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Electrical Anisotropy of W-Doped $ReSe_2$ Crystals

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Single crystals of W-doped $ReSe_2$ have been grown by chemical vapor transport process with bromine as the transporting agent. Single crystalline platelets up to 3×3 mm surface area and 100 μm in thickness were obtained. From the X-ray diffraction patterns, the doped crystals are found to crystallize in the triclinic-layered structure. The electrical anisotropy has been investigated along and perpendicular to the ***b***-axis on the van der Waals plane by temperature-dependent conductivity and Hall effect measurements. The influence of the dopant will be compared and discussed.
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Rhenium diselenide ($ReSe_2$) is a diamagnetic indirect semiconductor belonging to the family of transition-metal dichalcogenides crystallized in a distorted layered structure of triclinic symmetry (space group $P\bar{1}$).[1,2] It is a subject of considerable interest because of its extremely anisotropic electrical, optical and mechanical properties,[3] as a promising solar-cell material in electrochemical cells.[4,5] Owing to the potential technological applications of the material, a variety of efforts have been devoted to the theoretical and experimental understanding of the solid-state properties of $ReSe_2$.[6-8] It is known that doping of semiconductor material can lead to a change of the electrical properties. To date, few related works concerning the effects of tungsten (W)-doped on the electrical anisotropy of $ReSe_2$ have been reported.[9]

In this article we report the electrical anisotropy of the W-doped $ReSe_2$ single crystals. $ReSe_2$ crystallizes in a distorted 1T-MX_2 structure with clustering of Re_4 diamond units forming a one-dimensional chain within the van der Waals (VdW) plane. The diamond chain clusters in the metal sheet of $ReSe_2$ resulted in a lattice distortion from the ideal octahedral layered structure resulting in an electrical biaxial character of the compound. Therefore, in-plane anisotropic response is expected for linearly electrical field along and perpendicular to the ***b***-axis.[1,2] The effects of dopant (W) on the anisotropic electrical properties were studied and discussed.

Experimental

Single crystals of W-doped and undoped $ReSe_2$ layered crystals were grown by the chemical vapor transport process, respectively with Br_2 as the transporting agent. The total charge used in each growth experiment was ~10 g. The stoichiometrically determined weight of the doping material (~0.5% nominal concentration) was added. Prior to the crystal growth, a quartz ampoule containing Br_2 (~5 mg/cm^3) and the elements (W, 99.99% pure; Re, 99.99% pure; Se, 99.999%) was cooled with liquid nitrogen, evacuated to 10^{-6} Torr and sealed. It was shaken well for uniform mixing of the powder. The ampoule was placed in a three-zone furnace and the charge pre-reacted 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. A temperature gradient of about 2°C/cm with the temperature range from 1050 to 1000°C over a reaction length of 25 cm gives optimal condition for the crystallization of the samples. After 360 h, the furnace was allowed to cool down slowly (40°C/h) to ~200°C. The ampoule was then removed and wet tissues applied rapidly to the end away from the crystals to condense the Br_2 vapor. When the ampoule reached room temperature, it was opened and the crystals removed. The crystals were then rinsed with acetone and deionized water. Figure 1 shows the scanning electron microscopy (SEM) photograph of the as-grown W-doped crystal with the ***b***-axis as indicated. Single crystalline platelets up to 3×3 mm surface area and 100 μm in thickness were obtained. The tungsten content x was estimated by energy dispersive X-ray analysis (EDX). A considerable discrepancy exists between the nominal doping ratio and that determined by EDX. The nominal concentration is much larger than the actual one because no W could be detected in EDX even though this method is sensitive to concentrations of $x >= 0.1\%$.[10] The Re and W metals are most likely to be chemically transported at different rates and most of the doping material must remain in the untransported residual charge.

