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Piezoreflectance Study of The Band-Edge Excitons of ReS_2:Au

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1. Introduction

The transition metal semiconductor rhenium disulphide (ReS_2) is a diamagnetic indirect semiconductor and belongs to the family of transition-metal dichalcogenides (TMDCs, MX_2 [1]. ReS_2 crystallized in a triclinic distorted $CdCl_2$ structure with strong covalent bonds within a layer consisting of S-Re-S sheets and weak van der Waals interactions between layers as shown in Fig.1 [2]. The unique parallelogram-shaped cluster formed by metal-metal bonds results in chains of metal atoms oriented along the in-plan b [010] axis. Layered ReS_2 semiconductor has attracted considerable interest because of possible applications as a promising solar-cell material in electrochemical cells. It is known that doping of semiconductor leads to a change in their optical and electrical properties. However, a few works discussing the doping effect on the properties of ReS_2 have been reported [3]. In this paper we report a detailed study of band-edge excitonic transitions of ReS_2:Au by using the temperature- and polarization-dependent piezoreflectance (PzR) measurements in the temperature range between 10 to 300 K. In order to polarize the monochromatic light, a Rochon prism with the measurement range of 400-4000 nm is equipped for PzR measurement.

2. Results and discussion

In Fig. 2 the solid lines show the temperature-dependent PzR spectra and the open circles are the least-squares fits using equation (1) in the temperature range from 14 to 300 K.

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

Where $A^{ex}{}_i$ and $\varphi^{ex}{}_i$ are the amplitude and phase of the Lorentzian lineshape function, and $E^{ex}{}_i$ and $\Gamma^{ex}{}_i$ are the energy and broadening parameter of the interband excitonic transition, respectively. The spectrum at 14 K exhibits three band-edge excitonic transitions labeled as $E^{ex}{}_1$, $E^{ex}{}_2$ and $E^{ex}{}_3$, which are correlated to the nonbonding Re 5d t_{2g} (d_{xy}, d_{x2-y2}) to 5d t_{2g}^{*} transitions. Furthermore, other four features indicated as A, B, C, and D, which have not been observed in the PzR spectra of pure ReS_2 crystal. We believe that they are induced by the doping of Au. The temperature dependent excitonic transition energies of $E^{ex}{}_1$, $E^{ex}{}_2$ and $E^{ex}{}_3$ have been fitted by Varshni semiempircal relationship and the results are shown in Fig. 3.

The experimental values of $\Gamma^{ex}{}_i(T)$ (half width at half maximum) of the $E^{ex}{}_1$, $E^{ex}{}_2$ and $E^{ex}{}_3$ transitions as obtained from the lineshape fit for ReS_2:Au are displayed in Fig. 4. The temperature dependent broadening parameters of semiconductor can be expressed as

$$\Gamma_i(T) = \Gamma_{i0} + \frac{\Gamma_{iLO}}{\left[\exp\left(\Theta_{iLO}/T\right) - 1\right]}, \qquad (2)$$

Where Θ_{iLO} is the energy of the LO phonon in ReS_2:Au and Γ_{i0} is the zero temperature broadening parameter, and Γ_{iLO} is a parameter describing the exciton-LO-phonon interaction. The fitted results are summarized in Table I.

The polarization-dependent PzR spectra of ReS_2:Au at lower temperature are shown by solids lines in Fig. 5. The open circles are the least-squares fits using equation (1). Three main band-edge excitonic transitions are indicated by arrows and labeled as $E^{ex}{}_1$, $E^{ex}{}_2$ and $E^{ex}{}_3$. From these spectra we can find that the $E^{ex}{}_1$ is obvious at polarization angle of 0°, and it gradually obscured with increasing polarization angle. While an opposite attitude is observed in the other two band-edge excitonic transitions $E^{ex}{}_2$ and $E^{ex}{}_3$. The amplitude of these three excitonic transitions are extracted and shown in Fig. 6. From this polarization selection result the origin of the excitonic transitions can be determined.

3. Conclusions

We have performed the optical characterization of ReS_2:Au using temperature- and polarization-dependent PzR measurement. From the temperature-dependent PzR spectra, the three excitonic energies have been obtained obviously. The polarization-dependent PzR measurements provide polarization information to identify the origin of $E^{ex}{}_1$, $E^{ex}{}_2$ and $E^{ex}{}_3$. The transition energies and broadening parameters of the band-edge excitonic transitions have been studied.

