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Optical anisotropy of Au-doped ReS_2 crystals

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ABSTRACT

Au-doped rhenium disulfide (Au-ReS_2) layer crystals were grown by chemical vapour method with iodine as the transporting agent. The thin samples were investigated by polarization-dependent transmittance (T) and photoreflectance (PR) at 20 K with the optical polarization along and perpendicular to the crystal b-axis. The Au-ReS_2 showed band gap anisotropy with respect to the b-axis. By comparing with the undoped sample, the indirect band gap deduced from the polarization-dependent T spectra shows a more pronounced red shift than the band edge excitonic transitions determined from polarization-dependent PR spectra.

1. Introduction

Transition-metal dichalcogenides (TMDC) crystals (MX_2) consist of stacks of hexagonal close-packed layers of transition-metal atoms (M) sandwiched between two layers of chalcogen atoms (X = S, Se) [1,2]. TMDCs crystallize with strong intralayer covalent bonds and weak van der Waals-type interlayer bonding forces. ReS_2 crystallizes in a distorted $CdCl_2$ structure of triclinic symmetry (space group $P\bar{1}$) [3,4], with clustering of Re_4 diamond units forming a one-dimensional chain within the van der Waals plane. ReS_2 semiconductors are of interest because of their potential for application in solar cell material for electrochemical cells [5–7]. The transporting agents are an important factor in determining the type of majority carrier in the crystal produced. For instance, transport of ReS_2 with bromine produces n-type crystals, while iodine produces p-type crystals [3]. In this article, we report on the growth and optical characterization of Au-ReS_2 crystals prepared by chemical vapour transport method with iodine as a transporting agent. Hall effects measurements confirmed the p-type semiconducting behaviour of the synthesized samples. The crystals formed thin layer plates with a typical surface area of 8 mm × 8 mm and thickness of a few microns. The strong anisotropy in the chemical bonds leads to anisotropy of the optical and electrical properties of these materials parallel and perpendicular to the b-axis [8]. The optical anisotropic properties were studied by polarization-dependent transmittance (T) measurements parallel and perpendicular to b-axis at 20 K, which yield information for determining the indirect band gap of the semiconductor. The polarization-dependent photoreflectance (PR) spectra were used for the determination of the excitonic transitions. The effects of Au dopant on the anisotropic optical properties were studied and discussed.

2. Experimental

Au-doped ReS_2 layer compounds were prepared by vapour transport methods. The total charge used in each growth experiment was about 10 g. For crystal growth, the elements (Au, 99.999%; Re, 99.99%; S, 99.999%) was placed in a clean quartz ampoule (22 mm OD, 17 mm ID, 20 cm length) with I_2 (~10 mg/cm^3) as the transport agent, evacuated to 10^{-5} Torr and sealed. The ampoule was placed in a three-zone furnace. The temperature gradient of about 3 °C/cm with the temperature range from 1050 to 990 °C over a reaction length of 20 cm gives optimal condition for the crystallization of the samples. This gradient was maintained for 4 weeks to complete the transported growth of sample from high to low temperature zones and allowed to cool down slowly (40 °C/h) to room temperature. When the ampoule reached room temperature, it was opened and the crystals removed. The XRD pattern (peak positions and intensities) of Au-ReS_2 crystals is similar to that of the undoped ReS_2 [2]. The details of the optical diagnostic techniques of polarization-

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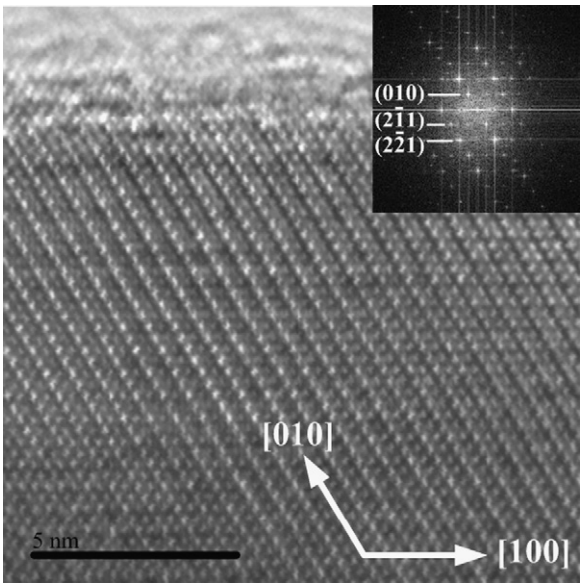

Fig. 1. TEM detailed image of the atomic arrangement and its fast Fourier transform (FFT) diffraction is shown in inset.

dependent transmittance and photoreflectance measurements have been described elsewhere [9].