For anisotropic electrical conductivity, a selected sample was oriented and cut into a rectangular shape. Electrical connections to the crystal were made by means of four parallel gold wires (parallel or perpendicular to b-axis) with spiral shape laid across the basal surface of the thin crystal and attached to the crystal surface by means of highly conducting silver epoxy. The wires near each end of the rectangular crystal acted as current leads, while the two contact wires on either side of the central line were used to measure the potential drop across the crystal. The voltage drop measured by a sensitive potentiometer is taken to be the average value obtained on reversing the current through the sample. The data was checked for ohmic contact quality. For Hall effect measurements, the Hall voltage was measured between side arms of the sample which are opposite to each other. The measurements were made by taking data

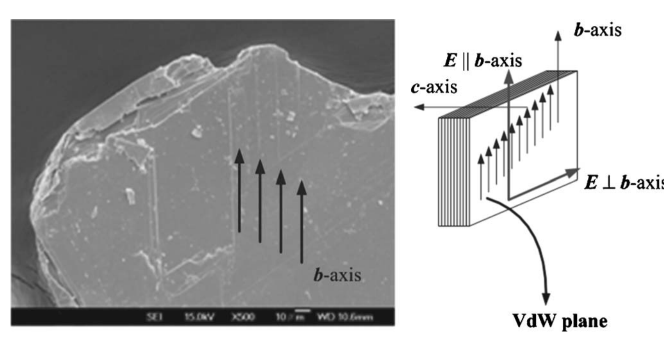

Figure 1. The SEM of as-grown W-doped $ReSe_2$ sample with the b-axis as indicated and the experimental polarization schemes for electrical anisotropy.

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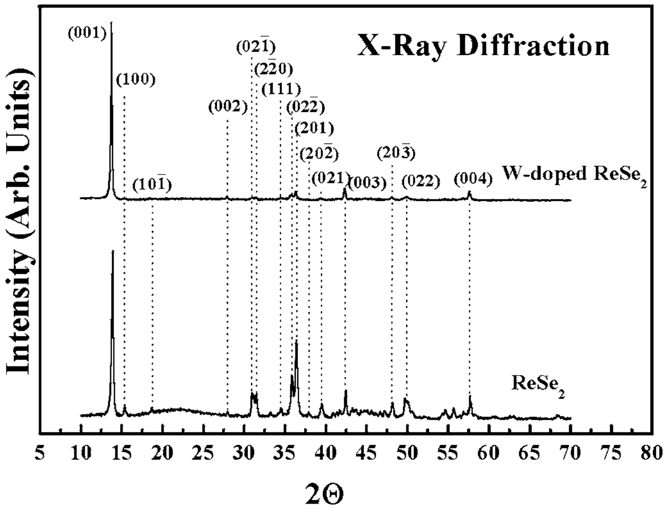

Figure 2. XRD patterns of W-doped $ReSe_2$ and undoped $ReSe_2$ single crystals.

for both directions of electrical and magnetic fields and averaging the results, thus eliminating errors caused by misalignment of Hall probes, thermal emfs, and all the thermomagnetic effects which are dependent on the direction of the electric or magnetic fields. A RMC model 22 closed-cycle cryogenic refrigerator equipped with a model 4025 digital thermometer controller was used for temperature-dependent measurements. The measurements were done between 20 and 300 K with a temperature stability of 0.5 K or better.

Results and Discussion

X-ray diffraction.— For X-ray diffraction (XRD) studies, several small crystals from batches of as-grown W-doped $ReSe_2$ were finely ground with a mixture of glass powder and the X-ray powder patterns were taken and recorded by means of a slow-moving radiation detector. The Cu Kα radiation ($\lambda = 1.542$ Å) was employed and a silicon standard was used for the experimental calibration. The structural parameters with reasonable standard errors (±0.01%) were determined by the least-squares fit of SPSS SigmaPlot mathematical software.[11] Figure 2 shows the XRD pattern of the undoped $ReSe_2$ together with W-doped $ReSe_2$ and confirmed the triclinic symmetry, while the lattice parameters *a*, *b* and *c* of Re-doped samples were carefully determined to be 6.715 ± 0.005 Å, 6.626 ± 0.005 Å and 6.739 ± 0.005 Å, respectively. These numbers are similar to that of the undoped $ReSe_2$ and consistent with those previously reported.[9]

