Possible negative correlation between electrical and thermal conductivity in p-doped WSe$_2$ single crystal

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Abstract

The materials with high electrical conductivity $\sigma$ and low thermal conductivity $\kappa$ are the driving force for an efficient thermoelectric device. In general, electrical and thermal conductivity cannot be controlled independently as both electron and phonon participate in transport processes. Two dimensional layered materials are one such kind where van der Waals inter-layer interaction and covalent intra-layer bond favours strong phonon mediated electronic interaction. Here, we report that the substitutional p-type doping of WSe$_2$ demonstrate negative correlation between $\sigma$ and $\kappa$ at wide temperature range from 5–300 K. Nominal 0.5% Nb doping of WSe$_2$ (WSe$_2$:Nb) increases the electrical conductivity by an order of magnitude and suppresses the thermal conductivity by the same magnitude. The formation of impurity band at close proximity (0.2 meV) of valance band display large delocalized carrier density and temperature independent mobility as compared to the undoped sample. Simultaneously, the strong delocalization of degenerate band impurity is also found to lower the thermal conductivity to 6 W m$^{-1}$K$^{-1}$ at 300 K.

1. Introduction

Two dimensional layered materials (2DLMs) have so far proved to be the most intriguing and promising candidate for multitude of applications [1–3]. The weak van der Waals interaction between the inter atomic layers in 2DLM bulk crystals has lead to existence of rich electronic states like metallicty, insulating, semiconducting, superconducting and charge density waves [4–7]. Recently, 2DLM which meets the requirement of low thermal conductivity and high electrical conductivity have been on high demand for the development of thin and small thermoelectric material devices. Till now, thermal and electrical transport in 2DLMs such as graphene, BP, PbTe, Bi$_2$Te$_3$, h-BN, MX$_2$ ($M = Mo, W, Zr, Hf$, Sn; $X = S, Se, Te$) have been intensely investigated over the past few years [8–11]. In the quest for finding promising thermoelectric materials, different types of nanostructures such as Si nanowires, quantum nanodot alloys (AgPb$_2$Sb$_2$Te$_6$)$_{x}$, heterostructures (Bi$_2$Te$_3$/Sb$_2$Te$_3$) have also been grown where decrease in thermal flow while suppressing the decrease in electrical conductivity is observed [12–14]. More recently, Lee et al. has reported one-third decrease in $\kappa$ and 30 times increase in $\sigma$ for 2D SnS$_2$ as compared to 3D SnS$_2$, thus fits practically well for thermoelectric applications [15].

Doping and intercalation are the two other important methods by which new electronic and vibrational modes near Fermi energy can modify the transport properties in 2DLMs and 3D bulk networks [16]. Furthermore, doping directly into conduction or valence band of 2DLM adds additional technological advantages like band to band tunneling, lower metal-semiconductor interfacial resistance, persistent mobility and good thermal stability [7, 17, 18]. In addition, a recent calculation by Parker and Singh indicates that the heavily doped PbSe of band gap around 65 meV shows improved thermoelectric performance which might be due to band flattening of $\approx$0.35eV below the valence band maximum [19, 20].
In this paper, we report the effect of degenerate doping on temperature dependent electrical and thermal conductivity in WSe$_2$:Nb bulk single crystal. Here, the degenerate doping refers to large concentration of impurity carriers which does not freeze at low temperature. Electrical Conductivity $\sigma$ and thermal conductivity $\kappa$ are performed on bulk samples in wide temperature range 5-300 K. The temperature dependent electrical and thermal conductivity for undoped WSe$_2$ is measured to be $\approx 10^2$ S m$^{-1}$ and 17 W m$^{-1}$ K$^{-1}$ at 300 K respectively. On the other hand the same properties when measured for WSe$_2$:Nb are found to be $\approx 10^3$ S m$^{-1}$ and 6 W m$^{-1}$ K$^{-1}$ respectively at same temperature. Moreover we have found from Hall measurement that the strong temperature dependent carrier density in pristine WSe$_2$ becomes temperature independent i.e. no carrier freeze out when the carrier density increase to $10^{19}$ cm$^{-3}$ by p-type doping. Theoretical calculation by Han et al. is in accord with our experimental results, that also confirms that Nb is a competent effective p-type dopant. Nb creates a shallow acceptor level where Fermi level lies in between valance band maxima and the ionization level.

