

OPTICAL PROPERTIES OF RHENIUM DISELENIDE SINGLE CRYSTALS DOPED WITH TRANSITION METALS

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Abstract

In this paper, we focus on optical properties of rhenium diselenide (ReSe₂) single crystals doped with Au, W, and Nb. The doping effect of the material was characterized by polarization-dependent piezorefectance (PzR) and photorefectance (PR) measurements in the temperature range of 15–300 K. The low temperature PzR and PR spectra reveal the observation of E_1^{ex} feature at $\mathbf{E} \parallel \mathbf{b}$ polarization as well as two features E_2^{ex} and E_3^{ex} at $\mathbf{E} \perp \mathbf{b}$ polarization. In comparison with the undoped ReSe₂, the excitonic transition energies remain practically unchanged, while the broadening parameter of the excitonic transition features slightly increases due to impurity scattering. The angular dependence of the excitonic features amplitudes agree well with the Malus law.

1. Introduction

Rhenium diselenide (ReSe₂) is a transition-metal dichalcogenide (TMDC) semiconductor which crystallizes in a lattice with strong covalent bonds within a layer consisting of Se-Re-Se sheets and weak van der Waals interactions between the individual layers [1]. ReX₂ (X=S, Se) crystallized in distorted CdCl₂ structure leading to triclinic symmetry unlike most of other groups of layer TMDC crystals. Re atoms in each ReX₂ crystal layer are actually displaced from the centre of octahedral coordination units forming a one-dimensional chain along the $\mathbf{b}$ -axis within the van der Waals plane [2]. Taking into account the structural properties, layered ReX₂ semiconductors were of a considerable interest for the past decade due to the anisotropy of optical and electrical properties in the van der Waals plane [3–5]. In particular, the experimental results clearly indicated that near-band-edge transitions, such as indirect band gap and excitons, are polarization dependent [4–6]. Owing to the polarization dependence of indirect band-gaps ($E_{g\parallel}$ and $E_{g\perp}$) of ReX₂ observed by transmission measurements at room temperature, a potential capability of this layer material was proposed to be used as an optical switch applied in polarized optical communication of near infrared region [7] and to fabricate a polarization sensitive photodetector applied in multi-channel optical communication [8]. A few works concerning the doping effect on the properties of ReX₂ compounds were reported [9–11].

In this paper, we study the polarization dependent optical properties of Au-, W-, and Nb-doped ReSe₂ single crystals in the temperature range between 15 and 300 K. The polarization-dependent PzR and PR measurements were used for the determination of the direct band-edge excitonic transitions. The angular dependence of the amplitudes of the excitonic features shows a sinusoidal variation with respect to the angular change of the linearly polarized light that corresponds to the Malus law.

2. Experimental

The ReSe_2 single crystals were grown directly from the composite elements (Re: 99.99% pure; Se: 99.999%) by the vapor transport method using iodine as a transport agent [12]. To obtain the nominal concentration $\sim 0.5\%$ of Au, W, or Nb, the weight of doping material was determined stoichiometrically. Like previously reported undoped ReSe_2 , Au-, W-, and Nb-doped ReSe_2 single crystals formed thin silver-colored graphite-like platelets up to $10 \text{ mm} \times 5 \text{ mm}$ in area and $\sim 100 \text{ }\mu\text{m}$ in thickness. The morphology, structure, and the composition of the ReSe_2 crystals were characterized by X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), energy dispersive X-ray analysis (EDX), and by selected area electron diffraction techniques (SAED). XRD patterns revealed the triclinic symmetry of the single crystals with all parameters consistent with those previously reported for undoped samples. HRTEM and SAED results which provide information of the structure on the atomic scale show a single-phase structure and confirm the results obtained by XRD (Fig. 1). The chemical composition of the obtained layer crystals analyzed by EDX shows an atomic Re: Se ratio of about 1.0: 2.0. No Au could be detected in EDX even though this method is sensitive to concentrations of dopant 0.1%. According to previous results on electrical properties, ReX_2 crystals grown with I_2 become p-type semiconductors due to compensation [13].

