Low temperature carrier transport mechanism and photoconductivity of WSe$_2$

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**ABSTRACT**

This work reports the temperature-dependent photoconductivity and electrical-transport in tungsten diselenide (WSe$_2$) thin films. The electrical transport is due to the Mott’s hopping mechanism at lower temperatures <190K, while middle region follows the Seto’s parameters and thermally activated conduction is dominated in higher temperature >273K region. A thin film of WSe$_2$ is prepared by thermal evaporation. The transient photoconductivity measurements show a consistent temperature-dependent behaviour. The role of disordered film and presence of trap states is discussed for the carrier transport and photoconductivity of WSe$_2$ thin films.

Transition metal dichalcogenides (TMD) materials have recently showed a new pathway to advance the energy-efficient optoelectronics and nanoelectronics$^{1-2}$. Although graphene offers remarkable high thermal conductivity and electrical mobility but its gapless nature limits the use$^{3-4}$. Tungsten diselenide (WSe$_2$) is an important TMD materials which overcome the limit of graphene owing to its band gap (~1.2–1.7 eV)$^{5-6}$. This feature makes them desirable for low-dimensional electronics$^{7}$. Unlike other TMDs, opto-electronic properties of WSe$_2$ has been less studied. WSe$_2$, a layered semiconductor, exhibits p-type conduction$^{8}$. The previous studies on the opto-electronic properties of WSe$_2$ shows promising results with high photo-responsivity.
but most of the studies were performed at room temperature or at high temperature. At lower temperature, device properties change drastically due to various effects such as -increase of contact resistance, decrease of thermionic emission, variation of recombination centres, trap states, etc. Thus, in order to further increase the applicability of material, realization of temperature-dependent properties especially low temperature is important. It is significant to understand how material behaves in the presence of light and at low temperature. For the deposition of WSe$_2$ thin films, various methods such as electrodeposition, chemical vapor deposition, chemical bath deposition, soft selenization, solid state reaction, thermal evaporation, galvanostatic routes, spray pyrolysis, van der Waals reheataxy, has been employed in previous reports$^{9-15}$. Structural and optical properties of the fabricated thin films are reliant on the method of deposition. Due to its suitability, high deposition rate, simplicity and reproducibility, thermal evaporation method is the most common in above said deposition techniques.

In the present work, we explore the temperature-dependent electrical conductivity of WSe$_2$ thin films. We have used thermal evaporation method to fabricate WSe$_2$ thin films and examined the possibility of a different type of carrier transport mechanisms and photoconductivity in the deposited films. It is found that three mechanisms are evident in carrier transport in WSe$_2$ thin films – low temperature Mott’s variable range hopping, middle temperature range Seto’s grain boundary effect whereas higher temperature range dominated by thermally activated band conduction. The photoconductivity mechanism is also discussed in detail.

WSe$_2$ has been synthesized by solvothermal approach. The synthesized powder used for thin film preparation by the thermal evaporation technique on pre-cleaned glass substrates. Thin film deposition was done in a vacuum controlled chamber using Hind HIVAC system (Model: BC-300) at a deposition rate of 10 Å/s. In the deposition process, boat was adjusted under the glass slide lid. Known amount (200 mg) of synthesized WSe$_2$ nanomaterial was put in the boat.
Pressure of chamber was maintained at $5.3 \times 10^{-6}$ mbar. After deposition, film was taken out from the chamber and characterized by various characterization techniques. Structural analysis was done using X-ray diffraction (XRD) technique. The surface morphology and cross-section analysis of deposited thin film was studied using scanning electron microscope (SEM). Elemental mapping was also done. To study the electrical properties, a simple device was fabricated. The temperature dependent electrical properties measurements were done using MS-TECH probe station with a Keithley Sourcemeter-2450. The photoconductivity measurements were done using white light of different intensities and blue light source. The light intensity is observed using a digital luxmeter. The photocurrent is calculated by subtracting the dark current ($I_D$) from the current obtained in the presence of light ($I_L$).