Temperature dependence electrical conductivity and Hall effect measurements.— The electrical transport along ($\boldsymbol{E} \parallel \boldsymbol{b}$) and perpendicular ($\boldsymbol{E} \perp \boldsymbol{b}$) to the **b**-axis polarization schemes are shown in Fig. 1. A study of electrical anisotropy was undertaken by performing the temperature-dependent conductivity measurement along different crystal orientations. Shown in Fig. 3a is the result of the temperature-dependent conductivity measurements along ($\sigma_{\parallel b}$) and perpendicular ($\sigma_{\perp b}$) to the **b**-axis of undoped $ReSe_2$ and W-doped $ReSe_2$. The results show the conductivity of the doped sample is found to be higher than that of the undoped one and the conductivity along the **b**-axis, $\sigma_{\parallel b}$ larger than that of the perpendicular one, $\sigma_{\perp b}$. The larger value of the conductivity parallel to the **b**-axis is related to the strongest bonding force of the samples, which exists along the crystal orientation of the Re-cluster chains. From the conductivity measurements, the anisotropic ratio of undoped $ReSe_2$ and W-doped $ReSe_2$ is around 4 and 3.5, respectively and is shown in Fig. 3b. The anisotropy shows a decrease with adding W dopant. The temperature variation of carrier concentration evaluated from the Hall measurement is similar to conductivity measurement in which a marked

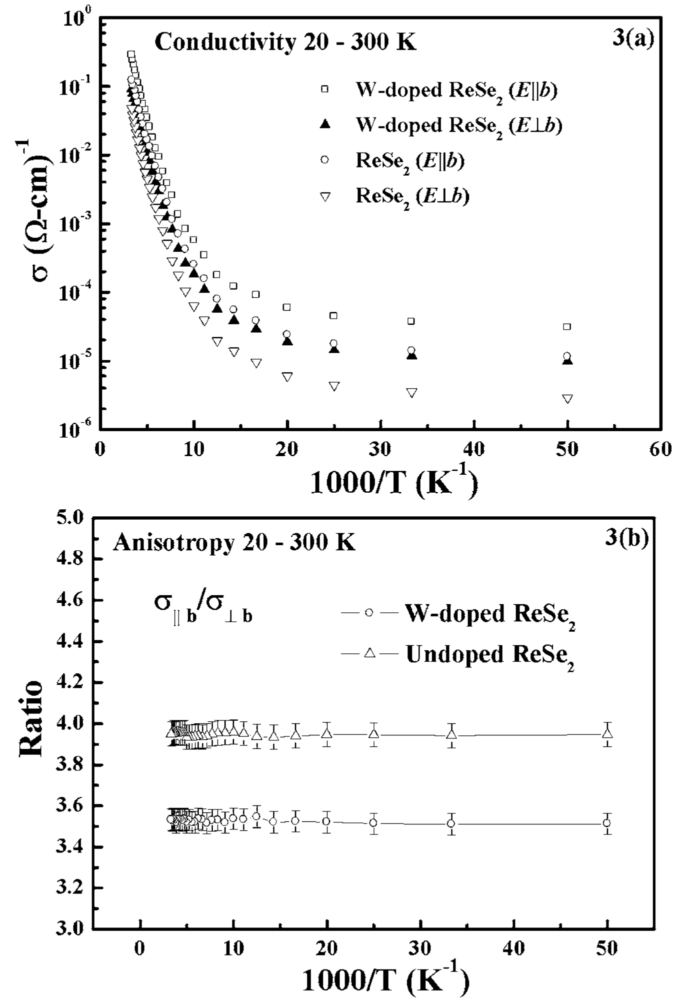

Figure 3. (a) Temperature dependence conductivity of W-doped $ReSe_2$ and undoped $ReSe_2$ single crystals. (b) Temperature dependence conductivity anisotropy of W-doped $ReSe_2$ and undoped $ReSe_2$ single crystals.

