Chapter-1

General Introduction

1.1 Overview of Thin Film Technology

In the development of modern science, thin films and devices play an important role. "Any object in solid or liquid form with one of its dimensions, called the thickness, is very much less than that of the other two is called a thin film". Basic properties of thin films are still the subject of considerable interest and investigation, because many features of their behavior may differ from those of materials in bulk form. The thin film is formed by atom to atom or molecule to molecule condensation process. Because of many properties of materials depend on the thickness of the thin film, it becomes very important. Depending upon the field of application the thickness of the thin film varies from a nanometer to a few micrometers [1]. Initially, the investigations on the thin films were made out of scientific curiosity. But in subsequent years due to the acquired capability of controlling properties of the thin films, the use of thin films in electronic, opto-electronic and other devices increased and as a result, the electronic industry has become the greatest beneficiary of thin film technology. On the other hand, the thin film technology has contributed to the development of various fields like space electronics, consumer electronics, microelectronics etc. The recent impact of thin films in the field of electronics is mainly based upon two features viz. compactness and integration. These features have many desirable results like low cost, reproducibility, high performance, low power requirement and especially reliability. Electronic device fabrication also demand certain chosen properties to be exhibited by the material for a particular application. For example, high electron mobility and large energy gap are desirable for the preparation of transistors and for solar cell application. Materials with high carrier mobility find applications in Hall generators and magneto resistors where as for thermoelectric applications, low thermal conductivity materials are preferred.

Thin films can be used to obtain information about the properties of the matter, because certain measurements can be made more conveniently using thin films. Examples of such research activities include studies of phase transformation,
chemical reactivity, superconductivity, electrical resistance, photoconductivity and magnetic properties. Also investigations are being made on thin films as they have certain interesting properties that are not exhibited by the same material in the bulk form. Many examples of this type of research include studies on chemical and mechanical behavior, electrical and magnetic properties etc.

The geometrical parameters of the material in thin film form play a key role in many applications. In addition, spectrally selective surfaces find numerous applications in space science and solar energy studies. In a way, it will be an unending process to list the usefulness of applicability of thin films of different materials as one would hardly find any area of technical value where thin films have no application.

The most important applications of thin films are in the photovoltaic devices as well as in various semiconductor devices [2, 3]. The investigations on thin films have led to the development of new kind of active devices and passive components, different types of sensors [4], storage of solar energy and conversion to other forms, magnetic memories [5], optical image storing devices [6,7], gas detecting transducer [8], reflecting and anti-reflecting coating [9] and many others. Because of a dramatic increase in the industrial usage of thin films with its applications in many diverse areas and the need for new and improved optical and electronic devices, thin film technology has become extremely important in recent years.

1.2 Metal - Semiconductor Schottky Contacts

The technological development in different fields like communication, space electronics, consumer electronics etc. has greatly affected today’s living standard of human being. Semiconductor devices are at the central stage in all these, either in form of transducer/sensor, signal conditioner, actuators, drivers or display units. The tremendous advancements in electronics industry are the result of recent developments in faster semiconductor devices. Metal-Semiconductor contacts are of great importance because they are always present in every semiconductor device in any of two forms, ohmic or rectifying. Today, the metal-semiconductor junctions are much used as rectifiers, microwave diodes, \textit{UV} detectors, switching diodes, photo sensors and solar cells [10-14]. Due to its fast switching effect, it is widely used in digital circuits and communications and radar applications also [13-15]. Thus, Metal-
Semiconductor contacts have become an important member of the device families of the modern electronic systems. Schottky barrier junction or Schottky diode has a rectification capability, with a large current in forward bias and very low leakage current in reverse bias. Because of their importance in direct current and microwave applications and as tools in the analysis of other fundamental physical parameters, metal-semiconductor contacts have been studied extensively. Thus, metal-semiconductor contacts are most common form of junction in integrated circuits. Hence research efforts related to the interaction of semiconductor surfaces with deposited metals are important for understanding many behavioural aspects of the microelectronic devices.

