Chapter 6
Preparation and Characterization of Metal - Semiconductor Rectifying Contacts

6.1 Introduction

Metal - semiconductor (MS) structures are important research tools in the characterization of new semiconductor materials. The fabrication of these structures plays an important role in developing some useful devices such as microwave field-effect transistors, radio frequency detectors, photo transistors and space solar cells [1-7]. Moreover, metal-semiconductor (MS) contacts are the most common form of junctions in integrated circuits. Therefore, research efforts regarding the interaction of semiconductor surfaces with deposited metals are very important for understanding many developmental aspects of the microelectronic devices. The great majority of metal-semiconductor junctions are used for ohmic contact. Ohmic contact has a very low resistance to make the electrons and holes move freely in and out of the devices. The other type of metal-semiconductor contact has a rectification capability, with a large current in forward bias and a very low leakage current in reverse bias and is called Schottky diode. Looking towards the importance of metal semiconductor contacts, specially rectifying contacts, in the field of electronic, it is necessary to have basic ideas regarding both types of MS contacts. In the initial part of present chapter author presents theoretical concept of both ohmic and rectifying MS contact. In the subsequent sections the fabrication of thin film Schottky diodes based on WSe$_2$ (Aluminum thin film/pWSe$_2$ thin film) with prior work done by other researchers is presented. In results and discussion section voltage – current characteristics of prepared thin film Schottky diodes has been discussed in detail with various methods for obtaining different Schottky diode parameters in wide temperature range.
6.2 Ohmic Contacts

The term "ohmic" refers in principle to a metal-semiconductor contact, which is non-injecting and has a linear current-voltage characteristic in both directions of current flow. In practice, the contact is usually acceptable if it can supply the required current density with a voltage drop which is very small compared to that across the active region of the device; even though its behaviour may not be strictly linear. Historically, metal-semiconductor contacts were predominantly used as rectifying contacts until suitable methods of fabricating $p - n$ junctions became available. Then, these contacts began to assume a less significant role as ohmic contacts for transporting current into and out of $p - n$ junctions. With greater understanding and technological advancements, there was a renaissance of the rectifying metal-semiconductor or Schottky contact in the 1960's. At the same time, the need for higher speed devices with their smaller and more complex geometries acted as the driving force behind the search for high performance ohmic contacts. In many cases, we wish to have a perfect ohmic metal-semiconductor contact for getting signals into and out of a semiconductor device. It is important that such contacts with minimal resistance and no tendency to rectify signals be ohmic and conducts in the same way for both polarities.

A metal-semiconductor junction results in an ohmic contact if the Schottky barrier height ($\Phi_B$), is zero or negative. In such case, the carriers are free to flow in or out of the semiconductor so that there is a minimal resistance across the contact. For an $n$-type semiconductor, this means that the work function of the metal must be close to or smaller than the electron affinity of the semiconductor. For a $p$-type semiconductor, it requires that the work function of the metal must be close to or larger than the sum of the electron affinity and the bandgap energy.
6.2.1 Ohmic Contact With Small Work Function Metal

If the metal work function is smaller than semiconductor (n type) work function ($\Phi_m < \Phi_{nt}$), then an ohmic contact is formed. The corresponding band diagram under thermal equilibrium, forward bias and reverse bias conditions are shown in figure 6.1(a), (b) and (c) respectively. (Here $J_{smo}$: current density flows from semiconductor to metal, $J_{mso}$: current density flows from metal to semiconductor, Subscript 'o' represents thermal equilibrium)

![Energy band diagram](image)

Figure 6.1: Energy band diagram (a) metal / n- semiconductor contact ($\Phi_m < \Phi$) under thermal equilibrium. $J_o = J_{smo} - J_{mso} = 0$ (b) metal / n - semiconductor contact ($\Phi_m < \Phi$) under forward bias. $J_f = J_{smf} - J_{msf} = J_{smf} - J_{mso} = J_{smf} > 0$ (c) metal / n-semiconductor contact ($\Phi_m < \Phi$) under reverse bias. $J_r = J_{smr} - J_{msr} = J_{smr} - J_{mso} = J_{smr} > 0$. 

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6.2.2 Ohmic Contact With Tunneling Current Mechanism

Mostly it is difficult to form ohmic contacts with the above stipulations and in this case, a highly doped layer in semiconductor is always useful. The heavily doped layer increases the junction barrier height and makes the thickness of the depletion width extremely narrow, which increases the probability of electron tunneling from the semiconductor to the metal. This tunneling mechanism thus increases the current flow through the junction and reduces the contact resistance (figure 6.2). For the metal - semiconductor (p type) junction, ohmic contact is mainly formed with the tunneling mechanism.

![Schematic diagram of the ohmic contact with tunneling current mechanism.](image)

It is seen that there are several possible ways of achieving a good ohmic contact:

- The most common method is to have a layer of very highly doped semiconductor immediately adjacent to the metal giving rise to a very narrow depletion / barrier width. Increased conduction is then dominated by quantum mechanical tunneling.

- Another approach is to have a negligible potential barrier, $\Phi_b$, to start with. In practice, this is harder to achieve for VIA - VIB covalent compounds such as WSe$_2$ where $\Phi_b$ is essentially determined by interface states rather than the difference between the work function of the metal and the electron affinity of the semiconductor as theory predicts.

- A third approach is to deliberately increase interface states. This in turn aimed at reducing the contact resistance by causing space-charge
recombination to dominate. But, in practice, this has adverse effects on the device stability.

The quality of an ohmic contact is ultimately assessed by determining its specific contact resistance \( (R_c) \). Other desirable properties of ohmic contacts include good adhesion to the semiconductor, smooth surface morphology (particularly where near micron size device geometry is concerned), ability to bond gold / silver alloy wires to connect the device to external circuitry and finally contact reliability.

6.3 Metal-Semiconductor Contacts: Schottky Contacts

Metal-Semiconductor (MS) contacts are an essential part of virtually all semiconductor electronic and optoelectronic devices. One of the most important properties of a MS interface is its Schottky barrier height (SBH). The SBH controls the electronic transport across the MS interface and therefore, it is of vital importance for the successful operation of any semiconductor device. Ever since the second half of the 20\textsuperscript{th} century, many textbooks and articles were published with efforts to unravel the SBH mystery. In this section, a theoretical background about the SBH formation and some experimental observations are discussed. A more extensive overview can be found in the review article of Tung [4]. The study of electrical behaviour of the SB is discussed and its analysis is presented for evaluation of various barrier parameters.

6.3.1 Metal - Semiconductor Junctions: Theoretical Background

Metal-Semiconductor junction shows non-ohmic characteristics when the metal work function \( (\Phi_m) \) (n-type semiconductor) is greater than the semiconductor work function \( (\Phi_s) \), as shown in the figure 6.3(a). When metal and semiconductor materials are in contact and under thermal equilibrium (no current flow) the Fermi levels of both must be at the same energy level and constant throughout this system (figure 6.3(b)).
Thus, if the work functions of the metal and the semiconductor are different, a potential-energy barrier exists between the connected materials at equilibrium. Assuming \( \Phi_m > \Phi_s \) this height \( \Phi_b \) is given by equation (Schottky 1938, Mott 1938) [8, 9, 10],

\[
q \Phi_{bn} = q (\Phi_m - \chi_s)
\]

(6.1)

Where \( q \) is the electronic charge, \( \chi_s \) is electron affinity and \( \Phi_m \) is work function of metal.

Opposite is equally true for \( p \)-type semiconductors with the condition \( \Phi_s > \Phi_m \). For \( p \)-type material, the barrier height is given by the difference between the valence band edge and the Fermi energy in the metal:

\[
\Phi_{bp} = \frac{E_g}{q} + \chi - \Phi_m = E_g - \Phi_{bn}
\]

(6.2)

A metal - semiconductor junction will therefore form a barrier for electrons and holes if the Fermi energy of the metal as drawn on the flat band diagram is somewhere between the conduction and valence band edge. In addition, we define the built-in potential \( \Phi_i \) as the difference between the Fermi energy of the metal and that of the semiconductor.

\[
\Phi_i = \Phi_m - \chi - \frac{E_c - E_{Fn}}{q} \quad \text{(for n type)}
\]

(6.3)

\[
\Phi_i = \chi + \frac{E_c - E_{Fp}}{q} - \Phi_m \quad \text{(for p type)}
\]

(6.4)
This theory of Schottky and Mott is rather simplistic in the sense that it assumes ideal conditions. The experimental barrier heights often differ from the one calculated using equation 6.3 or 6.4. This is due to the complex structure of the metal-semiconductor interface as postulated by Schottky and Mott. The ideal metal-semiconductor theory assumes that both materials are pure, and there is no interfacial layer.

One of the first explanations for the departure of experimental observations from this theory was given in terms of localized surface states or "dangling bonds". This is because at the surface of a solid the atoms have neighbors on one side only. This causes a distortion of the electron cloud belonging to the surface atoms, so that the centers of the positive and negative charge do not coincide. This means that, in practice, surface dipole layers do arise. It was observed that \( \Phi_b \) does not depend on \( \Phi_m \) in contradiction to equation 6.1. Thus, the assumption of constancy of the surface dipole cannot be justified. The surface states are continuously distributed in energy within the forbidden gap and are characterized by a neutral level (\( \Phi_0 \)) such that if the surface states are occupied up to \( \Phi_0 \) and empty above \( \Phi_0 \), the surface is electrically neutral.

In general, the Fermi level does not coincide with the neutral level. In this case, there will be a net charge in the surface states. If, in addition, there is a thin oxide layer between the metal and the semiconductor the charge in the surface states together with its image charge on the surface of the metal will form a dipole layer. This dipole layer will alter the potential difference between the semiconductor and the metal. Thus the modification to the Schottky-Mott theory is expressed as follows [2],

\[
\Phi_b = \gamma'(\Phi_m - \chi) + (1 - \gamma')(E_g - \Phi_0)
\]

where, \( E_g \) is bandgap of the semiconductor in eV and \( \Phi_0 \) is the position of neutral level (measured from the top of the valence band) and,
\[ \gamma' = \frac{\varepsilon_f}{(\varepsilon_f + q\delta D_s)} \]  

(6.6)

where, \( \varepsilon_f \) is permittivity of oxide layer, \( \delta \) is thickness of oxide layer and \( D_s \) is the density of surface states.

Hence if there are no surface states, \( D_s = 0; \gamma' = 1 \) and equation 6.5 becomes identical to equation 6.1, which is the original Schottky-Mott approximation. But if the density of states is very high, \( \gamma' \) becomes very small and \( \Phi_0 \) approaches the value \( E_g - \Phi_0 \). This is because a very small deviation of the Fermi level from the neutral level can produce a large dipole moment, which stabilizes the barrier height by a negative feedback effect [2]. When this occurs, the Fermi level is said to be \"pinned\" relative to the band edges by the surface states.

