CHAPTER – 1

INTRODUCTION
1.1 Semiconducting Materials

During the recent decades, advances in semiconductor materials resulted in the development of a wide range of electronic and optoelectronic devices that affected many aspects of the technological society. From semiconductors to microelectronic and optoelectronic devices (i.e., integrated circuits and devices for the generation and detection of light) for information applications (i.e., computing, memory storage, and communication), these advances and applications were catalyzed by an improved understanding of the interrelationship between different aspects (i.e., structure, properties, synthesis and processing, performance, and characterization of materials) of this multidisciplinary field [1]. Semiconductors are a group of materials having electrical conductivities intermediate between metals and insulators. It has an electrical resistivity in the range between those of typical metals and typical insulators (i.e., between about $10^{-3}$ and $10^9 \, \Omega \cdot \text{Cm}$). An important (and distinctive) property of a semiconductor is its temperature dependence of conductivity, i.e., the fact that the conductivity in semiconductors increases with increasing temperature, whereas the conductivity in metals decreases with increasing temperature.

One of the important parameters that often determine the range of applications of a given semiconductor is the fundamental energy band gap, or as it is referred to in the subsequent description, the energy gap, (i.e., the energy separation between the valence and conduction bands) as shown in figure 1.1, which is typically in the range between 0 and about 4eV for semiconductors [1-4]. Semiconductors have attracted considerable attention particularly after the discovery of transistors in 1947 and are the most important materials for fabrication of electronic and optoelectronic devices today [5]. Compared with other materials, semiconductors have unique properties that make them very suitable for the detection of ionizing radiation. Furthermore, semiconductors – especially silicon – are the most widely used basic materials for electronic amplifying elements (transistors) and more recently for complete microelectronics circuits. Thus part of the process technology that already existed in (micro) electronics could be taken or adapted for detector production. Integration of detector and electronics can be envisaged [6].
Nowadays, semiconductor devices are the basic components of integrated circuits and are responsible for the startling rapid growth of the electronics industry in the past 50 years worldwide. Because there is a continuing need for faster and more complex systems for the information age, existing semiconductor devices are being constantly studied for improvement and new ones are being invented. Whether it is for higher speed, lower power, higher density, higher Efficiency, or new functionality, the number and types of semiconductor devices have been growing steadily in this fascinating field. There now exists approximately 110 semiconductor devices, depending on the definition of the device.

Kwok [7] presented an approach, which is to serve as a tool to help in digesting the vast number of devices that exist the present a complete collection of semiconductor devices. A total of 67 “major” devices have been identified, together with about 110 device variations which are considered to be “related” devices to the former. These devices are organized into groups and subgroups. Some of these categories are shown in figure 1.2 and the justification for such classification of semiconductor devices is discussed by him.
Some examples of common semiconductors that are widely used in electronic and optoelectronic applications are group IV elemental semiconductors (e.g., Si and Ge), group III–V semiconductor compounds (e.g., AlAs, GaAs, GaP, GaN, InP, InAs, and InSb), group II–VI compounds (e.g., ZnS, ZnSe, ZnTe, CdS, CdSe, and CdTe), and group IV–VI compounds (e.g., PbS, PbSe, and PbTe). The interest in these semiconductor alloys stems from the desire to control the energy band gap, which ultimately dictates the spectral range over which the optical detectors and sources and other optoelectronic devices operate, and also to engineer the lattice parameter of the substrate to match that of the epitaxial layer. A wide variety of semiconductor compounds, mentioned earlier, are commonly used in optoelectronic applications such as laser diodes, light-emitting diodes and photodiodes [2,7] It should be noted that it is the energy gap of a semiconductor that determines the energy (or wavelength) of the emitted or absorbed electromagnetic radiation (in the ultraviolet, visible, or infrared ranges); the availability of a wide variety of semiconductors with appropriate energy gaps makes various semiconductor devices suitable for the detection and emission of electromagnetic radiation in these ranges.