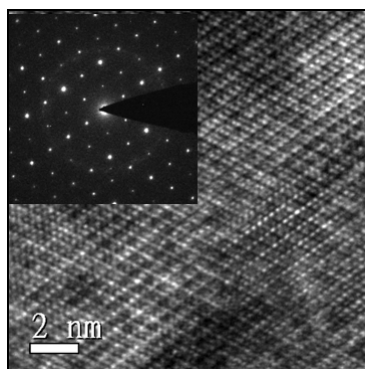


Fig. 1. Experimental HRTEM image and SAED pattern (insert) of an Au-doped ReSe_2 crystal.

The PzR measurements were achieved by gluing the thin samples on a 0.15 cm thick lead zirconate titanate piezoelectric transducer driven by a 200 Vrms sinusoidal source at 200 Hz. For PR measurements, an internally modulated 670 nm laser diode served the pumping beam. The CASIX Rochon prisms were employed for polarization dependent measurements. Detailed PzR and PR configurations have been described elsewhere [11, 14]. For temperature dependent measurement, a closed-cycle cryogenic refrigerator equipped with a digital thermometer controller was used for the low temperature measurements with a temperature stability of 0.5 K or better.

3. Results and discussion

The direct band-edge excitonic transitions are studied by polarization-dependent PzR at 15 K. The $\mathbf{E} \parallel \mathbf{b}$ and $\mathbf{E} \perp \mathbf{b}$ polarized spectra of Nb-, W- and Au-doped, as well as undoped ReSe_2 in the vicinity of direct band edge are shown by the open-square and open-diamond curves, respectively, at 15 K in Fig. 2. The two dominant structures located between 1.35 and 1.43 eV for X-doped ReSe_2 (X = pure, W, Au, Nb) are associated with band-edge excitonic transitions from different origins and were previously assigned as E_1^{ex} and E_2^{ex} [3].

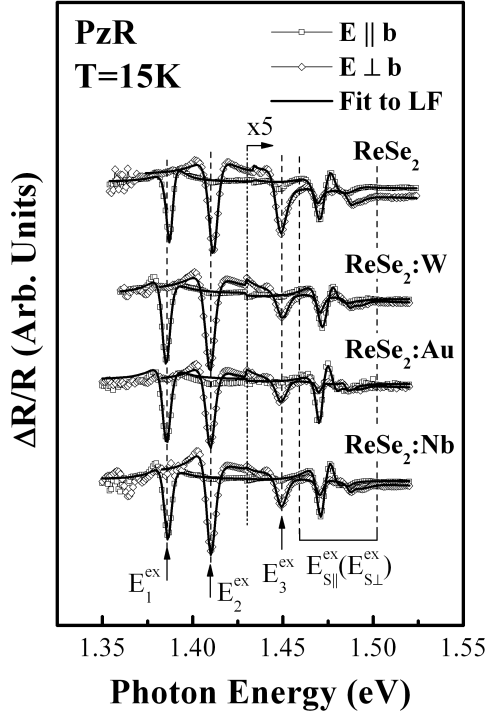


Fig. 2. Polarized PzR spectra of undoped, W-, Au- and Nb-doped ReSe_2 crystals at 15 K. The open-square and open-diamond curves correspond to $\mathbf{E} \parallel \mathbf{b}$ and $\mathbf{E} \perp \mathbf{b}$ polarizations, respectively. The solid curves are the least-square fits to Eq. (1).

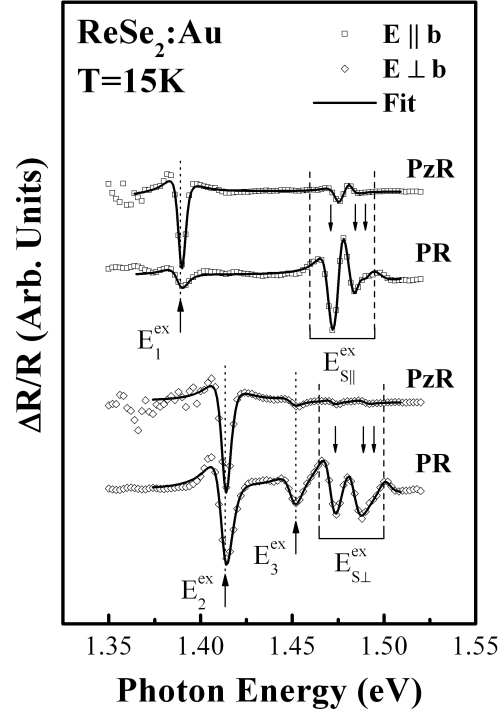


Fig. 3. Polarized PzR and PR spectra of $\text{ReSe}_2:\text{Au}$ at 15 K. The open-square and open-diamond curves correspond to $\mathbf{E} \parallel \mathbf{b}$ and $\mathbf{E} \perp \mathbf{b}$ polarizations, respectively. The solid curves are the least-square fits to Eq. (1).