1.3 Purpose and Objectives of the Present Investigations

The field of electronic devices is full of challenges due to various demands generated time to time for modified functions and operations of an electronic gadget of simple nature like consumer electronics items to sophisticated research analytical tools. To meet such demands the basic instrumentation techniques require devices of different nature to give refined characteristic. The advances in the devices and development of more functional devices are based on understanding the basic physical aspects involved in their working. Metal-Semiconductor contacts form an area of wide interest in this context. Metal-Semiconductor contacts have been used in electronics, optoelectronics and microwave devices such as solar cells, MESFETs and microwave mixers [16]. In these devices, the perfection of Schottky interface plays an important role on the device characteristics.

Thus, M-S contacts are not only interesting but also hold great potential for a number of technological applications. On the other hand, metal-semiconductor structures are important research tools in the characterization of semiconducting materials and fabrication of such type of structures plays an important role in the realization of some useful devices [17]. Extraction of device parameters using characteristics measured over a wide temperature range provides the more satisfactory information for understanding the different aspects of conduction mechanisms [18].

Despite research efforts of more than a century or so led to technological advancements in the field of fabrication of Schottky barrier devices, our knowledge of
evolution of such barriers is not complete. It is known that observed barrier heights are the result of band lineup and accompanying charge transfer across the interface. The resultant barrier heights should correspond to that predicted by Mott Schottky model [19]. But reported experimental barrier heights are found to have deviation from the above predictions. Perhaps the multiplicity of charge transport mechanisms that come into play at the interface instead of single mechanism along with other physical and chemical interface situations that arise in practical diodes may be the reason for that. This makes the interface a very complex region, which in turn reflects in their terminal physical characteristics. All these have created different challenges in these areas. The physical properties of the interfaces between metal and semiconductors depend on surface preparation conditions [20, 21]. Many models have been developed to understand the origin and behavior of potential barrier at the interface of M-S contacts by various workers. But significant efforts are still being made on ways and means to arrive at a more realistic interpretation of characterizing parameters of real Schottky diodes [18, 22, 23].

Semiconducting materials of group IV-VI compounds are extensively used in modern technology because of their great potential in the different applications like cathode-ray and television phosphors, electroluminescent devices, phosphorescent and UV-responsive pigments, scintillation counters, electron-microscope and x-ray screens, storage devices etc. Originally, IV-VI compounds were studied and applied in powder form only. Powdered phosphors are still used in cathode - ray screens and electroluminescent lamps, but photoconductors are generally employed in sintered - layer form, whereas radiation sensitive devices are prepared from single crystals.

Compounds of this group have proved their viability for the applications in the field of detectors and optoelectronic devices. Hence in recent years, the group IV-VI compounds has been very extensively studied.

Tin selenide (SnSe) is among these semiconductor compounds, which has band gap of about 1.1 eV and possess layered structure. This material has not been investigated much in its pure and doped form for Schottky barrier applications compared to other semiconductors. But now it is finding increasing interest for the different applications.
In light of this it was decided to study the deposition of SnSe thin films by thermal evaporation method to optimize various optical, physical and electrical properties. For this thin films of SnSe were deposited at different substrate temperatures having different thicknesses also. These well characterized thin films were used to prepare SBDs and they were studied to extract the diode parameters at different temperature using I-V and C-V characteristics. It was also planned to study the possible conduction mechanisms in these Schottky diodes. Objective is also to study the effect of variation in stoichiometry on different properties.

1.4 History of Semiconductors for Device Development

The social change and transformation in the quality of human living conditions from primitive to the present days is widely related to the understanding of materials. This rapid change in last many decades is due to scientific, industrial and electronic revolutions which has been based on the capability to understand, mould, shape and design the various materials in a desirable fashion to serve the needs of various applications. Out of various kinds of materials, semiconducting materials have been playing a vital role in present electronic and fast developing information age. It is due to the vast range over which the electrical behavior of semiconducting materials can be profitably maneuvered and controlled [24].