MS diode electrostatics and the general shape of the MS diode \( I-V \) characteristics are similar to \( p-n \) junction diodes, but the mechanisms of current flow are different. In \( p-n \) junction diode dominant current mechanisms arise from recombination in the depletion layer under small forward bias and also arise due to injection of hole from \( p \) side under larger forward bias.

But in the MS Schottky diodes electron injection from the semiconductor to the metal is the dominant current flow. The reverse leakage current for Schottky diode is generally much larger than that for a \( p-n \) junction diode. Since MS Schottky diode is a majority carrier device, the frequency response of the device is much higher than that of equivalent \( p-n \) junction diode (figure 6.4).

Based on this concept the first theory on the formation of Schottky barrier (SB) was proposed by Walter Schottky [9] and Sir Neville Mott [10] individually. They propose that the Schottky Barrier Height (SBH) \( (\Phi_{bh,n}) \) between a metal with work function \( \Phi_m \) and a semiconductor with an electron affinity \( \chi_s \) should be \( \Phi_{bh,n} = \Phi_m - \chi_s \), where the subscript \('n'\) denotes the
SBH measured on an n-type semiconductor. Unfortunately, the strong dependence of the SBH on the metal work function predicted by the Schottky-Mott theory, has received little support from experiments. The insensitivity of the SBH to the metal work function has been attributed to the 'Fermi level (F_l) pinning'. A lot of theories, trying to explain this 'F_l' pinning, made assumptions, which make the SBH insensitive to the interface structure.

![Figure 6.4: Current transport mechanisms in p-n junction diode and MS Schottky diode.](image)

But from a stand point of general physics and chemistry, such assumptions were hard to rationalize. One would expect the SBH to depend on the identity of the semiconductor and the metal, but also on the interface bonding and structure. The latter was shown in the mid-1980s with the dependence of the SBH on the orientation/structure at single crystalline MS interfaces [11]. A few years later, it was pointed out that the SBHs at polycrystalline MS interfaces were often inhomogeneous [12-14], which settled some of the disagreements on the 'F_l' pinning at those interfaces. New spatially resolved techniques like the Ballistic Electron Emission Microscopy (BEEM) [15], gave direct evidence for this SBH inhomogeneity [16]. The inhomogeneity of the polycrystalline interfaces was consistent with the structure dependent view.

In 2000, Tung published a new view on things by associating the interface dipole with the chemical bonding at the MS interface: the 'Bond
Polarization\' theory [17]. In his theory, he uses a method from molecular chemistry, namely the electrochemical potential equalization (ECPE) method, which allows an estimation of all the atomic charges of a large molecule. To apply this ECPE method in order to estimate the charge transfer and electric dipole at a MS interface, Tung regarded the entire MS region (the 'interface specific region') as a giant molecule. A few planes of atoms each from the semiconductor and metal lattices are included in this molecule. A further assumption is that the charge transfer only occurs between atoms that are directly involved in the interface bonds. By giving the atoms bulk characteristics, the Mulliken electronegativity and the hardness can be written as,

\[ \Phi_m, Y_m = 0, U_s = \chi_s + E_g/2 \text{ and } Y_s = E_g \]  

(6.7)

where \( \Phi_m \) is the work function of the metal and \( E_g \) is the band gap of the semiconductor. Finally the SBH can be written as [17],

\[ \Phi_b^0 = \gamma_b (\Phi_m - \chi_s) + (1 - \gamma_b) \frac{E_g}{2} \]  

(6.8)

where the 'interface parameter' is:

\[ \gamma_b = 1 - \frac{e^2 d_{ms} N_b}{\varepsilon_{\text{int}} (E_g + k)} \]  

(6.9)

\( d_{ms} \) is the distance between the metal and semiconductor atoms at the interface, \( N_b \) the uniform density of chemical bonds, \( \varepsilon_{\text{int}} \) is the permittivity of the interface region, and \( k \) is sum of all the hopping interactions.

Equation 6.8 predicts the same weak dependence of the SBH on the metal work function, as predicted by other 'gap state models' (e.g. MIGS [13-20]. There are however, quite some issues, which remain unsettled about the application of the ECPE method at MS interfaces. But most important is the validity of the overall view on the bonding-related charge transfer at the interface.
6.3.1.1 Charge transport mechanisms in Schottky junctions

The current across the Schottky junction is mainly due to majority carriers. Four distinctly different mechanisms i.e. (a) Emission of electrons from the semiconductor over the top of the barrier into the metal, (b) Quantum-mechanical tunneling through the barrier, (c) Recombination in the space-charge region, and (d) Recombination in the neutral region ('hole injection') exist for the flow of charge carriers across the barrier under biased condition. One can understand it from figure 6.5 as below,

![Figure 6.5: Charge transport processes in a forward-biased Schottky diode.](image)

(a) Emission of electrons from the semiconductor over the top of the barrier into the metal;

According to this mechanism, for transport of majority carriers over the Schottky barrier, they must be transported from interior neutral region of the semiconductor to the interface. The usual process for this is the drift and diffusion through the space charge region. Therefore the emission of such carriers over the barrier may be either limited by their transport up to the interface or by their capability of crossing the barrier after arrival at the interface.

(b) Quantum-mechanical tunneling through the barrier;

Tunneling from the neutral regions of the semiconductor will have a significant probability in the forward biased case only when doping concentration is so high as to make the barrier very thin.
(c) **Recombination in the space-charge region;**

This occurs through the localized centers within the space charge region. However, most effective recombination centers are the one lying near the center of the semiconductor bandgap.

(d) **Recombination in the neutral region ('hole injection');**

In case where Schottky barrier height is more than the semiconductor band gap, the nature of the semiconductor near the interface may be inverted and as a result minority carrier injection into the neutral region of the semiconductor may assume significance.

6.3.1.2 Schottky diode current

The current transport through the device by emission over the barrier is essentially a two-step process: first, the electrons have to be transported through the depletion region, and this is determined by the usual mechanisms of diffusion and drift [21, 22]; secondly, they must undergo emission over the barrier into the metal (Bethe 1942) [23], and this is controlled by the number of electrons that impinge on unit area of the metal per second. Quantum-mechanical tunneling through the barrier takes into account the wave-nature of the electrons, allowing them to penetrate through thin barriers [24, 25]. In a given junction, a combination of all three mechanisms could exist. However, typically one finds that only one mechanism limits the current, making it the dominant charge transport mechanism.

6.3.1.3 Thermionic emission: Rectification

The thermionic emission theory assumes that the current is controlled only by the transfer of carriers across the top of the barrier; provided they move towards the barrier and the drift and diffusion that occur as a result of collisions within the space charge region are considered unimportant. The actual shape of the barrier is hereby ignored.
For an \( n \)-type semiconductor under forward bias assuming \( q\Phi_b \gg kT \), the electrons emitted over the barrier from semiconductor into the metal will be in equilibrium with the electron population in the semiconductor and thus will have a Maxwellian energy distribution. The resultant current \( I_{TE} \) due to thermionic emission for an applied bias \( V \) (measured \( +ve \) with respect to the \( n \)-type semiconductor) is given by S. M. Sze [26],

\[
I_{TE} = AA^*T^2 \exp \left( \frac{-q\Phi_b}{kT} \right) \left[ \exp \left( \frac{qV}{kT} \right) - 1 \right]
\]  

(6.10)

where, \( A^* \) is cross-sectional area of the metal - semiconductor interface, \( A^* \) is Richardson constant for metal - semiconductor interface given as,

\[
A^* = \frac{4\pi q m_e^* k^2}{h^3} \quad \text{for } n \text{ type semiconductor}
\]  

(6.11)

\[
A^* = \frac{4\pi q m_h^* k^2}{h^3} \quad \text{for } p \text{ type semiconductor}
\]  

(6.12)

Here; \( m_e^* \) and \( m_h^* \) are effective mass of the electrons and holes respectively, \( T \) is temperature in Kelvin, \( k \) is Boltzmann constant, \( h \) is Plank's constant, \( q \) is electronic charge, \( V \) is effective bias across the interface and \( \Phi_b \) is the Schottky barrier height.

If the barrier height is assumed to vary linearly with bias as,

\[
\Phi_b(V) = \Phi_{b0} + \gamma V
\]  

(6.13)

where \( \Phi_{b0} \) is the barrier height at zero bias and \( \gamma (=\partial \Phi_b / \partial V) \) is positive. Substituting equation 6.13 in equation 6.10,

\[
I_{TE} = I_{TE0} \exp \left( \frac{-qV}{kT} \right) \left[ \exp \left( \frac{qV}{kT} \right) - 1 \right]
\]  

(6.14)

\[
I_{TE0} = AA^*T^2 \exp \left( \frac{-q\Phi_{b0}}{kT} \right)
\]  

(6.15)
this is called as thermionic emission saturation current and hence one can write equation 6.15 in the form of,

\[ \Phi_{b0} = \frac{kT}{q} \ln \frac{AA^*T^2}{I_{TE0}} \]  

(6.16)

Now, introducing a parameter 'n' such that \( l/n = 1 - \gamma \), equation 6.14 can be written as,

\[ I_{TE} = I_{TE0} \exp \left( \frac{qV}{\eta kT} \right) \left[ 1 - \exp \left( - \frac{qV}{kT} \right) \right] \]  

(6.17)

The one minus term in the square bracket ensures that the current is zero if no voltage is applied as in thermal equilibrium any motion of carriers is balanced by a motion of carriers in the opposite direction. The ideality factor (\( \eta \)) in equation 6.17 gives a measure of the quality of the junction which is highly process dependent. For an ideal Schottky junction, when \( \eta = 1 \) (or \( \gamma = 0 \)), equation 6.17 reduces to the case of pure thermionic emission-diffusion (equation 6.18). This mode of current transport is commonly referred to as the "thermionic emission" current [27, 28]. In practice, however, larger values for 'n' are obtained due to the presence of non-ideal effects or other contributing components to the total current through the junction.

Normally, the neutral region of the semiconductor, outside the depletion region and back ohmic contact, offers a series resistance (\( R_s \)) and so a significant voltage drop (= \( IR_s \)) occurs across it at large forward currents. This amounts to a reduction of the voltage across the barrier region from that actually applied to the terminals of the diode. This is accounted for by replacing \( V \) by \( V - IR_s \) in equation 6.18. The current equation then becomes,

\[ I_{TE} = I_{TE0} \exp \left( \frac{q(V-IR_s)}{\eta kT} \right) \left[ 1 - \exp \left( - \frac{q(V-IR_s)}{kT} \right) \right] \]  

(6.18)
6.3.1.4 Quantum mechanical tunneling

It may be possible for the electrons having energies below the barrier height to penetrate the barrier by quantum mechanical tunneling under certain conditions. One type is known as field emission and the other, thermionic field emission.