Figure 1.2: The categories of semiconductor devices.
In addition, in the ternary and quaternary alloys, the energy gap is tunable by alloying various semiconductors, and that allows the flexibility of producing materials with desired properties by varying the composition (i.e., $x$ and $y$ in the chemical formulas) [1]. A brief review of the crystal structure and physical properties of group II–VI compounds is presented here.

### 1.2 Purpose and Objectives of The Present Study

In the past few years, many researchers have been started to investigate II–VI compound semiconductors due to features that made it very effectively and efficiently used as the sensitive materials in various terrestrial and extraterrestrial applications. Though researchers have been investigating several possible applications of semiconductors for the last few years, this field is still far from well understood. The majority of a wide-bandgap II–VI compounds are expected to be one of the most vital materials for high-performance optoelectronics devices such as light-emitting diodes (LEDs), laser diodes (LDs) operating in the blue or ultraviolet spectral range, detectors, sensors, optical windows, modulators, photovoltaic cells etc.

Additionally, the high ionicity of these compounds makes them good candidates for high electro-optical and electromechanical coupling. But, due to complex defect structures in these materials, the behavior of dopants and related problems with reproducible fabrication of n- and p-type materials, progress in the application of these compounds has remained slow.

Therefore, one of the most important aims is the growth of cadmium sulfide by direct vapour transport (DVT) technique which are still rare due to several difficulties and also the rare of research works in its various properties in last few years. Therefore, this work provide us a serious attempt to study the growth of cadmium sulfide with an overall look to some conditions and difficulties which might be affect on the grown crystals and their habits, optical characteristics and electrical characteristics.

Cadmium sulfide (CdS) is one of the most important members of the metal chalcogenide family and has great potential applications in optoelectronic devices such as multilayer light emitting diodes, photodiodes, phototransistors and metals/CdS interfaces. Particularly cadmium sulfide (CdS), In spite of having a relatively large band gap, CdS is suitable for use as a sensor material due to its broad spectral response and sensitivity. CdS is widely used as a detector of radiation in the
visible range. The band gap of CdS is approximately 2.40 eV, which corresponds to green light in the visible spectrum, thus making it useful in detecting visible radiation.

In most of the work, photocurrent or photoluminescence spectra were measured along with transmission spectra, which is another way to understand surface and bulk semiconductor physics. Based upon the metal/semiconductor interfaces deserve more investigations for confirmation especially in metal/ n-CdS, The main aim of present work concentrated on Al/n-CdS Crystal Schottky diode in order to develop devices based on them.

Undoubtedly, Metal/ n-CdS interfaces play an important role in optoelectronic device such as solar cells [8-10] and based upon their successful use depends heavily on the understanding of electrical contacts to these materials therefore the future research should address the following areas in order to develop devices based on these materials.

Thus, efforts have been made to study the properties of the interfaces through the measurements of I-V characteristics in Au-CdS junction by Chavez et al [11] and by Patel et al [12]. Also electrical studies have been made by Gupta et al [13] for Cu-CdS and Zn-CdS Schottky junctions by determining various junction parameters. However, very few efforts have been made in order to study the properties of interfaces in the case of Al/CdS thin film [8, 14, 15]. But, in case of Schottky barrier diodes based on CdS in form of Crystals no any reports are available regarding I-V or C-V characteristics over a wide temperature range. In view of this, thesis focuses on the fabrication of Al/n-CdS Crystal to get Al/n-CdS Schottky to be in parallel with that studies using thin films form that is in case of comparison studies.

In light of the above mentioned, the most important purpose for this study is the new addition for the studies presented in the field of Schottky diode by using aluminum based on cadmium sulfide in crystal form in general as well as that is a new addition to the advanced research on Al/CdS junction in thin films in particular. Where the most interesting of this study is that the Al/CdS junction using CdS in crystal form are still not available.
1.3 Morphology, Structure and Defects in Semiconducting Crystals

1.3.1 Morphology of Crystals

Interest and understanding of the morphology of crystals which started in the 17th century, independently one of dendritic forms and the other of polyhedral forms bounded by flat faces, have now advanced to a state to be understood from a unique viewpoint, the atomistic process of crystal growth. This was due to the development of the science of crystal growth in the 20th century, particularly after the 1950s. For simple and pure model systems, it is now possible to explain at the atomistic level why and how the same crystal can take a variety of forms, from dendritic, hopper, to polyhedral forms, and why different crystal species exhibit different characteristic forms or habits. The understanding of morphology and growth mechanism of crystals has developed and recently summarized by Sunagawa [16, 17]. How crystals nucleate and grow, and how their forms are controlled, still problems waiting for proper answers.