2. Experimental details

Crystals of WSe$_2$ and nominal 0.5% Nb doped WSe$_2$ are grown by chemical vapor transport technique in which iodine is used as a transport agent. The details of growth process are discussed in our earlier report by Mukherjee et al. [7]. Single crystals of various sizes with dimensions $5 \times 5 \times 0.1$ mm$^3$ are obtained. The quantitative analysis by wavelength dispersive x-ray (WDS) spectometry shows actual dopant concentration of WSe$_2$:Nb is 0.42 at.%. Electrical and thermal measurements are measured in closed cycle cryostat from Advanced Research Systems. High purity silver paste from SPI Supplies and 25 $\mu$m diameter gold wires are used for electrical four point resistivity measurements. Due to the limitations on the sample size, the steady state method is used to determine the thermal conductivity of samples where constantan is used as reference sample [21]. Extra care is taken to maintain the high vacuum at $\sim 10^{-7}$ Torr, as it minimises the error due to thermal loss during the transport measurement. 100$\Omega$ SMT chip is used as heater and thin copper wires of thickness 0.05 inch are used for making electrical contacts. T-type differential thermocouple is used to measure temperature gradient across the samples. Stycast is used for thermal anchoring and gluing the sample with the gold plated copper sink.

3. Results and discussions

3.1. Resistivity measurement on bulk

Figure 1 shows the in-plane electrical conductivity $\sigma$ measured for the pristine WSe$_2$ (in red) and niobium doped WSe$_2$ (in blue) from 5–300 K using four point contact technique. In case of undoped WSe$_2$, the $\sigma$ at 300 K is found to be $\sim 80$ S m$^{-1}$ and falls down below the detection limit as temperature decreases below 110 K. Thermally activated conduction behavior (not shown here) $\propto e^{E_a/K_B T}$, where $E_a$ and $K_B$ are the activation energy and Boltzmann constant respectively, confirms the semiconducting behavior with $E_a \approx 70$ meV in WSe$_2$ crystal. On the other hand, the electrical conductivity of WSe$_2$:Nb shows around $10^3$ S m$^{-1}$ at room temperature and is found to decreases almost linearly with lowering of temperature. The absence of thermal activated

![Figure 1. Temperature dependent electrical conductivity of WSe$_2$ (in red) and WSe$_2$:Nb (in blue). Thermally activated behavior shows exponential behavior for WSe$_2$ and linear temperature dependence is observed for WSe$_2$:Nb. Inset: Mobility of pristine (in red) and doped WSe$_2$ (in blue) is shown as a function of temperature.](image-url)
behavior in doped WSe$_2$ is primarily attributed to degenerate doping which has significantly lowered the
activation energy to 0.2 meV. The persistent conductivity in WSe$_2$:Nb at low temperature is limited by weak
impurity scattering where the delocalized electrons in valence band are mostly scattered by ionized dopants
[7, 22]. The inset in figure 1 shows the temperature dependent mobility of WSe$_2$ which is \( \sim 80 \text{cm}^2 \text{V}^{-1} \text{S}^{-1} \) at
300 K is higher than that of WSe$_2$:Nb (\( \sim 4 \text{cm}^2 \text{V}^{-1} \text{S}^{-1} \)), thus indicating strong impurity scattering in the later
case. To shed more light into the conduction behavior, the variation of carrier density as function of temperature
is measured and plotted in figure 2. On substitutional doping, the carrier concentration \( n \) increases by 3 orders
of magnitude at room temperature. In addition, the pristine WSe$_2$ shows freezing of charge carriers with
decreasing temperature. However, WSe$_2$:Nb shows the variation to be almost independent of temperature. This
property further confirms the degenerate doping and formation of strong delocalized charge carriers in
WSe$_2$:Nb [7, 23].

3.2. Thermal conductivity measurement
Furthermore, to understand the phonon-electron interaction in degenerate semiconductor, we have measured
the thermal conductivity in both pristine and doped WSe$_2$ crystal.

Thermal conductivity \( \kappa \) in solids are in general contributed by oscillating lattice \( \kappa_L \) and conduction electrons
\( \kappa_E \). According to Debye model the lattice contribution to thermal conductivity is described as
\[
\kappa_L \propto T^3 \int_0^{\theta_D/T} x^4 e^{x}/(e^x-1)^2 \tau(\omega, T) dx
\]
where \( x = (h\omega/2\pi K_B T) \), \( \theta_D \) is the Debye temperature and \( \tau \) is the relaxation time of a phonon [24]. Figure 3
shows the lattice part of thermal conductivity of bulk undoped WSe$_2$ from 6 K to 300 K. At 300 K, the \( \kappa_L \) is found
to be \( \sim 17\text{W m}^{-1}\text{K}^{-1} \) and grows to maximum of \( \sim 180\text{W m}^{-1}\text{K}^{-1} \) with low temperature phonon peak appearing
around 20 K. Above the peak temperature, the thermal conductivity is dominated by Umklapp process which
reduces the phonon mean free path as the temperature increases [25]. Correspondingly, \( \kappa_L \propto 1/T \) is observed
and agrees well by theoretical fitting as shown in green in the range 30–300 K.