3. Results and discussion

The photograph displayed in Fig. 1 is the transmission electronic microscope (TEM) image of the crystal morphology for Au-ReS_2 while the inset in Fig. 1 showed the fast Fourier transform (FFT) of the TEM image. TEM investigations were done employing a Philips Tecnai G2 F20 using an acceleration voltage U_{acc} = 200 kV. The *b*-axis corresponds to the longest edge of the plate and is parallel to the Re cluster chains [8]. From FFT, the orientation of the *b*-axis is determined to be along the [0 1 0] direction. Mechanically, one can also determine *b*-axis direction to be along the edge of easy cleaving of the crystal plate.

The indirect band-edge transitions of the Au-ReS_2 were studied by means of near-normal incident polarization-dependent transmittance at 20 K. The experimentally measured transmittance data were utilized to derive the absorption coefficient α (depicted in Fig. 2) using the equation [10].

$$T = \frac{I_T}{I_0} = \frac{(1-R)^2 \exp(-\alpha d)}{1 - R^2 \exp(-2\alpha d)} \quad (1)$$

In performing the calculation, we assumed that the temperature dependence of reflectivity *R* is negligible. In Eq. (1), *d* is the thickness, I_T is the transmitted intensity, and I_0 is the incident intensity. Also displayed in Fig. 2 is a plot of $(\alpha h\nu)^{1/2}$ vs. $h\nu$, where the open circles (open squares) are deduced data points from the $E||b$ ($E\perp b$) polarization measurements and the solid lines are least-squares fits to the expression [10].

$$\alpha h\nu = \frac{A(h\nu - E_g^{ind} + E_p)^2}{\exp(-E_p/kT) - 1} + \frac{B(h\nu - E_g^{ind} - E_p)^2}{1 - \exp(-E_p/kT)} \quad (2)$$

The fitted values of the energy gaps and phonon energy of the Au-ReS_2 crystals at 20 K are $E_{g\parallel}^{ind} = 1.49 \pm 0.02$ eV, $E_{g\perp}^{ind} = 1.51 \pm 0.02$ eV, and $E_p = 20 \pm 5$ meV. The error for the estimation of $E_{g\parallel}^{ind}$, $E_{g\perp}^{ind}$, and E_p were derived by considering different range of data points in the estimation and also from the slight deviation of incident angles due to non-smooth sample surface. Here, $E_{g\parallel}^{ind}$ and $E_{g\perp}^{ind}$ refer, respectively, to the indirect gap for $E||b$ and $E\perp b$ polarizations. Analysis of the absorption spectra revealed band gap anisotropy with $E_{g\perp}^{ind} > E_{g\parallel}^{ind}$ and their values are red shifted by about 10 meV comparing to that of the pure samples [9,11]. The physical origin of the shift may come from the existence of impurity, which in general will contribute to the absorption near the band tail.

Displayed by the curves in Fig. 3 are the polarization-dependent PR spectra in the vicinity of the direct gap of Au-ReS_2 at 20 K. The solid lines in Fig. 3 are least-squares fits to the derivative Lorentzian line shape [12], which yield parameters of the transition energies