6.3.1.5 Field emission and thermionic field emission

As the concentration of the dopant is increased in the semiconductor, another mechanism for current flow across a metal - semiconductor interface becomes important. Here the width of the depletion layer decreases with increasing doping, probability of quantum mechanical tunneling of electrons through the barrier increases. At very high doping, the barrier can be thin enough to permit appreciable field emission at the bottom of the barrier. At moderately high doping, the barrier is somewhat wider. Hence, those electrons with sufficient thermal energy can tunnel near the top of the barrier to produce an appreciable current. This latter process is known as thermionic field emission. Field emission is independent of temperature, while thermionic field emission is temperature dependent.

The transmission probability \( P \) for an electron of energy \( E \) to successfully tunnel through a triangular shaped potential energy barrier with diffusion potential \( V_d \) is given by [26],

\[
P = \exp \left[ -\frac{2}{3} \frac{(qV_d - E)^{3/2}}{E_{00}(qV_d)^{1/2}} \right] \tag{6.19}
\]

\( E_{00} \) is a parameter, which is inherently related to material properties of the semiconductor and is very useful in determining the range of doping and temperature for which field emission, thermionic field emission or thermionic emission is valid [27]. \( E_{00} \) has the dimensions of energy divided by charge and is given by,
\[ E_{00} = \frac{1}{2} \hbar q \left[ \frac{N_A}{m^* \varepsilon_s} \right]^{\frac{1}{2}} \]  

\[ E_{00} = 1.85 \times 10^{-15} \left[ \frac{N_A}{m^* \varepsilon_s} \right]^{\frac{1}{2}} eV \]  

Where 'm*' (=\(m,m\)) is the effective mass of electrons in the semiconductor, '\(\varepsilon_s\)' is permittivity and the concentration 'N_A (=\(\eta\) in Chapter 5)' is expressed in \(m^3\).

Assuming uniform concentration 'N_A', complete depletion of the space charge region and ignoring image force lowering, analytical expression for the I-V characteristics as given by Padovani and Stratton can be summarized as follows.

1. At very high doping or at low temperatures, where \(E_{00}>>kT\),

\[ I_{FE} = I_{0FE} \exp \left( \frac{qV}{E_{00}} \right) \]  

where, 'I_{FE}' is resultant current due to field emission for an applied bias, 'I_{0FE}' is field emission saturation current.

2. At moderate temperatures and doping levels where \(E_{00} \approx kT\),

\[ I_{TFE} = I_{0TFE} \exp \left( \frac{qV}{E_{0}} \right) \]  

where, 'I_{TFE}' is resultant current due to thermionic field emission for an applied bias V, 'I_{0TFE}' is thermionic field emission saturation current.

\[ E_0 = E_{00} \coth \left( \frac{E_{00}}{kT} \right) \]  

3. At high temperatures or low doping where \(E_{00}<<kT\), the carriers are thermionically emitted over the barrier and the current can be expressed as,

\[ I_{TE} = I_{0TE} \exp \left( \frac{qV}{\eta kT} \right) \]  

where, 'I_{TE}' is resultant current due to thermionic emission for an applied bias 'V', 'I_{0TE}' is thermionic emission saturation current.
In brief, taking the expressions for the three dominant mechanisms, the current is determined by (29),

\[ \exp\left(\frac{\Phi_b}{kT}\right) \] for Thermionic Emission (TE) \hspace{1cm} (6.26)

\[ \exp\left(\frac{\Phi_b}{E_{00}\coth(E_0/kT)}\right) \] for Thermionic Field Emission (TFE) \hspace{1cm} (6.27)

\[ \exp\left(\frac{\Phi_b}{E_{00}}\right) \] for Field Emission (FE) \hspace{1cm} (6.28)

Thus, for \( kT/E_{00} \ll 1 \), TE dominates;

for \( kT/E_{00} \gg 1 \), FE dominates; \hspace{1cm} (6.29)

for \( kT/E_{00} \approx 1 \), TFE dominates. \hspace{1cm} (6.30)

Hence, FE and TFE are caused due to quantum mechanical tunneling of electrons through the barrier. It may be noted that both TE and TFE are temperature dependent while FE is not.

6.3.2 Other Current Transport Mechanisms

In addition to thermionic emission and quantum mechanical tunneling, there are a number of other effects and current transport mechanisms, which also contribute to the electrical properties of the metal-semiconductor interface albeit to a much lesser extent. These include generation - recombination effects, leakage and barrier inhomogeneity etc.

6.3.2.1 Generation-recombination effects

Generation - recombination effects within the depletion region give rise to a parallel component to the thermionic emission current transport mechanism. This is particularly significant at moderately low temperatures.
The current contribution, \( I_{GR} \), due to this mechanism can be represented by [28],

\[
I_{GR} = I_{GRO} \left[ \exp \left( \frac{qV}{2kT} \right) - 1 \right]
\]

where,

\[
I_{GR} = \frac{qniAdW}{2\tau}
\]

\[
n_i = (N_cN_v)^{1/2} \exp \left( -\frac{E_g}{2kT} \right)
\]

\[
N_v = 2 \left( \frac{2\pi m^*_h kT}{\hbar^2} \right)^{3/2}
\]

where, \( I_{GRO} \) is generation-recombination saturation current, \( \nu \) is thickness of the depletion region, \( \tau \) is carrier effective lifetime within the depletion region, \( n_i \) is intrinsic carrier concentration, \( N_c \) is effective conduction band density of states and \( N_v \) is effective valence band density of states.

6.3.2.2 Barrier lowering due to image force effects

The electric field in the semiconductor may be considered to be identical to that of the carrier itself and another carrier with opposite charge at equal distance but on the opposite side of the interface (figure 6.6). Consider an electron, in vacuum, at a distance \( x \) from a metal surface. A positive charge will be induced on the metal at a distance \( -x \) from its surface. This charge is called the image charge and will give rise to an attractive force between the two, known as the image force. This force has associated with it an image potential energy which corresponds to the potential energy of an electron at a distance \( \pm x \) from the metal.

When an external field, \( E_{ext} \), is applied this electric field causes the image-force-induced lowering of the potential energy for charge carrier emission [26]. Thus at high fields, the Schottky barrier is considerably lowered.
The difference between the actual surface charges and the image charge is that the fields in the metal are distinctly different. The image charge concept is justified on the basis that the electric field lines are perpendicular to the surface of a perfect conductor, so that, in the case of a flat interface, the mirror image of the field lines provides continuous field lines across the interface. The amount of reduction due to the induced image force, $\Delta\Phi_{imf}$, is given by Rhoderick et al. [2],

$$\Phi_{imf} = \left(\frac{q^{3}N_{A}}{8\pi\varepsilon_{0}^{2}}\right)\left(\Phi_{b0} - V - \xi - \frac{kT}{q}\right)^{1/4}$$  \hspace{1cm} (6.36)

6.3.2.3 Leakage current

The leakage current, $I_{L}$, is another parallel component of the total current. It is caused by surface leakage and can usually be significantly reduced by various designs and fabrication techniques such as guard ring structure etc. In practice, it is the component, which appears to by-pass the metal/semiconductor interface altogether and is often thought of as a large leakage resistor, $R'_{L}$, in parallel to it. Thus the leakage current can be expressed as,

$$I_{L} = \frac{V - IR_{L}}{R_{L}}$$ \hspace{1cm} (6.37)
6.3.2.4 Barrier height inhomogeneity

It has been reported that the increase in ideality factors ($\eta > 1$) of abrupt Schottky contacts without interfacial oxide layers between the metal and a moderately doped semiconductor may be due to the spatial / lateral inhomogeneity at the metal – semiconductor interface (figure 6.7). This inhomogeneity can be explained by using an analytical potential fluctuation model based on spatially inhomogeneous barrier height at the interface [30, 31].

![Figure 6.7: The band diagram of an inhomogeneous Schottky contact under bias ’$V_a$’.](image)

Suppose that the distribution of the barrier height is Gaussian in character [$P(\Phi_b)$] with a standard deviation '$\sigma_b'$. So the Schottky barrier '$\Phi_b$' depend on the location within the interface plane with this barrier distribution '$P(\Phi_b)$', around the mean Schottky barrier $\Phi_b$. The Gaussian barrier distribution can be expressed as [30, 31],

$$P(\Phi_b) = \frac{1}{\sigma_b \sqrt{2\pi}} \exp \left( \frac{\Phi_b - \Phi_{b0}}{2\sigma_b^2} \right)^2$$  \hspace{1cm} (6.38)

Now, the current across a homogeneous Schottky barrier at a forward bias '$V$', when $V > 3kT/q$, based on the thermionic emission theory is given by [2],

$$I = AA^*T^2 \exp \left( -\frac{q\Phi_{b0}}{kT} \right) \left[ \exp \left( \frac{q(V-IR_s)}{\eta kT} \right) \right]$$  \hspace{1cm} (6.39)

According to Werner and Guttler [30, 31] the net current '$I$' through an inhomogeneous Schottky contact is controlled by the effective /
apparent barrier height $\Phi_{ap}$ and the corresponding ideality factor is $\eta_{ap}$. For most non homogeneous Schottky diodes, the current – voltage characteristics can still be well described with the help of the thermionic emission theory, except that $\Phi_{bo}$ and $\eta$ should be replaced by $\Phi_{ap}$ and $\eta_{ap}$ in equation 6.39.