Particularly elemental semiconductors have been playing prominent role in various applications in the area of electronics and applied fields. The variability of electrical properties by changing temperature, optical excitation and impurity content makes the semiconducting materials natural choice for electronic device investigations. The group-IV semiconductors i.e. Si and Ge have been the prime materials for such applications. But these semiconductors alone could not satisfy all the requirements of materials to be used for applications like detection systems, electroluminescent devices etc. Therefore Scientists were in need for search of new materials to cope up with the requirements of above mentioned applications. Many new materials have been investigated as a result of endeavor towards this direction. The research activities in the field of semiconductors and applications have shown that many interesting binary, ternary and quaternary compounds offer high potentials towards their applications in the area of electronics and communication. Some of
more investigated materials belongs to different groups like group $III-V$, group $II-VI$, group $I-III-VI$, group $IV-VI$ etc. have already shown their potential in the fabrication of optoelectronic devices. The layered chalcogenide compounds occupy a prominent place of current interest in material science. The versatility of these compounds is demonstrated by the remarkable range of properties they exhibit. In recent years studies on group $IV-VI$ of compounds have been very much in progress due to their device applications in many fields as mentioned earlier.

1.5 An Overview of Group $IV-VI$ Semiconductor Compounds

In the quest for a new semiconducting thin film material for solar-energy conversion, the binary $IV-VI$ compounds are being increasingly studied. Besides their suitable properties, the abundance and low environmental impact of their constituent elements are additional advantages for large scale applications [25, 26]. Group $IV-VI$ semiconductor compounds have attracted growing interest since many decades due to their important specific properties and various applications in different fields like solar energy conversion, sensor, phase change memory devices, thermoelectric cooling material etc.. This group of semiconductor is classified into three categories according to the crystal structure. The lead chalcogenides ($PbS$, $PbSe$ and $PbTe$) crystallize in a cubic structure. Compounds like $GeTe$ and $SnTe$ posses rhombohedral structure and other compounds like $GeSe$, $SnS$ and $SnSe$ have an orthorhombic structure. Each one of these possesses different physical as well as electronic properties and hence application areas [27-29]. The cubic semiconductors of this group are the narrow band semiconductors which are mainly used for infrared sensor devices, especially in thermal imaging applications [30]. They are also used for Schottky diodes [31]. The static dielectric constant $\epsilon_s=218\epsilon_o$ for $PbSe$ [32] and $\epsilon_s=400\epsilon_o$ for $PbTe$ [33] while $\epsilon_s=17\epsilon_o$ for $SnSe$ [34]. Thus static dielectric constant in $PbSe$ and $PbTe$ compounds are unusually very different.

Because of great potential of group $IV-VI$ compounds in the different applications mentioned above, semiconducting materials of this group are extensively used in modern technology. Compounds like $PbS$, $PbSe$, $PbTe$ and $SnSe$ have proved their viability for the applications in the field of detectors and optoelectronic devices.
These groups of semiconductor compounds have been successfully used as various detectors, sensors, modulators and optical windows in space and military applications.

### 1.6 Choice of Material and Its Importance

Group $IV-VI$ semiconductor compounds have attracted considerable attention since many decades due to their important specific properties and various applications in different fields. Among this group, tin selenide ($SnSe$) is having orthorhombic layered structure. It has attracted attention of many researchers because of higher absorption coefficient which is useful for different applications in the fields like optoelectronics [35], holographic recording systems [36-38], electronic switching [39, 40] and infrared production and detection system [41]. Moreover $SnSe$ is a semiconductor with energy gap of 1 $eV$ having a potential as an efficient solar material [42, 35]. The interest in the properties of these materials either in the form of a single crystal, polycrystal or a thin film with large dimensions for an optimum photo conversion has been shown several times [43-47]. A great amount of interest therefore, has been shown by various workers in the study of these materials.

$SnSe$ has attracted considerable interest as it is an important technological semiconductor having a potential for solar cell material particularly $PEC$ Solar cell electrode material [42]. As per survey it was found that many students of our thin film laboratory have been working on semiconductor of group-$VI$ TMDCs with a layer type structure. The semiconductor compounds of group $IV-VI$ have attracted attention of many researchers due to their specific important properties and various applications in different fields like solar energy conversion, sensor, phase change memory devices, thermoelectric cooling material etc. Many of them have been realized but still a lot of work is needed for complete understanding of these materials in different device forms. Tin selenide belongs to this group. There are few reports of devices like Schottky barrier diodes based on bulk crystalline $SnSe$ as per our literature survey. However, reports have been scarce in case of thin film $SnSe$ and off-stoichiometric $SnSe$ for such applications. This has motivated us to study $SnSe$ thin film based Schottky barrier devices and to study about the processes responsible for dominant conduction mechanism. As $SnSe$ possesses layered structure which is an extra
incentive to device research, it is less studied material compared to other layered materials, we have chosen tin selenide (SnSe) for such study in present investigations.