As shown in Fig. 2, the two features have different polarization dependence with E_1^{ex} and E_2^{ex} features allowed, respectively, for $\mathbf{E} \parallel \mathbf{b}$ and $\mathbf{E} \perp \mathbf{b}$ polarization only. The additional strongly polarization-dependent feature denoted by E_3^{ex} is observed near 1.45 eV just in $\mathbf{E} \perp \mathbf{b}$ polarized PzR spectra. This provides the conclusive evidence that features E_1^{ex} and $E_2^{\text{ex}}/E_3^{\text{ex}}$ detected in the vicinity of the direct band edge are associated with the excitonic transitions from different origins. The observation of E_3^{ex} is different from the isostructural compound ReS_2 where only two strongly polarization-dependent features E_1^{ex} and E_2^{ex} have been detected [12]. Each of the PzR spectra in Fig. 2 shows a region of close-located excitonic features $E_{S\parallel}^{\text{ex}}$ and $E_{S\perp}^{\text{ex}}$ positioned at the higher-energy side with respect to the band-edge excitons E_1^{ex} and E_2^{ex} , respectively. We have fitted the polarized curves to a functional form appropriate for excitonic transitions that can be expressed as a Lorentzian line-shape function of the form [15]

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

where A_i^{ex} and φ_i^{ex} are the amplitude and phase of the line shape, respectively, and E_i^{ex} and Γ_i^{ex} are the energy and broadening parameter of the band edge excitonic transitions, respectively. The solid curves in Fig. 2 are the least-squares fits using Eq. (1). The arrows at the bottom of Fig. 2 show the peak positions of the main interband excitonic features, E_1^{ex} and

E_2^{ex} / E_3^{ex} for $\mathbf{E} \parallel \mathbf{b}$ and $\mathbf{E} \perp \mathbf{b}$ polarization, respectively. The energies and broadening parameters obtained for these features show that the direct band edge excitonic transition energies are relatively unaffected by the small concentration of W, Au, and Nb, and broadening parameters are slightly increased for doped samples reflecting directly the increase of impurity scattering due to the dopant incorporated into the as grown sample.

The typical polarization-dependent PR spectra of $\text{ReSe}_2\text{:Au}$ in the energy range 1.35–1.53 eV are presented in Fig. 3 together with PzR spectra for comparison. The spectra with $\mathbf{E} \parallel \mathbf{b}$ and $\mathbf{E} \perp \mathbf{b}$ polarization are shown by open-square and open-circle curves, respectively. In order to determine the energy positions associated with observed excitonic transitions, the PzR and PR spectra of excitonic transitions have been fitted by Eq. (1). The fitting results illustrated as solid lines (Fig. 3) are the least-square fits to the experimental data. The arrows at the bottom of PzR and PR spectra show the peak positions of the main excitonic features. The values of transition energies and broadening parameters at 15 K analyzed by Eq. (1) are fitted to be $1.386 \pm 0.002 / 1.409 \pm 0.002 / 1.448 \pm 0.002$ eV and $4.8 \pm 1.0 / 5.9 \pm 1.0 / 6.0 \pm 1.0$ meV for $E_1^{ex} / E_2^{ex} / E_3^{ex}$, respectively. In comparison with undoped ReSe_2 [11], the fitting results of $\text{ReSe}_2\text{:Au}$ samples confirm that the direct band-edge excitonic transition energies E_1^{ex} and E_2^{ex} are not sensitive to a small concentration of Au doping and broadening parameter values are slightly increased due to impurity scattering. These observations agree with the results reported previously for Mo- and W-doped ReSe_2 single crystals [11]. The values of transition energies and broadening parameters obtained from PzR spectra are consistent with those of the PR spectra.