In natural crystallization, growth rates may fluctuate or abruptly change during their growth processes, and morphology and element partitioning are influenced accordingly. Crystals may be partially dissolved during the process of formation, or experience transformation in their post growth histories. We are unable to observe in situ the growth or post growth process of mineral formation, but we can investigate samples that experienced these processes, provided that these processes are recorded in the samples in some form and can be visualized by appropriate methods.

In nearly perfect single crystals, these are recorded in the form of various physical imperfections and chemical heterogeneities, preserving the records of morphological evolution during the growth or post growth processes. Various optical microscopy techniques, such as atomic force microscopy (AFM), and scanning tunneling microscopy (STM) can visualize and measure growth steps of nanometer height. Natural diamonds occur in a variety of forms, to which different variety names have been given. Orlov [18] classified natural diamonds into ten types on the morphological basis, whereas Sunagawa [19] classified them into three major types, based on the relation between morphology and driving force. According to Sunagawa’s classification, diamonds of single crystalline type are formed under small driving force conditions, polycrystalline type are formed under much higher driving
force conditions and coated stone and cuboid are those that experienced two different driving force conditions.

1.3.2 Structure of Crystals

Semiconductors can crystallize in several different structures depending on temperature or pressure, leading to polymorphism and the existence of different polytypes. For example, ZnS can exist in several different structural forms, such as a cubic (zincblende) structure, or as a hexagonal (wurtzite) structure, or as various polytypes [1]. In the majority of the II – VI compounds exists in two possible structures form from such a tetrahedral – (1) the zinc blende (cubic type) structure and (2) the wurtzite (hexagon type) structure. Therefore in this section will be looked over these structures.

1.3.2.1 Diamond and Zinc Blende Structures

Most semiconductors of interest in electronics and optoelectronics have an underlying FCC lattice. Figure 1.3 (a, b) gives this important structure. If the two atoms of the basis are identical, the structure is called diamond. Semiconductors such as Si, Ge, C, etc., fall in this category. If the two atoms are different, the structure is called the zinc blende structure. Semiconductors such as GaAs, AlAs, CdS, etc., fall in this category. Semiconductors with diamond structure are often called elemental semiconductors, while the zinc blende semiconductors are called compound semiconductors [20].

Silicon is an elemental semiconductor and is present in group IV of the periodic table. Group IV elements are exceptional in the sense that outer orbital of an individual atom is exactly half filled. So each atom can complete its outer shell by sharing electrons with four other atoms of the same kind through covalent bonds. Hence group IV elements can only crystallize in a diamond structure in the whole periodic table. It should be noted that semiconducting properties of a material are related to the crystal structure and the number of valence electrons per primitive unit cell [1].
The hexagonal close pack (hcp) structure is an important lattice structure and many metals have this underlying lattice. Some semiconductors such as BN, AlN, GaN, SiC, etc... The hcp structure is formed as shown in figure 1.4. The hexagonal structure of alternating layers is shifted so its atoms are aligned to the gaps of the preceding layer. The atoms from one layer nest themselves in the empty space between the atoms of the adjacent layer just like in the FCC structure. However, instead of being a cubic structure, the pattern is hexagonal. The hexagonal close packed structure can be made by piling layers in the A - B - A - B - A - B . . . sequence. Moreover, the wurtzite structure corresponds to the hexagonal packing ABABAB... (denoted as 2H), whereas the polytypes 4H and 6H can be represented by ABACABAC... and ABCACBABCACB..., respectively. In the majority of the II – VI compounds, the interatomic distance in the tetrahedral of both modifications are very similar.

