature [14,15]. The solid curves in Fig. 4 are least-squares fits to Eq. (4), which made it possible to evaluate Γ_{i0}, Γ_{iLO} and Θ_{iLO} for the excitonic transitions of ReS$_2$ and ReSe$_2$. The obtained values of these quantities are listed in Table 2 together with the numbers for GaAs [20] and ZnSe [21].

Our values of Γ_{10} and Γ_{20} for the excitonic transitions are approximately 5 and 7 ~ 8 meV, respectively, for ReS$_2$ and ReSe$_2$. This resolution is an indication of the high quality of our single crystals. The values for the coupling constants Γ_{1LO} and Γ_{2LO} for ReS$_2$ and ReSe$_2$ are in the range of 40–90 meV, which are considerably larger than those reported for a number of semiconductors, such as GaAs (~ 20 meV) [20] and ZnSe (~ 24 meV) [21]. At this point we suspected that the large values of Γ_{LO} may be a general characteristic of crystals with a layered structure. However, a more systematic experimentation should be carried out to verify this property.

Table 2
Values of the parameters which describe the temperature dependent broadening function Γ(*T*) for the excitonic transitions of ReS$_2$ and ReSe$_2$, and the direct band-edge transitions of GaAs [20] and ZnSe [21]

Feature	Materials	Γ_0 (meV)	Γ_{LO} (meV)	Θ_{LO} (K)
E_1^{ex}	ReS$_2$	7.0 ± 0.5	70 ± 10	395 ± 50
E_2^{ex}	ReS$_2$	7.2 ± 0.5	40 ± 8	363 ± 50
E_1^{ex}	ReSe$_2$	6.8 ± 0.5	90 ± 20	340 ± 50
E_2^{ex}	ReSe$_2$	7.5 ± 0.5	70 ± 8	375 ± 50
E_g^{d}	GaAs [20]	2	20 ± 1	417
E_g^{0}	ZnSe [21]	6.5 ± 2.5	24 ± 8	360

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