Below the maximum, a reasonable fitting of \( \kappa_L \propto T^{1.5} \) (shown in blue line) indicates that the phonon-point
induced defect scattering dominates at low temperature. This effect has further barred thermal conductivity
from following T$^3$ law. The inset of figure 3 shows the electronic contribution of thermal conductivity \( \kappa_E \) in the
same temperature range. The electronic contribution is extracted using Wiedemann–Franz law \( \kappa_E = LT\sigma \),
where L is Lorenz number equal to \( 2.44 \times 10^{-8} \text{W} \text{K}^{-2} \). From the plot, \( \kappa_E \) is found to increase monotonically
with increasing temperature and reaches to \( 0.6 \text{mW} \text{m}^{-1}\text{K}^{-1} \) at 300 K.

The low magnitude of electronic contribution i.e. \( \kappa_E \) comprises of <1% of the total thermal conductivity.
This confirms the negligible contribution by the conducting charge carriers carrying phonons in the entire
experimental temperature range. On the other hand, doping the WSe$_2$ by niobium, surprisingly suppresses the
magnitude of thermal conductivity as shown in figure 4. The room temperature \( \kappa_L \) for WSe$_2$:Nb is found to be
\( \sim 6 \text{W m}^{-1}\text{K}^{-1} \) and falls down to minimum of \( 0.5 \text{W m}^{-1}\text{K}^{-1} \) at 6 K. The maximum value of \( \kappa_L \) is also found to
reduce by an order of magnitude in WSe$_2$:Nb. The overall reduction of $\kappa_L$ in the entire temperature range is held accountable by phonon scattering from point defects as induced by heavy impurity (degenerate) carriers. A similar kind of suppression of $\kappa_L$ is also reported in Fe, Ni doped CoSb$_3$ single crystal [26]. The broadening and shifting of phonon peak to higher temperature $\sim 114$K indicates the presence of long range point defect concentration in WSe$_2$:Nb. A theoretical fitting (blue line) on our experimental data shows $T^0$ dependence of $\kappa_L$ at low temperature ($T < 30$K) where $\alpha$ is found to be 1. The observation that $\kappa_L \propto T^1$ for $T < 30$K also indicates the presence of electron-phonon interaction which arises from delocalized impurity band. At temperature range from 300 K to 150 K, $\kappa_L \propto T^{-0.6}$ (fitted with green line) indicates absence of phonon-phonon umklapp scattering which has an usually exponential temperature dependence [27]. The inset of figure 4, shows that the $\kappa_E$ of WSe$_2$:Nb is one order magnitude higher than WSe$_2$. On optimizing the carrier concentration and type of charge carrier in host WSe$_2$, it has improved the $\kappa$ ratio significantly. It would be further interesting to study the comparison of lattice thermal conductivity with same defect concentration and different carrier concentration for better understanding.

Figure 3. Lattice thermal conductivity as a function of temperature for WSe$_2$ in linear scale. Theoretical fitting of $1/T$ (in green) and $T^{1.5}$ (in blue) is overlapped with the experimental data at high and low temperature respectively. Inset: Temperature dependent electronic part of thermal conductivity in the same temperature range.

Figure 4. Lattice thermal conductivity with broad peak as a function of temperature for WSe$_2$:Nb is plotted. Theoretical fitting of $\propto T^{-0.6}$ (in green) and $T^1$ (in blue) overlaps with the experimental data at high and low temperature respectively. Inset: Small contribution of $\kappa_E$ as a function of temperature.
4. Conclusion

In summary, degenerate substitutional doping of WSe$_2$ by nominal 0.5% niobium shows improved electrical conductivity by an order of magnitude. The increase is mainly attributed to large delocalized carrier concentration which does not freeze out at wide range of cryogenic temperature. From thermal measurement, the lattice part of thermal conductivity is found to be suppressed upon niobium doping in WSe$_2$. This suppression of $\kappa_L$ is caused by strong electron-phonon scattering which shows $T^2$ dependence at low temperature. From this perspective, this work is a proof of concept that lowering the Fermi level close to valance band maximum improve the electrical conductivity and lowers the thermal conductivity as found in WSe$_2$:Nb system. By the same token, there is considerable room for improvement of negative correlation effect for the development of more efficient and reliable two dimensional thermoelectric materials in near future.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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