1.7 A Review of Prior Work on Tin Selenide Thin Films

The electrical and optical properties of tin selenide, both in the bulk and thin film form, had been investigated by a number of scientists [48-76]. Anomalous variation of the Hall coefficient of crystalline SnSe was observed by Asanabe [48]. Maier & Daniel [49] studied the electrical properties of single crystals of SnSe grown by sublimation method. J.G.Yu et al.[50] have reported the electrical and optical properties of the crystals grown by the close-tube vapor-transport technique. X-ray photoemission studies of the valence band of SnSe were performed by Shalvoy [51] and IR and Raman spectra were analysed by Chandra Shekhar et al. [52]. Absorption spectra analysis has been carried out by Mochida [53], Takashashi [54], Guseinova et al. [55], Elkorashy [56,57] and Garg [58]. A variety of physical and chemical deposition techniques have been employed for the preparation of amorphous and polycrystalline thin films of tin selenide [59-76]. They can be generally classified into two, viz; vacuum evaporation and chemical deposition. Engelken et al. [59] have prepared SnSe films by electro-deposition and studied their optical properties and photo conductance. An energy gap of 1.3 eV for annealed polycrystalline films was observed by them. Pramanik and Bhattacharya [60] have deposited amorphous SnSe films with n-type conductivity by a chemical method and conducted its optical absorption studies. Nuriev et al. [61], Mikolaichuk et al. [62], Chopra [63] and Avilov et al. [64] have been concentrated their studies on the structural aspects of SnSe thin films while Ganesan and Sivaramakrishnan [65] have examined the gas absorption effects on the electrical properties of these films. The electrical properties and optical absorption of evaporated SnSe films [66] and the films obtained by solid state reactions [67] have been reported by Quan. Structural analysis of these films showed that the crystallites of the films have preferential orientation on the substrate surface. Subba Rao and Chaudhuri [68-70] have investigated the structural, electrical and photo-electronic properties of the thermally evaporated films of SnSe. They have observed the formation of the high temperature phase of SnSe films, when deposited at substrate temperatures of 473 K and above. Photoelectric and optical properties of evaporated polycrystalline SnSe films have been studied by Bennouna et al. [71]. The
electrical and optical absorption of the flash evaporated SnSe films [72] and the films grown by hot wall epitaxy [73] were reported by Singh & Bedi. Hot wall expitaxial films had a preferred orientation with their (111) planes parallel to the substrate plane. Bhatt et al. [74] have also investigated the electro-optic properties of vacuum evaporated SnSe thin films. A number of techniques are employed in the formation of high quality thin films such as chemical vapor deposition, molecular beam epitaxy, electrochemical, physical vapor deposition and sputtering by Sankara et al and Guziewiez et al [75]. However there is an interest to investigate other techniques, which could find new possibilities in terms of device properties, structure etc. Chemical bath deposition (Wang et al) belongs to these alternative techniques that could also produce high quality films of IV–VI semiconductor materials [76]. It seems to be an inexpensive, simple, low temperature method that could produce good quality films for device application. Wang et al. [77] have reported a systematic investigation on the synthesis of SnSe in several alkaline media. The method adopted by them is less complicated compared to earlier methods reported in the literature for the preparation of SnSe using high temperature or toxic reagents. The effect of different annealing conditions over the tin selenide obtained from a chemical route was studied by Ana Claudia Bernardes-Silva et.al. [78]. Samsudi Sakrani et. al have investigated A.C. properties of tin selenide thin films prepared by an encapsulated selenization method [79]. Electrical transport properties of SnSe single crystals grown by DVT technique has been studied by B. B. Nariya et. al [80]. R. Mariappan et. al studied the compositional, surface morphological, structural and electrical properties of SnSe thin films deposited by Spray-pyrolysis technique [81]. They found that various structural parameters such as crystallite size, strain and dislocation density are temperature dependent. The average grain size is found to be 478 nm and crystallinity of the films increased with increasing temperature. The effect of substrate temperature on the structural, morphological, optical and electrical properties of SnSe thin films deposited using thermal evaporation method have been studied by N. Kumar et. al [82]. Thin films deposited are found to be polycrystalline in nature and having preferred orientation of grains along the (111) direction. N. A. Okereke and A. J. Ekpunobi have prepared SnSe thin films using chemical bath deposition technique at various deposition conditions and studied the effect of these parameters on thin film properties. They found that the grain size of thin film increases with the film thickness and greater thickness minimizes imperfection [83].
1.8 Properties of Tin Selenide