As shown in Fig. 3, each of the polarized PR spectra shows prominent and enlarged features of the excitonic series $E_{S\parallel}^{ex}$ or $E_{S\perp}^{ex}$, positioned at the higher-energy side with respect to the band-edge excitons. Photo-induced modification of the reflectivity has been proposed to account for the enhancements of excitonic series in the low-temperature PR spectra [16]. The analysis of higher energy side sequences $E_{S\parallel(S\perp)}^{ex}$ reveals that excitonic features can be further analyzed by using the Rydberg series starting with principal quantum number $n = 2$ [17]. Through accurate fitting with the Rydberg sequence formula, the transition energies in the excitonic sequence are matched well with the energy positions of exciton levels $n = 2, 3, 4$. These excitonic transitions are similar to the so-called yellow exciton series 2p, 3p, 4p as observed in Cu_2O [17]. The values of the threshold energy $E_{S\parallel}^{n=\infty} = 1.495 \pm 0.004$ eV ($E_{S\perp}^{n=\infty} = 1.502 \pm 0.004$ eV) and the effective Rydberg constant $R_{S\parallel}^* = 101 \pm 7$ meV ($R_{S\perp}^* = 128 \pm 7$ meV) corresponding to the 1s orbital binding energy ($n = 1$) are obtained from the fits, respectively. The crystal anisotropy along and perpendicular to $\mathbf{b}$ -axis results in the splitting of the valance band and hence in the difference of threshold energies, determined to be $\Delta E \approx E_{S\perp}^{n=\infty} - E_{S\parallel}^{n=\infty} \approx 7$ meV. The results are in a good agreement with those previously obtained for ReS_2 [16].

The polarized nature of band-edge excitons E_1^{ex} , E_2^{ex} , and E_3^{ex} in $\text{ReSe}_2\text{:Au}$ were further characterized using angular dependent PzR measurements at 15 K. The polarized PzR spectra with polarization angles ranging from $\theta = 0^\circ$ ($\mathbf{E} \parallel \mathbf{b}$) to $\theta = 90^\circ$ ($\mathbf{E} \perp \mathbf{b}$) are shown in Fig. 4. The signal intensity of E_1^{ex} decreased, while the amplitudes of E_2^{ex} and E_3^{ex} enlarged when the angle θ of linearly polarized light increased from 0° to 90° . The solid curves in Fig. 4 are the least-square fits to Eq. (1). It was found that angular dependence of the normalized transition intensities of E_1^{ex} , E_2^{ex} , and E_3^{ex} for $\text{ReSe}_2\text{:Au}$ shows a sinusoidal variation of transition prob-

abilities with respect to the angular change of linearly polarized light. The variation of the normalized amplitudes of the interband excitonic transition E_1^{ex} , E_2^{ex} , and E_3^{ex} matches well with the functional form $I_n(\theta) = \frac{1}{2}[1 + \cos 2(\theta + \theta_M)]$, where θ_M is the angle that corresponds to the maximum intensity of the excitonic transitions (i.e., $\theta_M = 0^\circ$ corresponds to E_1^{ex} whereas $\theta_M = 90^\circ$ to E_2^{ex} and E_3^{ex}). This dependence of the linearly polarized light confirmed by the Malus law is observed also in polarization-dependent transmittance measurements [7] and spectral quantum efficiency determination [8]. The polarization sensitive behavior of E_1^{ex} and E_2^{ex} / E_3^{ex} provides potential usage for ReSe₂ to fabricate a polarization sensitive photodetector applied in multi-channel optical communications to detect the various orientations of linearly polarized light [7].