**Figure 1.3:** The sphalerite (cubic type) crystal structure; (a) Silicon (Diamond) structure; (b) (Zinc-Blende) structure.
In view of the two structures, zinc and cadmium chalcogenides prepared from the gaseous phase crystallizes not only in the three-layer (cubic) or two-layer (hexagonal) forms, but they can also have structures in which the sequence of layers is different. This would give rise to multilayer polytypic forms, similar to those observed for silicon carbide. It has been reported/ that ZnS crystals prepared by the sublimation method have complex two- and three-layer or, rarely, four- and six-layer hexagonal structures which may be present in the same crystals in various proportions. It has also been reported that ZnS may exist in the rhombohedral modification which is intermediate between the wurtzite and sphalerite structures.

Depending upon the experimental condition, ZnSe crystals are of purely cubic form with a three-layer packing of the sphalerite type or with a mixed two- and three-layer packing in which the two-layer and three-layer packets alternate. ZnTe also forms a mixture of cubic and hexagonal crystals. The hexagonal structures have a fifteen-layer rhombohedral packing of the 15R type. There have been reports of cadmium chalcogenides also showing similar observations. The hexagonal crystals of CdS and CdTe exhibit a system of lines indicating a 24-layer packing (24H type) and the cubic CdTe has ‘defects’ resulting a twelve layer hexagonal packing (12H type) [21-23].
1.3.3 Defects in Semiconducting Crystals

In fact, the real crystals are never perfect; one invariably has some defects that are introduced due to either thermodynamic considerations or the presence of impurities during the crystal growth process. The real crystals always contain a considerable density of defects and imperfections that affect their physical, chemical, mechanical and electronic properties. A real crystals contain large numbers of defects (typically more than $10^4$ per milligram), ranging from varying amounts of impurities to missing or misplaced atoms or ions. These defects occur for three main reasons:

1. It is impossible to obtain any substance in 100% pure form. Some impurities are always present.
2. Even if a substance were 100% pure, forming a perfect crystal would require cooling the liquid phase infinitely slowly to allow all atoms, ions, or molecules to find their proper positions. Cooling at more realistic rates usually results in one or more components being trapped in the “wrong” place in a lattice or in areas where two lattices that grew separately intersect.
3. Applying an external stress to a crystal, such as a hammer blow, can cause microscopic regions of the lattice to move with respect to the rest, thus resulting in imperfect alignment [24].

Having defects in crystals, however, has very wide implications in various technological processes and phenomena such as annealing, precipitation, diffusion, sintering, oxidation and others. Defects can mostly be used as control parameter for getting desired characteristics in a system. The effects of imperfections or crystal defects on a few properties of solids nowadays are most useful, for example, is largely controlled by imperfections inside the crystal and the development of the transistor and the entire field of solid state device technology has been originated from this fact. In general, these defects in crystalline semiconductors may take a variety of forms:

1. Point defects (zero-dimensional) such as substitutional and interstitial impurity atoms and vacancies
2. Line defects (one-dimensional) such as dislocations.
3. Planar defects (two-dimensional) associated with grain boundaries in a polycrystalline material; and defects associated stacking faults.
4. Volume defects (three-dimensional) such as voids and inclusions.
It should be emphasized that defects in real semiconductors may interact and form a variety of possible combinations. Any of the above defects (to be discussed in brief below) can play a variety of electronically active roles that affect the electrical and optical properties of a semiconductor and the performance of semiconductor devices [24, 25].

### 1.3.3.1 Point Defects (0D)

A point defect is a highly localized defect that affects the periodicity of the crystal only in one or a few unit cells. There are a variety of point defects, as shown in figure 1.5 (a-d). Point defects are interstitials in which an atom is sitting in a site that is in between the lattice points as shown in figure 1.5(a), and if an impurity atom found in the interstice between matrix atoms is called an interstitial impurity atom. Figure 1.5(b), impurity atoms which involve a wrong chemical species in the lattice in which occupies a normal lattice site is called a substitutional impurity atom figure 1.5(c), and a vacancy is an atom site and it is usually occupied in the perfect crystal, from which an atom is missing figure 1.5(d).