1.8.1 Properties of tin

Tin is a chemical element with the symbol Sn and atomic number 50. It is a main group metal in group 14 of the periodic table. Its electronic configuration is \([Kr] 4d^{10} 5s^2 5p^2\). Tin is the element of the periodic table with a large number of stable isotopes. Tin compounds sprayed onto glass are used to produce electrically conductive coatings. These have been used for panel lighting and for frost-free windshields. Most window glass is now made by floating molten glass on molten tin (float glass) to produce a flat surface. Tin is the basis for many eutectic alloys and the discovery by early man that copper could be better formed and crafted if tin were added producing the first bronze and launching what we refer to as the "Bronze Age" and the first Neolithic metal tools, cooking utensils, and jewelry produced from rudimentary bronze. An important tin compound is the chloride, which is used as a reducing agent and as a mordant in calico printing. Tin is also used in various metal alloys, most notably tin/lead soft solders, corrosion-resistant tin plating of steel etc. Some important properties of tin are given in table 1.1.

1.8.2 Properties of selenium

Selenium is a chemical element with the symbol Se and atomic number 34. It is a nonmetallic chemical element, member of the XVI of the periodic table. Its electronic configuration is \([Ar] 3d^{10} 4s^2 4p^4\). Selenium exhibits both photovoltaic action, where light is converted directly into electricity, and photoconductive action, where the electrical resistance decreases with increased illumination. These properties make selenium useful in the production of photocells and exposure meters for photographic use, as well as solar cells. Below its melting point, selenium is a p-type semiconductor and has many uses in electronic and solid-state applications. Selenium is available as metal and compounds with purities from 99% to 99,9999% (ACS grade to ultra-high purity); metals in the form of foil, sputtering target, and rod, and compounds as submicron and nano-powder. Some important properties of Selenium are given in following table 1.1.
Table 1.1 Physical and chemical properties of Sn and Se.

<table>
<thead>
<tr>
<th>Property</th>
<th>Sn (Tin)</th>
<th>Se (Selenium)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic Number</td>
<td>50</td>
<td>34</td>
</tr>
<tr>
<td>Atomic Weight</td>
<td>118.710 g/mol</td>
<td>78.96 g/mol</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>2876 K</td>
<td>958 K</td>
</tr>
<tr>
<td>Melting Point</td>
<td>505.12 K</td>
<td>494 K</td>
</tr>
<tr>
<td>Density</td>
<td>7.31 g/cm³</td>
<td>4.79 g/cm³</td>
</tr>
<tr>
<td>Crystal Structure</td>
<td>Tetragonal</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>Heat of Vaporization</td>
<td>290.37 kJ/mol</td>
<td>26.32 kJ/mol</td>
</tr>
<tr>
<td>Heat of Fusion</td>
<td>7.2 kJ/mol</td>
<td>5.54 kJ/mol</td>
</tr>
<tr>
<td>Electrical Conductivity</td>
<td>8.7×10⁶ ohm⁻¹cm⁻¹</td>
<td>8×10⁶ ohm⁻¹cm⁻¹</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>66.6 Wm⁻¹K⁻¹</td>
<td>2.04 Wm⁻¹K⁻¹ (at 300 K)</td>
</tr>
<tr>
<td>Specific Heat Capacity</td>
<td>0.228 Jg⁻¹K⁻¹</td>
<td>0.32 Jg⁻¹K⁻¹ (at 300 K)</td>
</tr>
<tr>
<td>First Ionization Potential</td>
<td>7.344</td>
<td>9.752</td>
</tr>
<tr>
<td>Atomic Volume</td>
<td>16.30 cm³/mol</td>
<td>16.50 cm³/mol</td>
</tr>
<tr>
<td>Atomic Radius</td>
<td>1.62 Å</td>
<td>1.40 Å</td>
</tr>
<tr>
<td>Covalent Radius</td>
<td>1.41 Å</td>
<td>1.16 Å</td>
</tr>
</tbody>
</table>