Considering equations 6.38 and 6.39 to describe the inhomogeneities of abrupt Schottky junctions, the total current $I'$ can be expressed as,

$$I(V) = \int_{-\infty}^{+\infty} I(\Phi_b, V) P(\Phi_b) d\Phi$$

(6.40)

Performing this integration from $-\infty$ to $+\infty$,

$$I(V) = A A^* T^2 \times \exp \left[ - \frac{q}{kT} \left( \Phi_b - \frac{q\sigma_0^2}{2kT} \right) \right] \times \exp \left( \frac{qV}{\eta_{ap} kT} \right) \left[ 1 - \exp \left( - \frac{qV}{kT} \right) \right]$$

(6.41)

With,

$$I_0 = A A^* T^2 \exp \left( - \frac{q\Phi_{ap}}{kT} \right)$$

(6.42)

The apparent barrier height $\Phi_{ap}$ and ideality factor ($\eta_{ap}$) at zero bias are given by \cite{33,34},

$$\Phi_{ap} = \Phi_{bo}(T = 0) - \frac{q\sigma_0^2}{2kT}$$

(6.43)

$$\left( \frac{1}{\eta_{ap}} - 1 \right) = \rho_2 - \frac{q\rho_3}{2kT}$$

(6.44)

The temperature dependence of $\sigma_3$ is usually small and thus can be neglected. However, $\sigma_3$ and $\Phi_{bo}$ are assumed to be linearly bias dependent on Gaussian parameters such that,

$$\Phi_b = \Phi_{bo} + \rho_2 V$$

(6.45)

$$\sigma_3 = \sigma_0 + \rho_3 V$$

(6.46)

where, $\rho_2$ and $\rho_3$ are the voltage coefficients that may depend on temperature and they quantify the voltage deformation on the barrier height distribution\cite{32,34}. Thus, the standard deviation $\sigma_3$ and hence the parameter $\sigma_0$ can be considered as a measure of the barrier inhomogeneity.
6.4 Experimental
6.4.1 Choice Of Material

Because of the importance of rectifying metal-semiconductor (MS) contacts in electronics, optoelectronics and microwave devices, which has been discussed earlier, it is necessary to study new MS structures for more efficient and fast rectifiers [35]. At the same time the authentic extraction of their characterizing parameters and correct understanding of their physical behaviour is absolutely important from both theoretical and application point of view. Although great efforts have gone into providing a systematic study of this seemingly simple system over the years, a complete determination of the detailed mechanisms responsible for Schottky barrier formation and charge transport across it have still proven quite elusive [2,12-14,26,31,36-42]. This was limited due to difference in the characteristics of the real system with that of the ideal one. Perhaps the reason for this may be due to the multiplicity of charge transport mechanisms that come into play at the interface instead of a single mechanism along with other physical and chemical interface situations those arise in practical diodes. This makes the interface a very complex region, which intern reflects on their terminal physical characteristics. Significant amount of work is still being made on ways and means to arrive at a more realistic interpretation of the characterizing parameters of real Schottky diodes [43-46].

In this context, aluminum deposited WSe₂ Schottky diodes have been fabricated and analyzed. According to Schottky's work-function difference model, the barrier height comes out to be 0.92eV with aluminum contacts. The reasons behind the choice of Al/pWSe₂ systems are based on the importance of WSe₂ that have already been pointed out in chapter 1. They include;
(i) The chemical inertness of the basal plane of the TMDC's where WSe$_2$ is a member, which makes it ideal active region for the fabrication of Schottky barrier devices [47].

(ii) Very limited numbers of current-voltage investigations were made on pWSe$_2$ based Schottky barrier systems over wide temperature ranges [48].

(iii) Most of the earlier reported work is based on Schottky barrier devices fabricated by deposition of metal thin films on TMDC single crystals, and till today there is no report on thin film Schottky diode based on WSe$_2$ thin films.

Aluminum (Al) is the most plentiful metal in the earth crust and never occurs in the free form. It is obtained by electrolysis from bauxite (Al$_2$O$_3$). Al is silvery, light weight, non-magnetic, non-sparking, malleable metal with atomic number 13. It has cubic face centered structure with atomic radius of 1.82Å and atomic volume of 10$\text{cm}^3$/mole. The electron work function of Al is 4.28eV and the melting point is 933.4K. Its electric and thermal conductivities are 0.377 * 10$^6$ $\Omega$.cm and 2.37 W/cm K respectively. Its density is 2.702 g/cc at 300K and the coefficient of linear thermal expansion is $2.39 \times 10^{-7}$ cm/cm/°C (0 °C) [49].

In general, several investigations have been made on TMDC's of MX$_2$ type with respect to Schottky barrier formation. Most of the work has been confined to MoS$_2$. Lince et.al.[50] studied Mn, Ti, V, Rh, Pd, In, Fe, Co, Au, Al and Ag on natural MoS$_2$ crystals. Among these, Mn was considered to lead to a surface reaction. Ti was almost oxidized during the experiment and hence has not been discussed further. In the subsequent studies a reactive interface with Fe and Mn on MoS$_2$ [51-53] has been observed. On the basis of Low Energy Electron Diffraction (LEED), auger spectroscopy and work function difference model, it has been reported Fe is reactive [54] while Ni and Pd are non-reactive [55,56]. Soft X-ray Photoelectron Spectroscopy (SXPS) studies on Cu, In, Ti and Mg by Mc. Govern et.al. [57] indicate that Cu and In do not react whereas Ti and Mg do react. In their study, in Al assumed to be
reactive, but no reaction could be observed with SXPS. Bortz et.al. [58] studied Au and Cu on MoTe$_2$ and WTe$_2$ which have chemically similar van der Waal's surfaces as a test of various models of heterogeneous nucleation. Different nucleation behaviours on the surfaces are observed and are found to be caused by the structural differences between MoTe$_2$ and WTe$_2$.

Regarding WSe$_2$ Schottky interfaces, various studies have been carried out in the past by different groups of researchers with different goals. In the work on the intercalation of metals with WSe$_2$, there was no reaction detected with Cu, Ag, Au and In whereas intercalated Na and K form a new bulk phase [59].

The adsorption of Cs on cleaved and Ar$^+$ sputtered WSe$_2$ surfaces at low temperatures (LT) and room temperature (RT) has been studied by LEED and photoemission spectroscopy using synchrotron radiation (SXPS) [60]. At low coverage, Cs is absorbed in an ionic state, Cs$^+$, whereas at high coverage, it forms metallic clusters. It has also been reported that clustering is stronger at room temperature than at low temperature. At low coverage (<0.1ML) strong band bending is observed which is again reduced at high temperature. In the case of Pt on WSe$_2$, chemical reaction is observed at the interface and the reactivity is attributed to the high condensation energy of the deposited metal rather than to a possible metal exchange reaction [59].

Jagermann et.al. [61] investigated the deposition of Cu/Ag on $p$ type WSe$_2$ interface with X-ray Photoelectron Spectroscopy (XPS) and LEED. There was no evidence for a surface reaction but they showed significant reduction of surface photo-voltage which was not according to TE model of Schottky barriers. The authors suggested an alternative interface model considering $n$ type doping of the semiconductor interface due to intercalation of the adsorbed metal atoms. This conclusion is supported by $I$-$V$ investigation of the Cu/$p$WSe$_2$ interface by Clemen et.al. [62]. Klein et.al. [63]
extended the investigation of Cu/pWSe$_2$ contacts with ultra-high vacuum (UHV) cleaved WSe$_2$ surfaces using high resolution photoelectron spectroscopy at few low temperatures. Here also, the studied interfaces show no interface reactions. The growth of the metal shows 3D islands at RT and continuous films at 85 K substrate temperature. They also observed non-ideal photo-voltages even for the case of the clustered interface, which is in support of the previous studies [62]. The authors concluded the diffusion of Cu into the space charge layer as the cause for the reduction of the photo-voltage which is similar to the interface of Ag with WSe$_2$. In contrast to Cu/pWSe$_2$ and Ag/pWSe$_2$, Au/pWSe$_2$ interface shows ideal photo-voltages in the case of a discontinuous metallic film and they concluded that thermionic emission is the dominant photo-carrier loss mechanism in this case [63].

Schellenberger and coworkers [64] reported that UHV deposited alkali metal atoms may be intercalated in $p$ type WSe$_2$ with electron transfer from the alkali metal to the conduction band of the host and the reactivity is discussed in terms of bulk thermodynamics. They extended the same work to RT as well as low temperature and stated that at room temperature, the alkali metal is intercalated and a degenerate $n$ type doped surface layer is formed, and the barrier resembles a $p - n^+$ junction. At low temperature, the Na intercalation is frozen out and a Na over layer is formed.

Studies on In/pWSe$_2$ by photoemission spectroscopy and SEM to investigate the lateral inhomogeneity aspects as well as the interface reaction with the deposited metal revealed that there is no such reaction at the interface with indium [48]. STM investigations on evaporation of sub-monolayer amounts of gold onto cleaved surfaces of WSe$_2$ revealed the formation of nano meter sized gold islands [65]. Nicolay et al. [66] reported that the deposition of Au and Ag on WSe$_2$ at 500Å leads to epitaxial growth and the growth is still preserved at deposition rates several orders of magnitude higher than previously reported.
The intercalation reaction has attracted technological interest because of its possible use in high energy density batteries [67]. The intercalation of alkali metals in layered compounds is important in heterogeneous catalysis and in application for solar energy conversion and electrochemical energy storage [68-72]. Nowadays, investigations of the opposite effect, deintercalation is also being made since it may affect the stability of intercalated systems when used in the form of devices. In this context, the reports on deintercalation of alkali atoms caused by electronegative adsorbates such as oxygens and halogens on WSe₂ host are noticeable [67, 73, 74]. In addition, Achamma et al [75, 76] have also reported the Al/pWSe₂ and In/pWSe₂ Schottky diodes and extracts the various diode parameters in wide temperature range. Again these Schottky diode systems are based on DVT grown single crystals of WSe₂.

Most of these studies have been focused on the efforts to find out device parameters at room temperature and at one or two low temperatures. But it is apparent that the extraction of device parameters from only room temperature and a few low temperature measurement data, may not lead to precise values. Therefore, it has been thought to make investigations of aluminum evaporated Schottky contacts on WSe₂ over a wide range of temperatures for a more precise analysis of device parameters adopting I-V measurement method. This will not only be helpful in obtaining more accuracy of device parameters but will also be useful to study the dominant conduction mechanisms in different temperature regions.

6.4.2 Fabrication Of Al/pWSe₂ Thin Film Schottky Diodes

WSe₂ semiconducting thin films of three different thicknesses (1000Å, 1732Å and 3226Å) were deposited by ė - beam evaporation technique for the fabrication of Schottky barrier devices, as described in chapter 2.

The metals which have been used for fabricating diodes are aluminum and silver for the present investigation. Since silver contacts with
WSe₂ thin films showed that the MS interface is ohmic in nature for p-WSe₂ from the Hall effect study as discussed in chapter 5. Hence metals with lower work function compared to silver have been selected i.e. aluminum.

In present investigation metal thin films were deposited using thermal evaporation technique as discussed in chapter 2. In order to get evaporated metals on a confined area on the WSe₂ thin film; thin films were masked with specially designed thin metal sheet mask having the opening area of 1 cm². After reaching a vacuum level of the order of 10⁻⁶ torr, pure aluminum metal was evaporated to achieve thickness of 5000Å from a W-helical boat onto the pre-deposited WSe₂ thin films surface. The rate of evaporation was kept very low (2Å/sec⁻¹) in order to make the deposition uniform over the whole area. Figure 6.8(a) and (b) shows the block diagram and photograph of prepared diode.