Figure S1(a) shows the XRD spectra of the crystalline WSe$_2$ powder which is used for the fabrication of thin film. The broad pattern in the case of WSe$_2$ film (Figure S1(b)) confirms the amorphous growth of film. Figure S2 shows the SEM image of the deposited WSe$_2$ film on a glass substrate which shows a uniform deposition of film via thermal evaporation of the material. The cross-section image shows the average thickness of ~100 nm for deposited film. The elemental mapping shown in Figure S3 confirms the presence of tungsten and selenide in deposited films. Figure 1(a) shows the resistivity variation with temperature for the WSe$_2$ film in the temperature range from 125 to 348 K. There is a decrease in resistivity with the increases in temperature which shows the semiconducting behaviour of deposited WSe$_2$ film.

The three different regions in resistivity plot with temperature indicates that there may be more than one carrier transport mechanisms involved in WSe$_2$ film. Firstly, the thermally activated band conduction mechanism has been analyzed in which, the conductivity ($\sigma$) can be expressed using Arrhenius relation;

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right)$$  \hspace{1cm} (1)
where $\sigma_0$ is a constant, $E_a$ is the activation energy for dc conduction, and $k$ is the Boltzmann’s constant. Figure 1(b) shows the $\ln \sigma$ vs $1000/T$ plot for WSe$_2$ film at temperature range from 350 K to 273 K. A straight line fit to the data (region I) shows that thermal conduction dominates in the high temperature range. Two distinct thermal activation energies have been found in the plot for WSe$_2$ film whose values are calculated to be $\sim$138 meV, 98 meV. This process includes thermal activation of carriers from donors to the conduction band.

The value of $E_a$ depends on the impurity energy levels and accepter carrier concentration. The Fermi level can be shifted up with an increase in the concentration of accepter carrier which leads to decrease of the $E_a$. The film deposition leads to the establishment of trap states within the amorphous disordered structures. In the range of 273–125 K, carriers do not have adequate amount of energy to jump to the conduction band due to entrapment in trap states. Thus, carriers can conduct via hopping from one to another energy level in the impurity band. It signifies the domination of hopping mechanism in lower temperature range than thermal conduction. Hopping conduction mechanisms are of two types – Nearest Neighbor Hopping (NNH) and Variable Range Hopping (VRH)$^{16}$. The carriers hop to the nearest neighbour empty site in NNH conduction. For NNH mechanism, temperature dependence can be written as$^{17}$

$$\sigma = \sigma_{0NNH} \exp\left(-\frac{E_{NNH}}{kT}\right) \quad (2)$$

Activation energy ($E_{NNH}$) is also required in this conduction which has lower value than the activation energy ($E_a$) of thermally activated conduction. But in Figure 1(b), $\ln \sigma$ vs $1000/T$ plot gives higher activation energy from 273 to 300 K, which means there is no dominance of NNH hopping. Hence, thermal conduction is the only possible mechanism to be responsible for conduction from 273 to 350 K with two activation energies.
(a) 

(b) Arrhenius model

(c) Seto's model

(d) Mott's model
Figure 1: (a) Electrical resistivity of WSe$_2$ film as a function of temperature (range 25 K to 350 K). The regions I to III have been fitted with different models; (b) Arrhenius model fits on the conductivity data in the temperature range 350 to 273 K; (c) Seto’s s model fits on the conductivity data in the temperature range 273 to 190 K; (d) Mott’s VRH model fits on the conductivity data in the temperature range 190 to 125 K.

We noticed the governance of Mott’s VRH conduction mechanism in the lower temperature region (T<190 K). In the Mott’s VRH, carriers hop between the levels close to the Fermi level regardless of spatial distribution. Hopping distance is not constant in VRH because carriers hop to a site which requires the minimum possible activation energy.$^{17}$ Density of states remains same near the Fermi level in this mechanism.$^{18}$ In Figure 1(d), we consider Mott-VRH at temperature range of 125 to 190 K.

In Mott’s VRH, for three-dimensional system, the temperature dependence of conductivity can be given as$^{18}$:

$$\sigma = \sigma_0 M T^{-1/2} \exp(-\left(T_M/T\right)^{3/4})$$  \hspace{1cm} (3)

where$^{19}$

$$\sigma_0 M = \frac{2e^2v_{ph}}{(8\pi)^{1/2}}\left[N_{\text{EF}}/\alpha kT\right]^{1/2};$$ \hspace{1cm} (4)

$$T_M = \left[\frac{\alpha^3}{kN_{\text{EF}}}\right]$$ \hspace{1cm} (5)