1.9 Existing Information about Tin Selenide

SnSe exhibits a strong anisotropy in its physical properties and has received considerable attention due to its possible technical applications in various fields. It can be used as cathodic materials in lithium intercalation batteries [84] and its solid-solutions with lead chalcogenides is a promising material for optoelectronic devices [85]. The energy gap of SnSe reported by different authors is in the range of 0.9 to 1.3 eV at room temperature. Because of its application as memory switching devices [86, 87] and being an efficient material for solar applications, thin films of SnSe have great potentialities. It is a semiconductor with layer-type character having orthorhombic structure. Tin selenide is transparent in the infrared region and thus used as optical windows.

1.9.1 Crystal structure of tin selenide

Crystal structure of SnSe is simple orthorhombic bravice lattice [88]. The unit cell of SnSe contains eight atoms with the symmetry of the space group $D_{2h}^{16}$.
Figure 1.1 Crystal structure of SnSe.

The Sn and Se atoms are arranged in two adjacent double layers orthogonal to largest cell dimensions [89]. The SnSe crystal is made up of tightly bound double layers of Sn and Se atoms stacked along the c-axis as shown in figure 1.1. Each atom has three strongly bonded neighbors within its own layer and three more distant weakly bonded neighbors, two of which lies within the same double layer and remaining one in the adjacent layer. In this compound the cation (Sn) and anion (Se) atoms form zigzag cation-anion chains perpendicular to c-axis. Each atom has the coordination environment of a heavily distorted octahedron [90]. Each atom forms six dominant heteropolar bonds, the strongest of which are in three bonds to nearest neighbors in the same double layer. Three weaker bonds are to further neighbors, two of which are in the same double layer, one to an atom in the next adjacent layer. The bonding between the layers is weak, being of van der wall’s type.
1.9.2 Optical properties of tin selenide

The study of optical properties of these semiconductors gives a good understanding of their electronic properties and band structures. The optical band gaps of semiconducting materials play an important role in deciding the photoelectric properties of the optoelectronic devices. The fundamental band gap $E_g$ is the most crucial optical parameter as far as the applications of the materials in optoelectronics devices is concerned. Thus, optical band gap ($E_g$) is, one of the main optical parameters for materials, while considering their use in device application.

The direct and indirect type band gap in SnSe is observed by many workers. Saravanan [91] reported a direct band gap of 1.23 $eV$. Nariya et al. [80] observed an indirect band gap of 1.0 $eV$ for by direct vapour transport technique. Zulkarnain group [92] reported indirect band gap of 1.25 $eV$ for by combination of chemical precipitation and vacuum evaporation technique. N. A. Okereke and A. J. Ekpunobi [83] found optical band gap to be indirect and it was equal to 1.5 $eV$. A direct band gap of 1.08 $eV$ was observed by R.Mariappan et al. [81]. R. Indirajith and co-workers [93] reported that the indirect band gap of SnSe thin films prepared at various substrate temperatures lies in the range of 1.2-1.4 $eV$ and the direct band gap value lies in the range of 0.6-1.2 $eV$.