![Figure 6.8: (a) Block diagram (b) prepared Al/pWSe₂ thin film Schottky diode.](image)

Front Schottky contacts with evaporated aluminum regions were taken by bonding low strain thin Ag alloy wires (LakeShore sample wires PN 671-260) using Ag paste (Eltec-1228C). Since silver gives good ohmic contact to p-WSe₂ the ohmic contacts were drawn again by bonding Ag alloy wires (LakeShore sample wires PN 671-260) using Ag paste (Eltec-1228C) onto the surface of WSe₂ thin films. The whole assembly was then mounted on the sample mount stage inside the Closed Cycle Refrigerator (CCR 75014) and contacts were soldered for external connections as described in chapter 5 for the low temperature Hall effect study.
6.4.3 Current -Voltage - Temperature Measurements

There are various methods that can be used for the determination of Schottky barrier parameters, e.g. Current - voltage (I-V) analysis, Capacitor - voltage (C-V) analysis, Photoelectron spectroscopy etc. Amongst these methods I-V is the basic and simplest of all methods since it involves direct measurement of current and voltage and provides first-hand information about the nature of the developed barriers across the interface. In the present investigation the I-V data were acquired using Keithley - Semiconductor Characterization System SCS-4200.

6.4.3.1 Keithley 4200 semiconductor characterization system (SCS)

The Model 4200-SCS provides a total system solution for DC characterization of semiconductor devices, test structures and materials. This advanced parameter analyzer provides intuitive and sophisticated capabilities for semiconductor device characterization. The Model 4200-SCS combines unprecedented measurement speed and accuracy with an embedded Windows NT-based PC and Keithley Interactive Test Environment (KITE) to provide a powerful single-box solution. KITE allows users to gain familiarity quickly with tasks such as managing tests and results and generating reports. Sophisticated and simple test sequencing and external instrument drives simplify performing automated device and wafer testing. The Keithley Model 4200 Semiconductor Characterization System (SCS) [77] can be programmed to characterize I-V and C-V of semiconductor devices and test structures, using up to eight Source-Measure Units (SMUs). A variety of supported external components enhance the capabilities.

The exceptional low current performance of the Model 4200-SCS makes it the perfect solution for research studies of single electron transistors (SETs), molecular electronic devices and other nano-electronic devices that requires I-V characterization. Figure 6.9 shows the complete block diagram of Keithley Model 4200 Semiconductor Characterization System (SCS).
The variation of current and voltage with temperature were accomplished by liquid helium close cycle refrigerator controlled by LakeShore temperature controller. The schematic representation of this has also been discussed in chapter 5. Keithley 4200 - Semiconductor Characterization System (SCS) is a versatile instrument, in which the start, stop and step for current or voltage values of the SMU’s are assigned initially. The switching of the terminals is to be connected to the device can be done using switch matrix unit coupled to the respective SMU’s. When these variables were set ready, temperature was also set constant at the desired level using LakeShore temperature controller and the data obtained were stored as spreadsheet in the computer memory. The experiment was repeated at different temperatures from room temperature to cryogenic temperature of around 100K in steps of 10K. The results can be observed either in the table form or in the graphical form and may be edited as needed. It also allows saving comma-separated values in text files that can be easily imported into most analysis and spreadsheet programs such as excel or origin. Provisions are also there to save the test configuration being done.

In the present investigation, adopting $I-V$ as the measurement technique, various Schottky barrier parameters were calculated by four different methods. They are [2, 4, 78, 79]:

Figure 6.9: Block diagram of Keithley Semiconductor Characterization System Model 4200-SCS.
(i) \( V \) versus \( \text{Ln} I \) plot

(ii) \( V \) versus \( \text{Ln} \{I/|I-\exp(-qV/kT)|\} \) plot

(iii) Norde method \( F(V) \) vs. \( V \) plot

(iv) Cheung method \( H(I) \) vs. \( I \) plot

\( V \) versus \( \text{Ln} I \) plot:

The plot of \( V \) vs. \( \text{Ln} I \) yield a straight line for \( V > (3kT/q) \) and this may cover two to three decades of change in current at low forward bias voltages. The intercept on \( y\)-axis of this straight line gives the value of saturation current \( 'I_d' \). From this \( '\Phi_{b0}' \) can be calculated using equation,

\[
\Phi_{b0} = \frac{kT}{q} \ln \left( \frac{AA^*T^2}{I_0} \right) \quad (6.47)
\]

Also from the slope of the \( V \) vs. \( \text{Ln} I \) plot, the ideality factor \( '\eta' \) can be calculated as,

\[
\eta = \frac{q}{kT} \frac{dV}{d(\text{Ln}I)} = \frac{q}{kT} \times \frac{1}{\text{slope}} \quad (6.48)
\]

The more realistic representation of barrier potential is done if the bands are flat across the interface. Under this condition the barrier potential as designated by flat band barrier height and is given by [80],

\[
\Phi_{bf} = \eta \Phi_{b0} - (\eta - 1) \frac{kT}{q} \ln \left[ \frac{N_V}{N_A} \right] \quad (6.49)
\]

Here \( 'N_A' \) is the carrier concentration \( (\eta) \) of WSe\(_2\) thin film obtained from Hall effect measurement as described in chapter 5. \( 'N_V' \) is the effective density of states in the valance band, which is given by [2],

\[
N_V = 2 \left[ \frac{2\pi m^*_e kT}{\hbar^2} \right]^{3/2} \quad (6.50)
\]
where, \( m_{\text{e}} \) is the effective mass of WSe\(_2\) and is given by 0.23\( m_0 \) [63, 75, 76]. Here \( m_0 \) is the rest mass of hole (9.1x10\(^{-31}\) kg), \( k' \) is Boltzmann’s constant (1.3808 x 10\(^{-23}\) J/K or 8.6175 x 10\(^{-5}\)eV), \( T \) is the temperature in K and \( h' \) is Plank’s constant. Using these values \( N_l \) comes out to be in the order of 10\(^{24}\) (m\(^{-3}\)).

\( V \) versus \( \ln \left( I / [1 - \exp(-qV/kT)] \right) \) Plot:

The analysis with \( V \) vs. \( \ln I \) plots gives reliable values of barrier parameters if:

(i) It is a straight line covering two to three decades of current change and

(ii) It should fit to several low forward voltage observation points. But in many practical devices this plot is neither a straight line because of large series resistance nor it covers much observed values of \( V \) and \( I \). Thus a \( V \) versus \( \ln I/[1-\exp(-qV/kT)] \) plot is made at each temperature mainly to cover the wide bias range including the regime \( V < (3kT/q) \) where the \( 1 - \exp(-qV/kT) \) factor is effective. The straight line portion of such a plot corresponds to the thermionic emission diffusion current with the intercept giving saturation current \( I_0 \). The slope of this line gives the ideality factor (\( \eta \)) according to the following equation,

\[
\eta = \frac{q}{kT} \times \frac{1}{\text{slope}} = \frac{q}{kT} \left[ \frac{dV}{d\ln \left( \frac{I}{1-\exp(-qV/kT)} \right)} \right]
\]

and \( \Phi_{\text{bo}} \) using equation 6.47.

\( \triangleright \) Norde method: \( F(V) \) vs. \( V \) Plot:

The series resistance is a very important parameter of Schottky diode. The resistance of the Schottky contact is the sum total resistance value of the series resistance \( R_S \) and parallel resistance of barrier region in the direction of current flow. Because of series high resistance, it is difficult to evaluate the accurate barrier height from the both standard \( \ln I \) vs. \( V \) method. Norde [78] proposed an alternative method to determine values of barrier
height of Schottky diode even for high series resistance. In this method Norde function $F(V)$ defined as,

$$F(V) = \frac{V}{2} - \frac{kT}{q} \ln \left( \frac{I}{AA^*T^2} \right)$$

(6.52)

which is used to plot against forward bias voltage. This plot normally shows slopes of $+1/2$ and $-1/2$ on both the side of minimum value of function $F(V)$ called $F(V)_{\text{minimum}}$. The effective Schottky barrier height is given by,

$$\Phi_b = F(V)_{\text{min}} + \frac{V_{\text{min}}}{2} - \frac{kT}{q}$$

(6.53)

Here, $F(V)_{\text{min}}$ is the minimum value of $F(V)$, $V_{\text{min}}$ is the corresponding voltage, and $I_{0}$ is the corresponding current at $V=V_{\text{min}}$, respectively, $A$ is the effective area of Schottky diode $(1cm^2)$ and $A^*$ is the Richardson constant $27.6 \ Acm^{-2}K^{-2}$ for $pWSe_2$ [75, 76].

Cheung method: $H(I)$ vs. $I$ Plot:

The Schottky diode parameters such as the barrier height $\phi_b$ and the ideality factor $\eta$ were also achieved using a method developed by Cheung and Cheung [79]. Cheung’s functions can be written as follows,

$$\frac{dV}{d(\ln I)} = IR_s + \eta \frac{kT}{q}$$

(6.54)

$$H(I) = V - \eta \left( \frac{kT}{q} \right) \ln \left( \frac{I}{AA^*T^2} \right)$$

(6.55)

$$H(I) = IR_s + \eta \Phi_b$$

(6.56)

where, $\phi_{\text{ho}}$ is the zero bias barrier height extracted from the lower – voltage part of forward $I$–$V$ characteristics, ‘$A$’ is the effective area of Schottky diode $(1cm^2)$ and ‘$A^*$’ is the Richardson constant $27.6 \ Acm^{-2}K^{-2}$ for $pWSe_2$ [75, 76].

Using equation 6.54 and from the plot of $dV/d(\ln(I))$ vs. $I$, one can obtain the value of barrier height ($\phi_b$) as the $y$ – axis intercept. Similarly using equation 6.56 and from the plot of $H(I)$ vs. $I$ one can obtain the value of barrier height ($\phi_b$) as the $y$ – axis intercept.
In order to study the charge transport mechanism in the WSe$_2$ thin film based Schottky diodes, three diodes with different thin film thickness (i.e., Al(5000Å)/pWSe$_2$(1000Å), Al(5000Å)/pWSe$_2$(1732Å) and Al(5000Å)/pWSe$_2$(3226Å)) were prepared for their analysis. Here Al(5000Å)/pWSe$_2$(1000Å) Schottky diode is only studied at room temperature and rest of them are characterized in wide temperature range 310K to 100K.

The total current passing through a Schottky barrier device may be because of one or a combination of several conduction mechanisms as outlined in beginning of this chapter. Generally identification of a dominant charge transport mechanism can be done by the comparison of the magnitude of characteristic energy $E_0$ with $kT/q$. The value of $E_0$ can be calculated from the equation 6.21. Since $N_A$ is a temperature dependent parameter the value of $E_0$ calculated for different region and the variation of $E_0$ for different values of $N_A$ is plotted in figure 6.10 for Al(5000Å)/pWSe$_2$(1732Å) and Al(5000Å)/pWSe$_2$(3226Å) Schottky barrier diodes.