$T_M$ is measure of the degree of disorder in the film, $\alpha$ is inverse of localization length, $k$ is Boltzmann constant, $N_{\text{EF}}$ is density of energy states at Fermi level, $v_{ph}$ is Debye frequency. We found that the plot of ln ($\sigma T^{1/2}$) vs. $T^{-1/4}$ fits very well the predicted Mott’s 3D VRH model in the temperature range of 125 to 190 K. By best fitting of the experimental data, Mott’s temperature ($T_M$) value obtained is 1217647 K. The high value of $T_M$ shows the disordered films which is also in agreement with the XRD spectrum showing amorphous nature of
deposited film. It has been found that $T_M/T >> 1$ which follows the condition of VRH transport in semiconductor\textsuperscript{16,20}. Hence, it can be assumed that VRH is the mode of carrier transport mechanism at lower temperature in WSe\textsubscript{2} films. Furthermore, the value of $N_{(EF)}$, mean hopping energy ($W$), hopping distance ($R$) has also been calculated by using the equations\textsuperscript{21} given below:

\begin{align*}
W &= \frac{3}{4\pi R^3} N_{(EF)} \\
R &= \left[\frac{9}{8\pi \alpha kT N_{(EF)}}\right]^{1/4}
\end{align*}  

To satisfy Mott’s VRH conduction mechanism, there are two conditions, $\alpha R > 1$ and $W > kT$\textsuperscript{21}. The calculated values for WSe\textsubscript{2} film satisfy these conditions. So at low temperatures ($<$190 K), thermal energy to the carriers decreases, that’s why carriers feel more interference for the electrical conduction. So, carriers become localized to small regions in the film at low temperatures.

We observed a region obtained between Mott’s VRH mechanism ($<$190 K) and thermal conduction ($>$273 K), which has been explained using Seto’s model. According to this model, grain boundaries act as defects which makes crossing of boundaries difficult for carriers\textsuperscript{22}. The linear plot between $\ln (\sigma T^{1/2})$ and $1000/T$ for WSe\textsubscript{2} film in the temperature range of 190 to 273 K is shown in Figure 1(c). This fitted data shows that Seto’s grain boundary model is applicable to WSe\textsubscript{2} film in this temperature range. The fitted equation is\textsuperscript{23}

\begin{equation}
\sigma = \sigma_{0S} \exp\left(-\Phi_B/kT\right)
\end{equation}

where,

\begin{equation}
\Phi_B = Le^2 n v_c/kT
\end{equation}

\begin{equation}
v_c = \left[kT/2\pi m^*\right]^{1/2}
\end{equation}

$\Phi_B$ is barrier height, $L$ is grain size, $e$ is charge of electron, $n$ is carrier concentration, $v_c$ is collection velocity, and $m^*$ is effective mass of charge. Barrier height is directly proportional
to grain size. From Seto’s model fitting, $\Phi_B$ has been found to be 0.0873 eV which is very small showing the improved mobility of carriers. This low barrier height may be ascribed to the more conductivity of WSe$_2$ thin film. The constant $\sigma_0S$ has been found to be 22.58 S cm$^{-1}$. All these three temperature regions fitted by Mott’s, Seto’s and Arrhenius model gives the detailed information of temperature-dependent carrier transport mechanism of WSe$_2$ thin film.