1.9.3 Electrical properties of tin selenide

Electrical transport properties of materials play an important role in determining the behavior of solid state devices and thereby their potential for such applications. Investigations regarding the electrical behavior of tin selenide thin films have been reported to be strongly depended on deposition conditions. For its application in the device fabrication as an active layer it must be thoroughly characterized for electrical transport properties. Hall Effect measurement is a unique tool to provide basic electrical parameters of material needed to find the suitability of its application. It is always interesting to investigate the nature of transport of carriers in a semiconducting material. The electrical conductivity of polycrystalline thin films prepared by vacuum deposition were measured by D. Pathinettam padiyan et al. [94] using van der Pauw technique in the temperature range 300-118 $K$. Activation energy was found to be 0.223 ,0.106 and 0.18 $eV$ in the temperature range 298-268 $K$,  13
268-193 K and 193-148 K respectively. G. Hema Chandra et al. [95] observed variation of electrical resistivity from 30 to 8.1 Ω.cm in the thickness range 150-300 nm with p-type conductivity for the film deposited at 513 K. Activation energy found by them was 0.26 eV in 303-473 K temperature range. N.Kumar et al. [96] deposited SnSe thin films by thermal evaporation technique and electrical data obtained by them shows that thin films indicating semiconducting behavior with p-type conductivity. The value of activation energy obtained by them was 0.14 and 0.24 eV in temperature range 300-400 K and 400-450 K respectively. The electrical properties of SnSe thin films were studied by R. Indirajith and their group [93] from room temperature Hall measurements in van der Pauw configuration. In these results positive sign of Hall co-efficient shows the p-type conductivity of films. The values of resistivity, hall mobility, carrier concentration and conductivity of the deposited thin films at 450 °C were shown in table 1.2. Some of reported electrical parameters of SnSe crystals and thin films are also shown in following table 1.2.

**Table 1.2** Reported values of electrical parameters of SnSe crystals/thin films.

<table>
<thead>
<tr>
<th>Techniques</th>
<th>Resistivity (\rho \times 10^{-2}) (Ω.m)</th>
<th>Hall Coefficient (R_H \times 10^4) ((m^3/C))</th>
<th>Hall Mobility (\mu \times 10^{-4}) ((m^2/V.s))</th>
<th>Carrier Concentration (n \times 10^6) ((m^{-3}))</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Evaporation</td>
<td>2.278x10^{-2}</td>
<td>-</td>
<td>6.047</td>
<td>4.531x10^{19}</td>
<td>[93]</td>
</tr>
<tr>
<td>DVT grown crystals</td>
<td>5.33</td>
<td>9.8</td>
<td>-</td>
<td>\sim 10^{18}</td>
<td>[97]</td>
</tr>
<tr>
<td></td>
<td>0.14</td>
<td>18</td>
<td>150</td>
<td>3x10^{17}</td>
<td>[56]</td>
</tr>
<tr>
<td></td>
<td>4.59</td>
<td>3.23</td>
<td>214</td>
<td>1.934x10^{16}</td>
<td>[98]</td>
</tr>
<tr>
<td></td>
<td>180.65</td>
<td>15.675x10^{-3}</td>
<td>86.76</td>
<td>8.53x10^{14}</td>
<td>[80]</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>115</td>
<td>\sim 10^{18}</td>
<td>[99]</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>700</td>
<td>3x10^{17}-2x10^{18}</td>
<td>[100]</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>154</td>
<td>9x10^{17}</td>
<td>[101]</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>\sim 10^{19}</td>
<td>[102]</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>10^{16}-10^{17}</td>
<td>[103]</td>
</tr>
</tbody>
</table>

It is seen from the table 1.2 that SnSe thin film/crystals shows semiconducting behavior with p-type conductivity and the carrier concentration is found to be in the range of \(10^{14}\) to \(10^{19}\) \(cm^{-3}\).
1.10 Review of Prior Work on Schottky Contacts

Most of semiconductor devices use the metal-metal, metal-semiconductor or semiconductor- semiconductor interface in one or other way. Because of their importance in direct current and microwave applications and as tools in the analysis of other fundamental physical parameters, metal-semiconductor contacts have been studied extensively.

A metal-semiconductor junction exhibiting rectifying behavior is commonly known as the Schottky barrier junction. The metal-semiconductor rectifying junction was the oldest solid state device used in electronics. But understanding of rectifying behavior of such contacts has taken almost a century of investigations starting from the pioneering work of Braun. History shows that the metal-semiconductor contact was first discovered by Braun in 1874 [104] and the first acceptable theory on the metal-semiconductor contact was provided by Schottky [105] in the 1930s. In his honor, M-S contact devices are also referred as Schottky barrier devices. In 1938, both Schottky [106] and Mott [107] independently suggested a model for the rectification mechanism that could be explained by supposing that electrons passed over a potential barrier through the normal process of drift and diffusion. According to this model Schottky barrier $\phi_{bn}$ and $\phi_{bp}$ at interface are given by,

