Optical and electrical properties of ReSe₂:Au and ReSe₂:Ag

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1. Introduction

ReSe₂ is a diamagnetic indirect semiconductor and belongs to the family of transition-metal dichalcogenides (TMDCs). This distorted octahedral structure leads to form a triclinic symmetry and metal-ion-clustering chains, they exist along the b axis [1]. It is crystallized in a lattice with strong covalent bonds within a layer and weak interactions, usually of the van der Waals type, between the individual layers [2]. In this paper, Single crystal ReSe₂ doped Au and Ag were grown by chemical vapor transport (CVT) method using iodine as a transporting agent. Furthermore, The optical properties are studied by transmittance spectra and polarized-thermoreflectance (PTR) spectra at different polarization angles and temperatures. Because the weak van der Waals interactions between layers, samples are easily to be torn off and separated into thin specimen. In absorption experiments, we find that the indirect band-edge transitions shift toward higher energy with decreasing the layer thickness. For very thin samples we can obtain the direct band-edge excitonic transitions E_1^{ex} , E_2^{ex} . Their unique polarization properties are studied at various polarization angles between 0° and 90°. Previous reports only observed the indirect band gap. We first time can detect the direct band-edge excitonic transitions by absorption spectra. The indirect band-edge transitions $E_{g\parallel},\,E_{g\,{\scriptscriptstyle \perp}}$ and direct band-edge excitonic transitions which show unique polarization dependence are measured by PTR in temperature range between 45 and 300 K and the temperature dependence of E_1^{ex} and E_2^{ex} are analyzed. On the other hand, the electrical conductivity were measured at different temperatures ranging from 20 to 300 K. From the experimental results, we observed that at low temperature the conductivity of ReSe₂:Au is ten times higher than that of ReSe₂:Ag. Furthermore, the activaction energies are determined to be 47 and 96 meV, respectively.

2. Results and discussion

We select some transmittance spectra of high quality samples with different thicknesses in Fig. 1. It can be observed that when the thickness is very thick, the incident light can not pass through the sample, and lead to a very weak or no signal can be detected resulting from a tiny obsition. The layer thickness blocked the way to observe the extronic absorption in high energy. After tearing off the thickness by 3M Scotch tape, we find that the absorption edge not only become clear but also shift to high energy with decreasing the sample thickness.

Fig. 2 shows the absorption spectra of ReSe₂:Ag and ReSe₂:Au taken at polarization perpendicular (solid lines) and parallel (dash lines) to b axis at different temperatures between 20K and 300 K. From these spectra, We obtain the temperature dependence of absorption edge of excitonic transitions $(E_1^{ex}, E_2^{ex}, E_3^{ex} \text{ and } E_s^{ex})$, which shift toward high energy with decreasing temperature. Moreover, the absorption edges of E_1^{ex} and E_2^{ex} show an unique polarization characteristic, which only appears as the incident light parallel or perpendicular to the crystal b-axis for E_1^{ex} and E_2^{ex} transitions, respectively. The detail polarization property of excitonic transitions have been studied at various polarization angles from $\theta=0^{\circ}$ to 90° . The clear excitonic transitions $(E_1^{ex}, E_2^{ex}, E_3^{ex})$ and E_s^{ex} are presented in Fig. 3. We also performed the PTR spectra of ReSe₂:Ag and ReSe₂:Au at polarization angles perpendicular (solid lines) and parallel (dash lines) to b axis at different temperatures from 45 to 300 K as shown in Fig. 4. Both the indirect and direct band-edge transitions are detected at the same spectra. Compared with the absorption spectra the clearly excitonic transitions (E_1^{ex}, E_2^{ex}) and E_3^{ex} at low temperature are confirmed. In Fig. 5 the solid-triangle lines and solid-square lines are least-square fits of Lorentzian line-shape function to summarize the temperature dependent excitonic transitions of E_1^{ex} and E_2^{ex} . In Fig. 6 the temperature dependence of the broadening parameters of E_1^{ex} and E_2^{ex} transitions, which are given by fits fit to varshni equation [3] and the expirical expression proposed by O'Donnel and Chen [4].

Fig. 7 show the PTR spectra of ReSe₂:Ag and ReSe₂:Au at various polarization angles changing from $\theta=0^{\circ}$ to 90°. The amplitude of E_1^{ex} decrease as increasing polarization angle from $\theta=0^{\circ}$ to 90°, while the signal intensities of E_2^{ex} is gradually enlarged. The E_s^{ex} series in higher-energy side, however, are not influenced at different polarization angles. Figure 8 shows the conductivity of ReSe₂:Ag and ReSe₂:Au at difference temperature. Activation energies for conduction are calculated by fitting experimental data to Eq. (4)[5]

$$\sigma = \sigma_0 \exp(\frac{-\Delta E}{kT}) \tag{4}$$

where ΔE is the activation energy for conduction, T is the absolute temperature, and σ_0 is a preexponential factor.



Fig. 1 Absorption spectra of ReSe₂:Ag and ReSe₂:Au at different thicknesses.



Fig. 2 Absorption spectra of ReSe₂:Ag and ReSe₂:Au at different temperatures.



Fig. 3 Polarization dependent absorption spectra of $ReSe_2$: Ag and $ReSe_2$: Au at 45 K.



Fig. 4 PTR spectra of ReSe₂:Ag and ReSe₂:Au at different temperatures.





ReSe₂:Ag and ReSe₂:Au.



Fig. 6 Temperature dependent linewidths of the E_1^{ex} , E_2^{ex} .



Fig. 7 Polarization dependent PTR spectra of ReSe₂:Ag and ReSe₂:Au at 45 K.



Fig. 8 Conductivity of ReSe₂:Ag and ReSe₂:Au at different temperatures.

3. Conclusions

We have observed indirect absorption edge and the excitonic transitions (E_1^{ex} , E_2^{ex} , E_3^{ex} and E_s^{ex}) of ReSe₂:Ag and ReSe₂:Au by absorption and PTR spectra. For the sample with thin thickness, we first time find the excitonic transitions by absorption spectra. We also present the unique polarization optical properties and the temperature parameters for excitonic transitions. The doping atoms affect the activation energies and degrade the crystal quality.

Acknowledgements

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