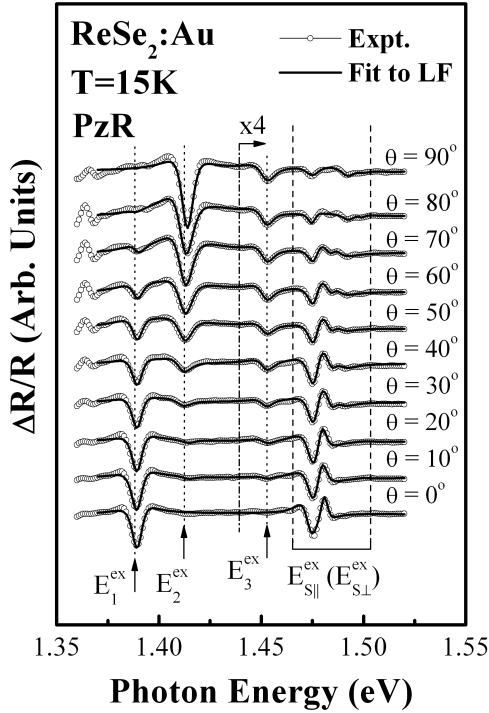


Fig. 4. Polarized PzR spectra of ReSe₂:Au (open-circle curves) with polarization angle ranging from $\theta = 0^\circ$ ($\mathbf{E} \parallel \mathbf{b}$) to $\theta = 90^\circ$ ($\mathbf{E} \perp \mathbf{b}$). The solid curves are the least-square fits to Eq. (1).

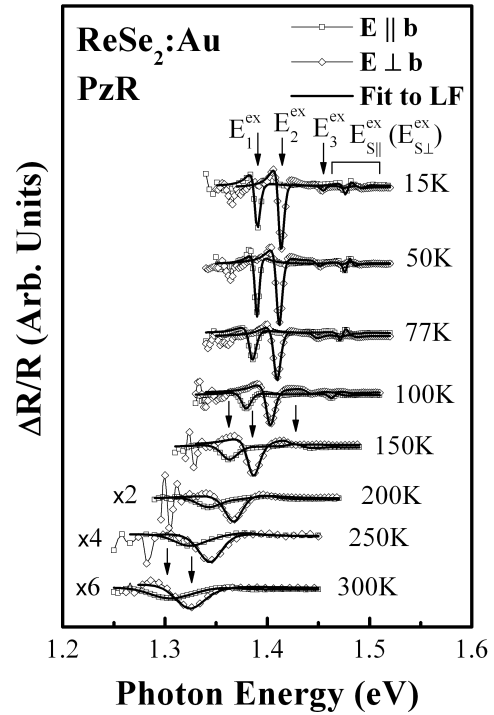


Fig. 5. Temperature-dependent polarized PzR spectra of ReSe₂:Au at temperatures between 15 and 300 K. The open-square and open-diamond curves correspond to the experimental data of $\mathbf{E} \parallel \mathbf{b}$ and $\mathbf{E} \perp \mathbf{b}$ polarizations, respectively; the solid curves are least-square fits to Eq. (1).

The temperature-dependent PzR spectra of ReSe₂:Au with $\mathbf{E} \parallel \mathbf{b}$ and $\mathbf{E} \perp \mathbf{b}$ polarizations at some temperatures between 15 and 300 K are shown in Fig. 5. The open-square and open-circle curves are the experimental PzR spectra of $\mathbf{E} \parallel \mathbf{b}$ and $\mathbf{E} \perp \mathbf{b}$ polarizations, respectively, while the solid curves are least-square fits to Eq. (1). As the general property of most semiconductors, the excitonic transitions in the PzR spectra exhibit a redshift and line-shape broadening when the temperature is increased. The results in Fig. 5 show that up to 175 K the higher order features of the excitonic sequence are ionized. At a still higher temperature, full ionization process renders the interband excitonic sequence undetectable. Up to 175 K the higher energy side feature E_3^{ex} corresponding to the $\mathbf{E} \perp \mathbf{b}$ polarization is practically ionized.

4. Summary

The anisotropic optical properties of doped ReSe₂ single crystals were studied by polarized PzR and PR measurements. The results reveal strongly polarization dependent E_1^{ex} feature at $\mathbf{E} \parallel \mathbf{b}$, as well as two features E_2^{ex} and E_3^{ex} were observed at $\mathbf{E} \perp \mathbf{b}$ polarization, that is different from the isostructural compound ReS₂ where only E_1^{ex} and E_2^{ex} features were detected. The values of band-edge excitonic transition energies E_1^{ex} , E_2^{ex} , and E_3^{ex} of doped ReSe₂ remain practically unchanged in comparison with undoped ReSe₂. Nevertheless, the doping effect shows up in a slight increase of the broadening parameter of the excitonic features. Enlarged in PR spectra, the higher energy excitonic series are similar to the so-called yellow exciton series as observed in Cu₂O, which starts from the excitonic level $n = 2$. The angular dependence of the excitonic feature amplitudes shows a sinusoidal variation with respect to the angular change of the linearly polarized light that corresponds to the Malus law.

Acknowledgments

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