Figures 6.11 shows room temperature I-V curves of Al(5kÅ)/pWSe$_2$(1kÅ), Al(5kÅ)/pWSe$_2$(1.732kÅ) and Al(5kÅ)/pWSe$_2$(3.226kÅ) respectively and they are showing good rectification ratio. A comparative study of their barrier height and ideality factor is shown in table 6.1. Figure 6.12(a) and (b) represent the forward and reverse bias LnI – V characteristics (known as Gamma plot) for prepared Al(5kÅ)/pWSe$_2$(1.7kÅ) and Al(5kÅ)/pWSe$_2$(3.2kÅ) Schottky diode at different temperatures. The values of saturation current $I_0$, zero bias barrier height $\Phi_0$, ideality factor $\eta$ and flat band barrier height $\Phi_f$ evaluated using equation 6.47, 6.48 and 6.49 with the help of these plots and given in tables 6.2.
Figure 6.10: Variation of $E_{oo}$ as a function of change in $N_v$ observed at different temperature using Hall effect measurement for (a) Al(5kÅ)/pWSe2(1.732kÅ) (b) Al(5kÅ)/pWSe2(3.226kÅ).

Table 6.1: The room temperature Schottky diode parameters of all prepared diodes.

<table>
<thead>
<tr>
<th>Prepared Diode</th>
<th>$I_0$</th>
<th>$\Phi_{be}$</th>
<th>$\eta$</th>
<th>Rectification Ratio (@ ±1V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(5kÅ)/pWSe2(1kÅ)</td>
<td>1.31\times10^{-9}</td>
<td>0.67</td>
<td>1.49</td>
<td>107</td>
</tr>
<tr>
<td>Al(5kÅ)/pWSe2(1.732kÅ)</td>
<td>6.14\times10^{-6}</td>
<td>0.69</td>
<td>1.07</td>
<td>17</td>
</tr>
<tr>
<td>Al(5kÅ)/pWSe2(3.226kÅ)</td>
<td>7.37\times10^{-7}</td>
<td>0.75</td>
<td>1.04</td>
<td>132</td>
</tr>
</tbody>
</table>
Figure 6.11: Room temperature $I$-$V$ curves of all three prepared diodes.

Figure 6.12: Temperature dependent forward and reverse bias $\ln I$-$V$ (Gamma Plot) characteristics for prepared Schottky diodes (a) $\text{Al}(5\text{kÅ})/\text{pWSe}_2(1.732\text{kÅ})$, (b) $\text{Al}(5\text{kÅ})/\text{pWSe}_2(3.226\text{kÅ})$. 
The $V$ against $\ln[I/1-\exp(-qV/kT)]$ graph for these Schottky barrier diodes at different temperatures are shown in figure 6.13. The parameters extracted using this method is tabulated in table 6.2.

To find out the accurate value of barrier height of prepared Schottky diodes, a method proposed by Norde [78] and using equation 6.52 and 6.53, a plot of $F(V)$ vs. $V$ is drawn as shown in figure 6.14 for three prepared thin film Schottky diodes at different temperatures.

From the $F(V)$ vs. $V$ plot the value of $\Phi_b$ for all three prepared diodes have been determined as mentioned in table 6.2.

To support the Norde method, the Cheung method [79] is also used to determine the barrier height of prepared thin film Schottky diodes. Using equation 6.54, 6.55 and 6.56, the $dV/d(lnI)$ vs. $I$ and $H(I)$ vs. $I$ plots were obtained as shown in figures 6.15 and 6.16 respectively. The values of ideality factor and barrier height from equation 6.54 and 6.56 were obtained and shown in table 6.2.

The dependence of barrier height and ideality factor on temperature is shown in figures 6.17(a), (b) for Al(5000Å)/pWSe2(1732Å) and Al(5000Å)/pWSe2(3226Å) Schottky diode. It has been observed that the ideality factor increases with decrease in temperature and its value increases from: 1.07 at 300K to 3.30 at 100K (for Al(5000Å)/pWSe2(1732Å)), 1.04 at 300K to 3.23 at 100K (for Al(5000Å)/pWSe2(3226Å)). On the other hand, the variation of zero bias barrier height $\Phi_{0b}$ and flat band barrier height $\Phi_f$, as a function of temperature is shown in figures 6.17(a), (b) which shows that both $\Phi_{0b}$ and $\Phi_f$ decrease with the fall in temperature. The zero bias barrier height decreases with decrease in temperature and its value at 300K is 0.69eV which becomes 0.21eV at 100K (for Al(5000Å)/pWSe2(1732Å)), and that is 0.74eV to 0.22eV for Al(5000Å)/pWSe2(3226Å)). Similarly, flat band barrier height decreases with decrease in temperature and its value at 300K is 0.73eV which becomes 0.63eV at 100K (for Al(5000Å)/pWSe2(1732Å)), 0.77eV to 0.66eV for Al(5000Å)/pWSe2(3226Å)).
Figure 6.13: \( \ln(I/\exp(-qV/kT)) \) vs. \( V \) plot for (a) Al(5k\( \text{Å} \))/pWSe\(_2\)(1k\( \text{Å} \)), (b) Al(5k\( \text{Å} \))/pWSe\(_2\)(1.732k\( \text{Å} \)), (c) Al(5k\( \text{Å} \))/pWSe\(_2\)(322k\( \text{Å} \)) Schottky diodes at different temperatures.
Figure 6.14: $F(V)$ vs. $V$ plot obtained from forward bias $I - V$ characteristics of the (a) Al(5kÅ)/pWSe$_2$(1kÅ), (b) Al(5kÅ)/pWSe$_2$(1.732kÅ), (c) Al(5kÅ)/pWSe$_2$(3226kÅ) Schottky diodes at different temperatures.
Figure 6.15: The experimental $dV/d(LnI)$ vs. $I$ plot obtained from forward bias $I - V$ characteristics of the prepared thin film Schottky diode at different temperature (a) Al(5kÅ)/pWSe$_2$ (1kÅ), (b) Al(5kÅ)/pWSe$_2$ (1.732kÅ), (c) Al(5kÅ)/pWSe$_2$ (3.226kÅ).
Figure 6.16: The experimental $H(I)$ vs. $I$ plot obtained from forward bias $I - V$ characteristics of the prepared thin film Schottky diode at different temperature (a) Al(5kÅ)/\text{pWSe$_2$}(1kÅ), (b) Al(5kÅ)/\text{pWSe$_2$}(1.732kÅ), (c) \text{Al}(5kÅ)/\text{pWSe$_2$}(3.226kÅ).
Figure 6.17: Plot of ideality factor, zero-bias barrier height and flat band barrier height as a function of temperature for (a) Al(5kÅ)/pWSe$_2$(1.732kÅ), (b) Al(5kÅ)/pWSe$_2$(3.226kÅ).
Table 6.2(a): Comparative values of Al(5000 Å)/pWSe₂(1732 Å) Schottky diode parameters extracted using various methods.

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>LnI vs. V</th>
<th>Ln[I/(I-\exp(-qV/kT))] vs. V</th>
<th>F(V) vs. V</th>
<th>H(I) vs. I</th>
<th>Series Resistance (Ω)</th>
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<td>$\Phi_{bf}$ (eV)</td>
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<td>$I_0$ (A)</td>
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<td>$\eta$</td>
<td>$I_0$ (A)</td>
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Table 6.2(b): Comparative values of Al(5000Å)/pWSe_3(3226Å) Schottky diode parameters extracted using various methods.
Various factors may be responsible for these large variations observed in ideality factor and apparent (experimental) barrier height. The ideality factor is simply a manifestation of the barrier uniformity and it increases for an inhomogeneous barrier [81]. An apparent increase in ideality factor and decrease in BH at low temperature are possibly caused by some other effects such as inhomogeneity of thickness and composition of the layer, non-uniformity of the interfacial charges or the presence of any thin insulating layer between the metal and the semiconductor [13, 31, 32, 81-85].

Since the current transport across the MS interface is a temperature-activated process, at low temperature, the current will be dominated by the current through the patches of low barrier height. Therefore at low temperature, electrons are able to overcome the lower barriers, and hence current transport will be dominated by current flowing through the patches of lower BH and resulting in to larger ideality factor. As the temperature increases, more and more electrons have sufficient energy to overcome the higher barriers. As a result both BH and η are strongly dependent on temperature. Moreover, simulation studies of Freeouf et.al.[40] on mixed-phase Schottky contact reveal that, below a critical size, low BH region pinched off and high barrier remains effective.

Schmitsdorf et.al. [86, 87] used Tung's theoretical approach and they found a linear correlation between the experimental zero-bias BH and ideality factors η. Figures 6.18 (a) and (b) shows a plot of the experimental SBH as a function of the ideality factors dependent on temperature for prepared Schottky diode. As can be seen from the figure there is nearly linear relationship between the experimentally observed effective BHs and ideality factors of Al/pWSe₂ SBDs that is explained by lateral inhomogeneity of the BHs in the SBDs [13, 82].

From the plot one can see that the ideality factor η =1 has a homogeneous BH of 0.74eV (Al(5000Å)/pWSe₂(1732Å)) and 0.78eV
y = -0.0708x + 0.8514

The temperature dependency of flat band barrier height \( \Phi_{bf} \) can be understood by \[26\],

\[
\Phi_{bf} = \Phi_{bf}(T = 0) + \alpha T
\]  

(6.57)
where $\alpha$ is the temperature coefficient of the barrier height. If we draw the plot of $\Phi_{bf}$ vs. $T$ (figure 6.19), it will give us a straight line and the slope gives the value of temperature coefficient $\alpha = 5.43 \times 10^{-4}$ eVK$^{-1}$ for Al(5000Å)/pWSe$_2$(1732Å) Schottky diode and $\alpha = 5.28 \times 10^{-4}$ eVK$^{-1}$ for Al(5000Å)/pWSe$_2$(3226Å) Schottky diode. The intercept on $y$-axis represents the value of $\Phi_{bf} = 0.58eV$ for Al(5000Å)/pWSe$_2$(1732Å) and $\Phi_{bf} = 0.62eV$ for Al(5000Å)/pWSe$_2$(3226Å) Schottky diode at $T=0K$.