Optical studies on the WSe$_2$ films have been performed and used to calculate the band gap by Tauc’s plot as shown in Figure S4. The calculate band gap for WSe$_2$ is $\sim$1.5 eV. Also, WSe$_2$ shows two PL peaks (as shown in Figure S5) at $\sim$1.71 and $\sim$1.74 eV which can be attributed to trions and excitons respectively. These peaks are well investigated in literature$^{24}$. Also, there is a peak at $\sim$1.59 eV which can be ascribed to the exciton bound to defects$^{25,26}$. This will result in mid-bandgap states above the maximum of valence band or below the conduction band minimum. These defect states play an important role in the photoconductivity of WSe$_2$ film. The photoconductivity of WSe$_2$ film is measured in the temperature range of 125-350K. Figure 2 (a) shows the temperature dependence comparison of dark and photo conductivity. The temperature dependent I-V curves of dark and photocurrent are shown in Figure S6 and S7. Photocurrent is calculated by subtracting dark current from current obtained in presence of light. The photocurrent is $1.19 \times 10^{-5}$ A at 125 K while at 350 K it was observed to be $3.12 \times 10^{-4}$ A (Figure S8). Figure 2(b) shows the photo-response cycle of WSe$_2$ film at room temperature when illuminated with white light (Intensity = 1750 lux). The rising and decaying edge follows the equations $I(t) = I_0[1-\exp(-t/\tau_r)]$ and $I(t) = I_0\exp(-t/\tau_d)$, where $\tau_r$ is rising edge time constant and $\tau_d$ is decaying edge time constant$^{27}$. By fitting curves (Figure 2(c) and 2(d)), $\tau_r$ and $\tau_d$ are found to be 28.39 s and 42.50 s. This shows the slow rise and decay of the photocurrent which can be found in disordered materials or due to the presence of trap states in the energy gap. According to previous reports, shallow traps generally leads to faster process while deep trap states results in slow increase or decrease in photoconductivity$^{28,29}$. 
Figure 2: (a) Variation of photoconductivity and dark conductivity with temperature at 1750 Lux intensity; (b) I-T curve measurement using white light illumination (1750 Lux) at room temperature; (c) Rising edge of single photo-response current cycle; (d) Decaying edge of single photo-response current cycle; (e) I-T curve measurement using white light illumination of different intensities 380 (I_1), 720 (I_2), 1270 (I_3), 1580 (I_4), 1750 Lux (I_5) at room temperature; (f) I-T curve measurement using blue light illumination at room temperature.
When I-T curves of photo-response was observed by repeatedly turning on and off light illumination (white and blue both). After various cycles, current can recover to its initial state. This shows that the WSe$_2$ thin film device is stable and has outstanding reversible properties. The I-T curve with variation of light intensity is shown in Figure 2(e). As white light illumination power densities increased from 4.75 to 21.87 mW/cm$^2$, photo current also increased in steps. The photo-current under illumination of different power intensities follows power law ($I \sim P^\gamma$) with intensity exponent $\gamma = 0.87$ as shown in Figure S9. Figure 2(f) shows the photo-response curve during ON and OFF state with blue light illumination. Shallow and deep level defects in the forbidden gap influences the rising and decaying edges of photo-response. The slow decaying edge can be ascribed to the presence of trap states generally deep defects. When light is shone, photogenerated carries formed in the film. Then these carriers move from valence to conduction band. Due to the presence of deep level defects these photogenerated carriers take longer time to relax. Hence, defect or trap states plays an important role in photoconductivity of WSe$_2$ films.

In summary, we present carrier transport mechanism and photo-response properties of WSe$_2$ at low temperatures. A simple thin film device with as synthesized WSe$_2$ was prepared which shows Ohmic contact nature. The obtained conductivity is high even at low temperatures. The carrier transport mechanism in the temperature range of 125-350 K follows three different mechanisms – Mott’s, Seto’s and Arrhenius models. Low temperature is dominated by hopping mechanism whereas high temperatures are dominated by thermal conduction. The photoconductivity also shows the same trend in different temperature regions. WSe$_2$ thin film also display stable and reversible photo-response properties which can be used in low temperature and high vacuum applications.
SUPPLEMENTARY MATERIAL

See the supplementary material for the XRD pattern, FESEM images, Elemental mapping images, I-V measurements, dark and photocurrent of WSe$_2$ thin film.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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**Results**

![Figure S1: XRD spectra of the crystalline WSe$_2$ synthesized by solvothermal method and the amorphous WSe$_2$ film prepared by thermal evaporation on a glass substrate.](image)

Figure S1: XRD spectra of the crystalline WSe$_2$ synthesized by solvothermal method and the amorphous WSe$_2$ film prepared by thermal evaporation on a glass substrate.
Figure S2: (a) SEM image of WSe$_2$ film; (b) Cross-section image showing thickness of deposited film.

Figure S3: Elemental mapping of WSe$_2$ film.
Figure S4: Tauc’s plot for WSe$_2$ film.

Figure S5: PL spectra of WSe$_2$ film.
Figure S6: I-V curves (in dark) at temperatures from (a) 125 to 273 K; (b) 273 to 343 K.

Figure S7: I-V curves (in presence of light) at temperatures from (a) 125 to 273 K; (b) 273 to 343 K.
Figure S8: Dark current and phototo-current dots at different temperatures.

Figure S9: Fitting curve to experiment data of different power densities.