Acknowledgements

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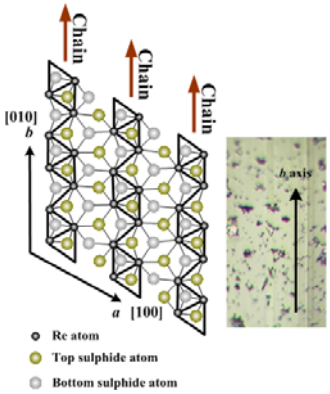

Fig. 1 Crystal morphology and crystal structure in the van der Waals plane of a ReS_2:Au cryatal.

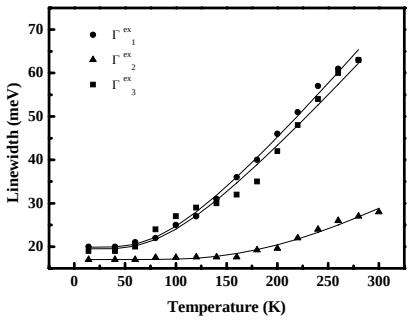

Fig. 4 Temperature dependent linewidths of the E^{ex}_1, E^{ex}_2 and E^{ex}_3. The solid lines are the least-squares fit equation (2).

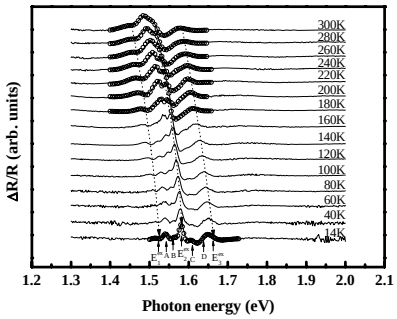

Fig.2 Temperature dependent PzR spectra of ReS_2:Au in the temperature range between 15 and 300 K. The exciton positions shift toward high energy indicated by the arrows as the temperature is decreased.

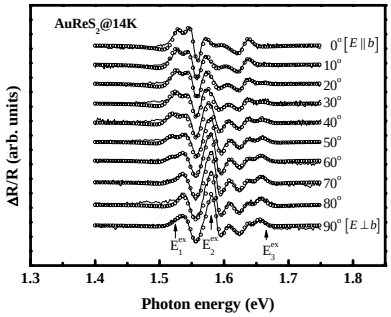

Fig. 5 Polarization-dependent PzR spectra at low temperature. The open lines are the least-squares fit equation (1). The results indicate that the E^{ex}_1 is present in E || b polarization while E^{ex}_2 and E^{ex}_3 only appear in E ⊥ b polarization.

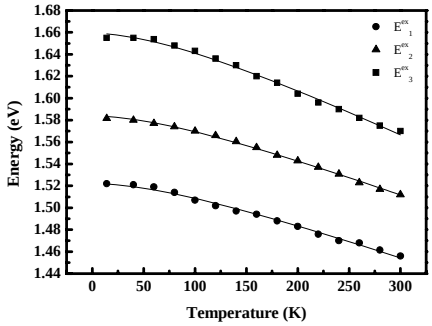

Fig. 3 Temperature dependence of the band-edge excitonic transition energies.

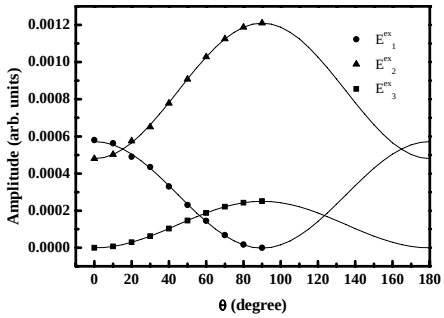

Fig. 6 Angular dependence of polarized PzR spectra of the E^{ex}_1, E^{ex}_2 and E^{ex}_3 at 14K.

Table I. Values of the Varshni-type and broadening function fitting parameter which describe the temperature dependent of the excitonic transition of ReS_2 and ReS_2:Au.

Feature	Materials	E(0) (eV)	a (meV/K)	b (K)	Γ_0 (meV)	Γ_{LO} (meV)	Θ_{LO} (K)
E^{ex}_1	ReS_2[a]	1.554±0.005	0.36±0.05	175±75	5.5±1.0	74±28	395±100
	ReS_2:Au[b]	1.522±0.005	0.34±0.05	152±75	20±1.0	82±30	288±100
E^{ex}_2	ReS_2[a]	1.588±0.005	0.37±0.05	150±75	7.8±1.0	42±8	363±50
	ReS_2:Au[b]	1.584±0.005	0.36±0.05	152±75	17±1.0	111±25	703±100
E^{ex}_3	ReS_2:Au[b]	1.659±0.005	0.47±0.05	159±75	19±1.0	77±30	288±100

[a]Reference[1]
[b]This work