\[ \phi_{m} = \phi_{m} - \chi_{s} \]  
\[ \phi_{np} = E_{g} - (\phi_{m} - \chi_{s}) \]

where $\phi_{m}$ is the work function of metal, $\chi_{s}$ is electron affinity and $E_{g}$ is the semiconductor band gap. Various workers observed experimental results which were found to be deviated from these predictions. To resolve this, Bardeen [108] proposed the presence of intrinsic surface states within the band gap and their occupancy should be taken into consideration. As a result, the Fermi level of semiconductor is not free to move for realignment on interface formation as it would be when there were no allowed energy levels in the energy gap as in the bulk. Therefore the Fermi level can be pinned by surface states and may not be free to vary for interface formation by different metals. Although the Bardeen’s attempt provided a way-out of this
impasse, it didn’t indicate how quantitatively one can estimate and control the contribution of surface states for barrier height. Later on Crowley and Sze attempted to describe the Schottky barrier variation by synthesizing the linear work function model of Mott and Schottky with Bardeen interface state model. Experimental results on barrier heights were not entirely explainable by above models, even though the attempts were also made for study of variation of BH with work function of metals, co-relation of BHs with electro-negativity etc. In this regards the work by Michelson, Kurtin, Bucher, Andrew, Philiphs, Hirose etc. are notable. These co-relation efforts exhibited that both bulk and interface condition contribute to barrier formation and thus more theoretical and experimental investigations in the field of Schottky barrier were continued. Since intrinsic surface states cannot exist on a bare surface, Heine showed that it is the metal induced gap states (MIGS) resulting from the tails of work functions of the atoms of metallic over layer that determine the interface contribution. The detailed investigations of extrinsic defects created during formation of the over layer have been discussed by Spicer’s group [109] and they have shown that these defects also play a significant role in the interfacial contribution to the Schottky barrier heights. These models and their results later on, inspired a large number of workers to devote more efforts for a closer and microscopic look at the evolution of Schottky barriers. Such efforts may develop the ability to produce tailor-made interface contacts with desired values of barrier height for applications of specific nature in future. Various efforts made in this direction are (1) by using metal alloy over layers [110-112], (2) by using intra-layer of metal over layers on semiconductors [113-114], (3) by using modifications of the chemical composition or doping level of the semiconductor surface [115-117] and (4) by using surface reconstructions at the interface [118-121].

The nature and origin of the temperature dependence of barrier height and ideality factor have been successfully explained on the basis of TE mechanism with Gaussian distribution of BHs by some studies since last decade or so. Large variation observed in BH and ideality factor with temperature by R.Singh et al.[122] was explained by lateral SBH inhomoginity model proposed by Tung [123, 124] and Werner and Gulter [125] which explains well the dependedance of SBH and ideality factor on temperature by considering the SBH inhomoginity at M-S interface in nanometer scale. The electron transport at inhomoginous M-S junction has been
treated by parallel conduction model. The current is assumed to be sum of current flowing in all individual patches each with its own area and SBH. The ballistic electron emission microscopy (BEEM) studies have also supported the existence of Gaussian distribution of BHs in Schottky diodes [126, 127]. Simulation studies on I-V characteristics of inhomoginious diodes with a Gaussian distribution have also yielded results similar to those observed in experimental data[128, 129]. The analysis of I-V measurements on Ag/p-SnSe Schottky barriers has been carried by H. Safak et al. [130]. The temperature dependence of I-V characteristics of Ag/p-SnSe SBD was successfully explained by N. Tugluoglu et al. [131] . In above both the cases SBDs were fabricated by depositing Silver on one side of p-SnSe crystals and Indium on back side of crystals for ohmic contact.

Most of the problems mentioned above have been overcome for specific systems, but general methods to unfold the contributing factors for ultimate barrier height and its measurement is still remains a topic of interest for researchers. As per our survey there are very few reports of devices like Schottky barrier diodes based on bulk crystalline SnSe. However, reports have been scarce in case of thin film SnSe and off-stoichiometric SnSe for such applications. Hence in this study efforts have been made to investigate tin selenide thin film based Schottky barrier diodes.

References