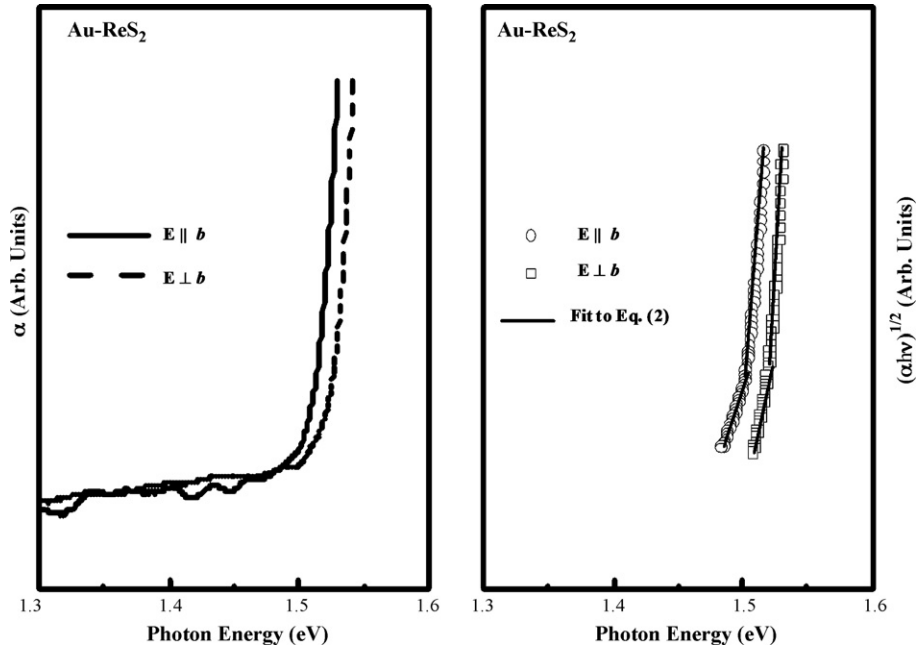

Fig. 2. Polarization-dependent absorption coefficient α vs. $h\nu$ and $(\alpha h\nu)^{1/2}$ vs. $h\nu$ for Au-ReS_2 at 20 K.

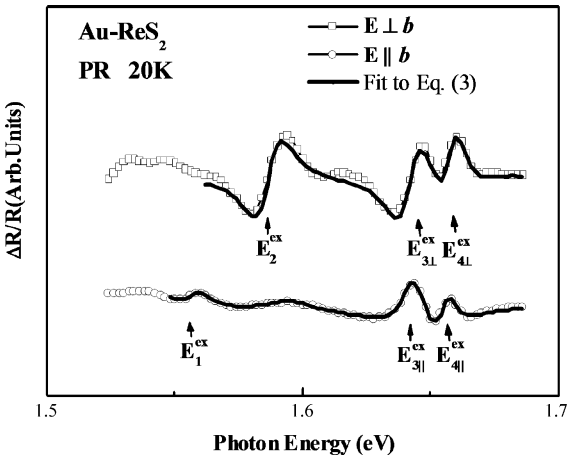

Fig. 3. The polarization-dependent PR spectra of Au-ReS_2 at 20 K.

indicated by arrows.

$$\frac{\Delta R}{R} = \mathrm{Re}[\sum_{i=1}^{n} A_i^{\mathrm{ex}} e^{j\varphi_i^{\mathrm{ex}}} (E - E_i^{\mathrm{ex}} + j\Gamma_i^{\mathrm{ex}})^{-2}] \quad (3)$$

In Eq. (3) the subscript i refers to the type of interband transition, E_i^{ex} and Γ_i^{ex} are the energy and broadening parameter of the interband excitonic transition, A_i^{ex} and φ_i^{ex} are the amplitude and phase of the line shape, respectively, and the value of n depends on the origin of the transition. For the first derivative functional form, $n = 2.0$ is appropriate for bounded states such as excitons or impurity transitions [12]. Arrows at the bottom of PR spectra show the peak positions of the main excitonic features, with $E_1^{\mathrm{ex}} = 1.554 \pm 0.002$ eV, $E_2^{\mathrm{ex}} = 1.585 \pm 0.002$ eV, $E_{3\|}^{\mathrm{ex}}$ ($E_{3\perp}^{\mathrm{ex}}$) = 1.642 ± 0.002 (1.645 ± 0.002) eV, and $E_{4\|}^{\mathrm{ex}}$ ($E_{4\perp}^{\mathrm{ex}}$) = 1.656 ± 0.002 (1.659 ± 0.002) eV. Comparing with the undoped sample [9], our results showed a small red shift of 1–2 meV for the band edge excitonic transitions. The E_1^{ex}, $E_{3\|}^{\mathrm{ex}}$ and $E_{4\|}^{\mathrm{ex}}$ features were detected for $E||b$ polarization while E_2^{ex}, $E_{3\perp}^{\mathrm{ex}}$ and $E_{4\perp}^{\mathrm{ex}}$ features were observed for $E \perp b$ polarization only [9]. The different polarization dependence of these observed excitonic transitions of ReS_2 lends evidence that E_1^{ex}, E_2^{ex}, and $E_{3\|}^{\mathrm{ex}}$ ($E_{3\perp}^{\mathrm{ex}}$)/$E_{4\|}^{\mathrm{ex}}$) ($E_{4\perp}^{\mathrm{ex}}$) are related to the interband excitonic transitions of different origins [9].

4. Summary

We have demonstrated the synthesis of single crystals of Au-doped ReS_2 with surfaces up to 8 mm × 8 mm and few micrometers thickness by chemical vapour transport method using iodine as a transporting agent. The indirect band gap and that of the direct band edge excitonic transition energies were deduced from the low temperature polarization-dependent T and PR measurements. The Au-doped ReS_2 showed both indirect and direct band gap anisotropy along and perpendicular to the crystal b-axis. Our measurements indicate that gold can incorporate into the host lattice ReS_2 and the effect of red shift on the indirect band gap is more pronounced than that of the band edge excitonic transitions.

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