increase is observed by adding W dopant. The corresponding value for undoped $ReSe_2$ and W-doped $ReSe_2$ at 300 K is 3.67×10^{16} cm^{-3} and 9.60×10^{16} cm^{-3}, respectively. This result together with the observation of increasing of conductivity shows that the incorporation of W into $ReSe_2$ could cause increases of the carrier concentrations of doped samples and hence improves electrical conductivity. Temperature-dependent Hall mobility along and perpendicular to the **b**-axis can be derived from the conductivity and Hall voltage by the relation $\mu_H = R_H\sigma$ and the results are shown in Fig. 4. For the samples, over the temperature range between 20 and about 160 K, the mobility increases with increasing temperature, characteristic of domination of impurity (or defect) scattering. Above 160 K the mobility decreases when temperature increases, which corresponds to the region where electron-phonon scattering effect is dominant. In general, the mobility of the doped sample is smaller than that of the undoped one. Hall mobilities are very low and the mobility along the **b**-axis, $\mu_{\parallel b}$ is larger than that of the perpendicular one, $\mu_{\perp b}$. The low values of mobility indicate the general semiconducting properties of layered crystals of undoped $ReSe_2$ and doped $ReSe_2$ due to the larger effective masses of carriers.[12] Electrical transport properties n, σ and μ_H from conductivity and Hall effect measurements at 300 K are summarized in Table I. In view of the low mobility, we may conclude that carrier concentration is the dominant factor in assisting the electrical conductivity for undoped and doped $ReSe_2$. Note also that the measured

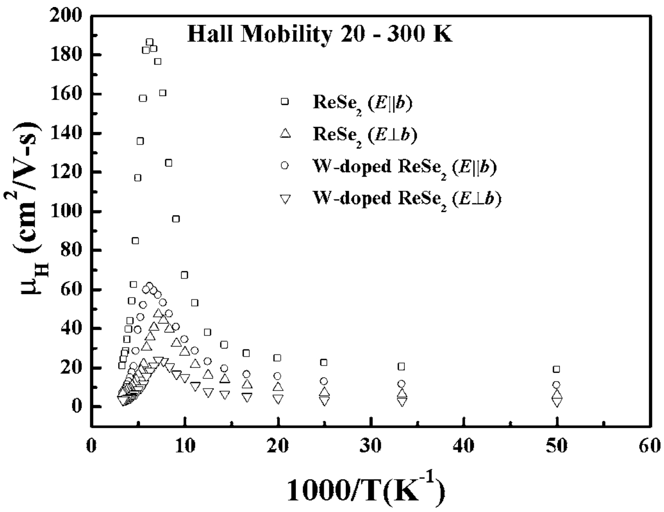

Figure 4. Temperature dependence mobility of W-doped $ReSe_2$ and undoped $ReSe_2$ single crystals along and perpendicular to ***b***-axis, respectively.

values vary considerably among crystals even when the crystals were taken from the same batch. Such differences are probably due to the different uncontrollable doping concentrations or nonstoichiometry of each crystal.[13]

Table I. Summary of electrical transport properties n, σ, and μ_H from conductivity and Hall effect measurements at 300 K.

Materials	Undoped $ReSe_2$	W-doped $ReSe_2$
Carrier type	n	n
Carrier concentration, n (cm^{-3})	3.67×10^{16}	9.60×10^{16}
Conductivity$_{\|b}$, σ (Ω-cm)$^{-1}$	0.122	0.149
Conductivity$_{\perp b}$, σ (Ω-cm)$^{-1}$	0.031	0.042
Hall mobility$_{\|b}$, μ_H (cm^2/V-s)	20.8	9.7
Hall mobility$_{\perp b}$, μ_H (cm^2/V-s)	6.8	4.2

Conclusions

Single crystals of W-doped $ReSe_2$ on the electrical anisotropy properties were studied via the temperature-dependent conductivity and Hall effect measurements. Hall effect measurements reveal that doped and undoped samples are all n-type semiconductors. The results indicate that incorporation of small amount of tungsten into $ReSe_2$ could cause increases of the carrier concentrations of doped samples and hence improves electrical conductivity. The larger value of conductivity parallel to ***b***-axis is most likely related to the strong bonding force of $ReSe_2$ which exists along the crystal orientation of Re-cluster chains and the anisotropy shows a decrease with adding W dopant.

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