To determine the $\Phi_{bf}(0)$ in another way, equation 6.16 can be rewritten in the form,

$$\ln \left( \frac{I_0}{T^2} \right) = \ln (AA^*) - \frac{q\Phi_{bf}}{kT} \quad (6.58)$$

The plot based on the above equation, known as Richardson plot, should yield in principle a straight line with slope determining the activation energy $E_a (= \Phi_{bf}$ here) and the intercept at the ordinate giving the Richardson constant $A^*$ for a known diode area $A$. However, in present case the plot is acceptably linear up to 140K and 180K for Al(5000Å)/pWSe$_2$(1732Å) and Al(5000Å)/pWSe$_2$(3226Å) respectively and deviation below this may be due to non-dominance of thermionic emission. Figure 6.20(a) and (b) shows the plot of $\ln(I_0/T^2)$ vs.1000/$T$. Here the value of $A^*$ obtained from the intercept of the straight portion at the ordinate is equal to 24.86 $Acm^{-2}K^{-2}$ and 27.87 $Acm^{-2}K^{-2}$ for both Al(5000Å)/pWSe$_2$(1732Å) and Al(5000Å)/pWSe$_2$(3226Å) Schottky diodes respectively. These values are closer with earlier reported data [75, 76]. But the value of $\Phi_{bf}(T=0)$ is very much comparable with the one obtained from the flat band barrier height such as 0.45$eV$ and 0.68$eV$ for both Al(5000Å)/pWSe$_2$(1732Å) and Al(5000Å)/pWSe$_2$(3226Å) thin film Schottky diodes.

The variation of ideality factor $\eta'$ and the series resistance $R_s$ with temperature are shown in figures 6.17 & 6.21. The series resistance in Schottky diode is the total resistance outside the depletion layer and the
resistance of the contacts. The values of series resistance are found to be around several ohms at 300 K, though it increases with decrease in temperature. Similarly the value of 'η' also increases considerably at low temperature. The decrease of zero bias barrier height with decreasing temperature indicates that the decrease may be attributed to one or more of the following reasons:

![Graph showing the temperature dependence of flat-band barrier height](image)

**Figure 6.19:** The temperature dependence of flat-band barrier height for (a) Al(5kÅ)/pWSe₂(1.732kÅ), (b) Al(5kÅ)/pWSe₂(3.226kÅ).
Figure 6.20: Richardson plot of \( \ln(I/V) \) versus \( 1000/T \) for (a) Al(5000 Å)\( /p\)WSe₂(1732 Å), (b) Al(5000 Å)\( /p\)WSe₂(3226 Å) Schottky diode.

Figure 6.21: Series resistance of Schottky diode with temperature.
1. Interface states [68, 89, 90]
2. Inhomogeneous nature of the fabricated diode [13, 14, 31, 30, 86, 83, 91, 92]
3. Multiplicity of operative transport mechanisms [2, 4, 44, 88]

The high magnitude of ideality factor \( \eta \) also can be considered as an indication in this direction. Moreover, the linear part in \( V \) vs. \( \ln(I/I_{0} - e^{-qV/kT}) \) plot do not extend much in forward bias region especially at low temperatures. All these factors point out that the observed decrease in the barrier height with temperature need to be re-examined more closely, and the first step towards this is to assess the barrier height inhomogeneities using Gaussian distribution as describes in the following section.

### 6.4.4 Barrier Height Inhomogeneities

Recent days, deviation of \( I - V \) characteristics based on thermionic emission diffusion (TED) model of real Schottky diodes with ideal one has been successfully explained by the presence of the barrier height inhomogeneities [3, 4, 6, 41, 75, 76]. These inhomogeneities can be readily expected in \( WSe_2 \) based Schottky diodes due to its specific nature of surfaces, which may contain defects, steps, kinks, voids etc. Thus interfaces may contain potential fluctuations in the lateral plane on a length scale smaller than the width of space charge region making the interface electrically inhomogeneous in nature. The approach assumes a continuous spatial distribution of Schottky barrier height (SBH) and the total current across a Schottky diode is simply calculated by integrating the current determined by the ideal TED model with an individual barrier height and weighed by the distribution function (parallel conduction model). Using the well accepted Gaussian distribution; the total current is described approximately by an analytical expression similar to the TED theory with an apparent barrier height and an apparent ideality factor, both of which are temperature dependent. The approach can explain anomalous behaviors which are usually observed in the \( I - V \) characteristics, such as a decrease of SBH and an increase
of ideality factor with decreasing temperature, difference of SBH determined from \( I - V \) and \( C - V \) methods, non-linearity in the Richardson plot etc.

Nevertheless, it is well known that the van der Waal's planes of WSe\(_2\) contain non-idealities in the form of chalcogen vacancies and steps. The non-idealities in the deposited metal overlayer morphology (grain boundaries, clusters etc) would also strongly influence the evolution of Schottky barriers at such interfaces. Under these circumstances, we assume that the distribution of the SBH \( P(\Phi_b) \) in the present case is Gaussian in character with a mean value \( \overline{\Phi}_b \) and a standard deviation \( \sigma_s \), having the form \([13,30,31]\),

\[
P(\Phi_b) = \frac{1}{\sigma_s \sqrt{2\pi}} \exp \left[ \frac{(\Phi_b - \overline{\Phi}_b)^2}{2\sigma_s^2} \right]
\]

(6.59)

Where, \( 1/(\sigma_s \sqrt{2\pi}) \) is the normalization constant of the Gaussian barrier height distribution. Here the implicit assumption is that there exist a number of parallel diodes of different SBH on the same surface contributing to the current independently. The mean SBH \( \overline{\Phi}_b \) and the standard deviation \( \sigma_s \) may be bias dependent. Werner and Guttler \([30,31]\) suggested a linear bias dependence of \( \overline{\Phi}_b \) and a quadratic bias dependence of \( \sigma_s \). Chand and Kumar \([12,68]\) suggested both \( \overline{\Phi}_b \) and \( \sigma_s \) are linearly dependent on the bias voltage. For simplicity, here also a linear bias dependence of both \( \overline{\Phi}_b \) and \( \sigma_s \) are assumed; the temperature dependence of \( \sigma_s \) being usually small can thus be neglected \([3,4,6,41,75,76]\). So \( \overline{\Phi}_b \) and \( \sigma_s \) can be expressed as,

\[
\overline{\Phi}_b = \overline{\Phi}_{b0} + \rho_2 V
\]

(6.60)

\[
\sigma_s = \sigma_0 + \rho_3 V
\]

(6.61)

Here \( \overline{\Phi}_b \) is the mean SBH at zero bias and extrapolated towards zero temperature. \( \sigma_0 \) is the standard deviation at zero bias. \( \rho_2 \) and \( \rho_3 \) are voltage coefficients of \( \overline{\Phi}_b \) and \( \sigma_s \) respectively, that may depend on the temperature.
and they quantify the voltage deformation on the barrier height distribution. [3,4,6, 30, 31, 41,75,76].

The total current for any forward bias \( V \) is given by

\[
I(V) = \int_{-\infty}^{+\infty} I(\Phi_b, V) P(\Phi_b) \, d\Phi_b
\]

(6.62)

where, \( I(\Phi_b, V) \) is the current at a bias \( V \) for a barrier of \( \Phi_b \) based on the ideal TED model. Performing this integration by substituting the value of \( I \) from equation 6.20 and neglecting the term including \( \rho_2 e^2 V^2 \), we get,

\[
I(V) = I_0 \left( \exp \left( \frac{q(V-I R_S)}{\eta kT} \right) - 1 \right)
\]

(6.63)

Here \( I_0 \) is the saturation current given by,

\[
I(V) = \frac{A \alpha^*}{2} e^x \left( -\frac{q \Phi_{ap}}{kT} \right)
\]

(6.64)

\( \eta_{ap} \) and \( \Phi_{ap} \) are the apparent ideality factor and barrier height at zero bias respectively, and is given by [30, 31],

\[
\Phi_{ap} = \overline{\Phi}_b - \frac{q \sigma_0^2}{2kT}
\]

(6.65)

\[
\left( \frac{1}{\eta_{ap}} - 1 \right) = -\rho_2 + \frac{q \rho_3}{2kT}
\]

(6.66)

However, the distribution may differ for each bias voltage; hence a more general form of equation 6.42 can be expressed as,

\[
\Phi_{ap}(V) = \Phi_b(V) - \frac{q \sigma_0^2}{2kT}
\]

(6.67)

which holds for all biases including zero bias. Thus equation 6.65 is a special case of equation 6.76 when the applied bias \( V \) is zero. Since equation 6.64 gives \( \Phi_{ap} \) and \( \eta_{ap} \) which should in turn obey equations 6.65 and 6.66. Thus, the plot of \( \Phi_{ap} \) vs. \( q/2kT \) should be a straight line giving \( \overline{\Phi}_b \) and \( \sigma_0 \) from the intercept and slope respectively. The plot of \( \Phi_{ap} \) vs. \( q/2kT \) for the Al/pWSe_2...
diodes with thickness 1732Å and 3226Å of tungsten diselenide deposition on the thermally evaporated aluminum thin film is shown in figure 6.22(a) and (b). Here also the straight line portion is deviated below 200K.

Considering the linear regions of this plot, the values of mean zero bias barrier height ‘\( \Phi_{b0} \)' and ‘\( \sigma_0 \)' was evaluated and was found to be 0.80 eV and 0.056V respectively for Al(5000Å)/pWSe\(_2\)(1732Å) thin film Schottky diode and 0.85eV and 0.064V respectively for Al(5000Å)/pWSe\(_2\)(3226Å) thin film Schottky diode. By comparing the values of ‘\( \Phi_{b0} \)' and ‘\( \sigma_0 \)' parameters, the percentage of inhomogeneity was found to be 7.0% and 7.5% of the mean barrier height for Al(5000Å)/pWSe\(_2\)(1732Å) and Al(5000Å)/pWSe\(_2\)(3226Å) thin film Schottky diode respectively. Also, the temperature dependence of the ideality factor can be understood on the basis of equation 6.66 which indicates that the \( (\ln(n)/\eta_{np}) - 1 \) vs. \( q/2kt \) plot should give a straight line with a y-axis intercept and a slope dependence on the voltage coefficients ‘\( \rho_2 \)' and ‘\( \rho_3 \)' respectively. The plot of \( (\ln(n)/\eta_{np}) - 1 \) vs. \( q/2kt \) is also shown in figure 6.23.

Here again in figure 6.23, considering the linear fit region of 200K to 300K, the voltage coefficients ‘\( \rho_2 \)' and ‘\( \rho_3 \)' where observed as 0.62V and -0.04V respectively for Al(5000Å)/pWSe\(_2\)(1732Å) Schottky diode and for Al(5000Å)/pWSe\(_2\)(3226Å) Schottky diode ‘\( \rho_2 \)' and ‘\( \rho_3 \)' where observed as 0.67V and -0.04V. In order to investigate the voltage sensitivity of the distribution of barrier height and standard deviation, the representative values of ‘\( \Phi_b \)' and ‘\( \sigma_b \)' were calculated according to the equations 6.60 and 6.61 for two biases viz. 0.0V and 0.4V. The values of \( \sigma_b(0V) = \sigma_0 \) and \( \sigma_b(0.4V) \) are found to be 0.056V and 0.04V respectively for Al(5000Å)/pWSe\(_2\)(1732Å) Schottky diode. Similarly the values of \( \Phi_b(0V) = (\Phi_{b0}) \) and \( \Phi_b(0.4V) \) comes out to be 0.8eV and 1.05eV respectively for Al(5000Å)/pWSe\(_2\)(1732Å) Schottky diode. In the case of Al(5000Å)/pWSe\(_2\)(3226Å) Schottky diode the values of \( \sigma_b(0V) = \sigma_0 \) and \( \sigma_b(0.4V) \) are found to be 0.064V and 0.05V respectively and the values of \( \Phi_b(0V) = (\Phi_{b0}) \) and \( \Phi_b(0.4V) \) comes out to be 0.85eV and 1.12eV respectively.
Figure 6.22: Apparent barrier height vs. \( q/2kT \) curves for Schottky diode, 
(a) Al(5k\(\AA\))/pWSe\(_2\)(1.732k\(\AA\)), (b) Al(5k\(\AA\))/pWSe\(_2\)(3.226k\(\AA\)).
Figure 6.23: Apparent ideality factor vs. $q/2kT$ curves for Schottky diode, (a) Al(5000Å)/pWSe$_2$(1732Å), (b) Al(5000Å)/pWSe$_2$(3226Å).

It could be noted that the value of $\sigma_s(0\,\text{V})$ is higher than the value of $\sigma_s(0.4\,\text{V})$ and the value of mean barrier height of $\langle \Phi_b \rangle$ increases with bias in the case of both diodes. These results reveal that a bias voltage obviously
homogenizes the barrier height fluctuation. Inhomogeneous interface contains a mean distribution of low and high barrier heights. When the bias voltage increases the smaller barrier height regions get pinched off gradually on account of interaction between barriers. Thus, the effective barrier maxima may get shifted deeper into the semiconductor, homogenizing the Schottky barrier height distribution. However, at lower temperatures these low barrier regions are more effective resulting in lower barrier heights.

Taking all the above facts into consideration, the Richardson plot is modified by combining equations 6.64 and 6.65 as,

\[ \ln \left( \frac{I_0}{T^2} \right) - \left( \frac{q^2 \sigma_0^2}{2k^2T^2} \right) = \ln (AA^{**}) - \frac{q\Phi_{b0}}{kT} \]  

(6.68)

The modified \( \ln(I_0/T^2) - (q^2\sigma_0^2/2k^2T^2) \) vs. 1000/T plot, thus should also be a straight line with the slope and the intercept at the ordinate yielding the mean barrier height \( '\Phi_{b0}' \) and modified Richardson constant, \( 'A^{**}' \) respectively. The modified Richardson plot for the data obtained (figure 6.24) shows quite a good linearity except for two or three points the very low temperature region. Here also, the activation energy which corresponds to the mean barrier height at zero Kelvin \( '\Phi_{b0}' \) was found to be 0.45eV and 0.68eV for both thin film Schottky diodes respectively. Further, the value of the modified Richardson constant \( 'A^{**}' \) comes out to be 24.86Acm\(^{-2}\)K\(^{-2}\) and 27.77Acm\(^{-2}\)K\(^{-2}\) which is in a closer agreement with the theoretical value of 27.6 Acm\(^{-2}\)K\(^{-2}\).

6.5 Conclusions

Thin film Schottky diodes of Al/pWSe\(_2\) have been successfully fabricated by depositing thermally evaporated aluminum thin film (5000Å) on pre deposited WSe\(_2\) (1000Å, 1732Å and 3226Å) thin films by e-beam evaporation technique and they were studied for their \( V-I \) characteristics in the temperature range 310K – 100K. The current voltage characteristics of the
fabricated diodes show good rectification ratio. Also it could be seen that the representative forward current characteristics do not exhibit exponential rise with voltage and reverse $I-V$ characteristics do not show saturating nature. This represents non-ideal nature for both forward and reverse bias conditions. Thus, it is concluded that the characterizing parameters of fabricated diodes might be associated with both bias and temperature dependent charge transport mechanisms arising from various physical reasons.

![Modified Richardson plot](image)

Figure 6.24: Modified Richardson plot of (a) Al(5000Å)/pWSe$_2$(1732Å), (b) Al(5000Å)/pWSe$_2$(3226Å) Schottky diodes according to Gaussian distribution of the barrier heights.

The dominant current conduction mechanism in this diode has been found to be thermionic emission (TE) from the temperature dependent
values of carrier concentration and the characteristic energy (tunneling parameter) \(E_{00}\). On the basis of this Schottky diode parameters were deduced. The value of zero bias barrier height has been calculated using four different methods i.e. \(\ln I\) vs. \(V\) method, \(\ln[I/(1-\exp(-qV/kT))]\) vs. \(V\) method, \(F(V)\) vs. \(V\) method and \(H(I)\) vs. \(I\) method for the temperature range 310K - 100K and it was revealed that the barrier height decreases with decrease of temperature for both prepared thin film Schottky diodes which is shown in table 6.2. The decrease of barrier height with decreasing of temperature may be attributed to the interface states, inhomogeneous nature of the fabricated diode, multiple transport mechanisms involved in the conduction of carriers etc. Further it has been observed that with increasing semiconductor thin film thickness the value of barrier height is also increases in association with increase in carrier concentration (chapter 5).

The diode ideality factor has also calculated by above mentioned method for the same temperature range of 310K - 100K which shows that as temperature decreases the ideality factor increases (Table 6.2). The inhomogeneous thickness and composition of the layer, non-uniformity of the interfacial charges, the presence of any thin insulating layer between the metal and the semiconductor etc. may be ascribed for the change of barrier height and ideality factor at low temperature.

Four different methods have been applied to extract the barrier parameters to subtract the effect of diode series resistance from barrier parameters as mentioned above. But, in present investigation there are no any large variation has been found in the values of barrier parameters extracted using four different methods (Table 6.2) which shows that series resistance does not affect the barrier parameters by large amount which is again confirmed by lower values of resistance in the order of few ohms (Table 6.2).

From the linear relationships of barrier height and ideality factor a homogeneous barrier height of 0.74eV and 0.78eV for Al/pWSe\(_2\) (1732\AA) and
Al/pWSe$_2$ (3226Å) thin film Schottky diode have been found respectively. The other barrier height values are deviating from this value due to local inhomogeneities.

The flat-band barrier heights calculated at various temperatures show that its value is much larger than the zero-bias barrier height at low temperatures. This may be due to the high value of ideality factor at low temperatures.

Also from the temperature dependent flat-band barrier the value of temperature coefficient of the barrier height has been deduced. These values are $5.43 \times 10^{-4} \text{eV K}^{-1}$ and $5.28 \times 10^{-4} \text{eV K}^{-1}$ respectively for both Al/pWSe$_2$ (1732Å) and Al/pWSe$_2$ (3226Å) thin film Schottky diodes. The flat-barrier height at zero Kelvin is found to be 0.59eV and 0.63eV respectively for both Al/pWSe$_2$ (1732Å) and Al/pWSe$_2$ (3226Å) thin film Schottky diodes.

The Richardson plot drawn for the given diode yields a straight line giving the Richardson constant $24.86 \text{Acm}^{-2}\text{K}^{-2}$ and $24.77 \text{Acm}^{-2}\text{K}^{-2}$ respectively for both Al/pWSe$_2$ (1732Å) and Al/pWSe$_2$ (3226Å) thin film Schottky diode.

The values of mean barrier height for Al have been found to be close to their Schottky model values of 0.92eV (Table 6.3). This suggests that there is an absence of sandwiching oxide layer formation, as is the case with Si based devices, between the two interfaces. In other words the faces of the metal and the semiconductor make intimate contact and this happens mainly because WSe$_2$ faces are inert, an observation in agreement with that of previous workers [70].

The value of modified Richardson constant 'A'' for both diode system comes out to be very close to the theoretical value ($27.6\text{Acm}^{-2}\text{K}^{-2}$).
Table 6.3: A comparative table of various Schottky barrier parameters extracted for the prepared thin film Schottky diodes.

| Thin film Schottky Diode | $\alpha$ ($\times 10^{-4}$) $(eVK^{-1})$ | $\Phi_{ho}(0)$ ($eV$) | $\Phi_{ho}(eV)$ | $\Phi_{ho}$ vs. Richardson Plot | $\Phi_{ho}$ vs. 1/2kT Plot | Modified Richardson Plot | $A^*$ $\text{Acm}^2K^{-2}$ | $A^{**}$ $\text{Acm}^2K^{-2}$ | $\sigma_0$ $(V)$ | $\rho_2$ $(V)$ | $\rho_3$ $(V)$ | % of inhomogeneity |
|-------------------------|-----------------------------------|-----------------|-----------------|--------------------------------|-----------------|------------------|------------------|----------------|----------------|----------------|----------------|-----------------|----------------|
| Al/pWSe$_2$ (1732Å)    | 5.43                              | 0.59            | 0.45            | 0.80                          | 0.45            | 0.45             | 24.86          | 24.86          | 0.056          | 0.62           | -0.04           | 7.0             |
| Al/pWSe$_2$ (3226Å)    | 5.28                              | 0.63            | 0.68            | 0.85                          | 0.86            | 0.86             | 27.77          | 27.72          | 0.064          | 0.68           | -0.04           | 7.5             |
Moreover, in light of the results obtained in present case, TE model with a Gaussian distribution of Schottky barrier heights as suggested by Werner and Guttler [30,31] is thought to be responsible for the electrical behaviour at temperatures above 200 K. But below 200 K, a combined effect of thermionic emission, generation recombination and tunneling prevails. For all two types of diodes, there is a particular temperature (200K) above which pure TE dominates and below which a combination of charge transport mechanisms exist [28].

The percentage value of inhomogeneity for Al/pWSe₂(1732Å) thin film Schottky diode is 7.0% and that for Al/pWSe₂(3226Å) thin film Schottky diode is 7.5% which is lower than the reported value of 14% [76] for diode fabricated on DVT grown WSe₂ single crystal. The reason for the higher inhomogeneity in the case of crystal [12-14] may be due to presence of more structural defects like screw dislocation on its surface and its morphology. This might result in a poor junction in comparison to smooth and flat thin films.

References


[77] Keithley 4200 SCS user manual.