Often the term “vacancy” is used to denote a Schottky defect, which is formed when an atom or an ion leaves a normal lattice site and repositions itself in a lattice site on the surface of the crystal. Many microwave diodes, which are devices that allow a current to flow in a single direction, are composed of materials with Schottky defects. In some cases the defect may involve several sites forming a defect complex [24].

![Figure 1.5: A schematic showing some important point defect in a crystal.](image-url)
One of important reason for that may be an atomic rearrangement in an existing crystal at a high temperature, which happens when atomic mobility is high because of increased thermal vibrations.

The process of crystallization, appearing as a result of local disturbances during the growth of new atomic planes on the crystal surface, might be taken another reason for vacancy formation. Vacancies are point defects of a size nearly equal to the size of the original (occupied) site; the energy of the formation of a vacancy is relatively lower - usually less than 1 eV. The presence of vacancies in solids can elucidate the diffusion of an atom through the material by its movement to a vacancy, resulting in a migration of a vacancy in the opposite direction. The atomic diffusion may also occur when atoms (or ions) change their interstitial positions. The equilibrium density \( n_v \) of vacancies in a crystal, containing \( N \) atoms per unit volume at a temperature \( T \), is given by:

\[
n_v = N \exp \left( -\frac{E_v}{K_B T} \right),
\]

\( E_v \) where is the energy of formation of a vacancy which is typically of the order of 1 eV [1,25-26]. The point defects create a local disturbance in the crystal structure of semiconductors. The effect of this crystal disturbance can be divided into two categories:

- The disturbance may create a potential profile which differs from the periodic potential only over one or a few unit cells. This potential is deep and localized and the defect is then called a deep level defect.
- Unlike the first case, the disturbance may create a long range potential disturbance which may extend over tens or more unit cells. Such defects are called shallow level defects.

**1.3.3.2 Line Defects(1D)**

In contrast to point defects, line defects (called dislocations) involve a large number of atomic sites that can be connected by a line. Dislocations are produced if, for example, an extra half plane of atoms are inserted (or taken out) of the crystal as shown in figure 1.6. Such dislocations are called edge dislocations. Dislocations can also be created if there is a slip in the crystal so that part of the crystal bonds are broken and reconnected with atoms after the slip. Dislocations can be a serious problem, especially in the growth of strained heterostructures. In optoelectronic
devices, dislocations can ruin the device performance and render the device useless. Thus the control of dislocations is of great importance.

![Figure 1.6: Schematic presentation of a dislocation.](image)

**1.3.3.3 Planar Defects (2D)**

Planar defects and volume defects are not important in single crystalline materials, but can be of importance in polycrystalline materials. In polycrystalline materials, lattice mis-orientations between the adjoining, randomly oriented crystallites result in grain boundaries. It should be noted that such grain boundaries could block the movement of dislocations.

When the mis-orientation between adjacent grains is small (up to about 15°), the boundary is called low-angle boundary, which consists of an array of well-separated dislocations. In such a case, low-angle boundaries are called (i) tilt boundaries if they consist of edge dislocations and (ii) twist boundaries if they consist of screw dislocations. For larger angles, i.e., for high-angle grain boundaries, the boundary structure cannot be resolved into dislocations and it must be analyzed as a defect in its own right.

In the case of a twin boundary, the atomic arrangements on each side of it are mirror images of each other. The grain boundary is considered as a two-dimensional defect, but in reality there is a specific thickness associated with this defect. In
general, the grain boundaries contain a high density of interface states that may trap free carriers, cause carrier scattering, and act as sinks for the impurity segregation.

Other surface defects are stacking faults. It’s well known that, crystalline structures can be described by their stacking sequence of layers in a close-packed arrangement. For example, the sequence ABCABC... corresponds to the FCC packing, and the ABABAB... represents the hexagonal close-packed structure. In these sequences, if a layer is missing (ABC A (?C) ABC...) or an extra layer is inserted (ABC A (C) BC ABC...) in the cubic structure, then a stacking fault is formed. Analogously, a stacking fault is formed in the hexagonal packing when a layer in the C position is introduced or when a C layer replaces an A or B layer as figure 1.7.

![Figure 1.7: Schematic presentation of stacking sequence and stacking faults of layers in a close-packed arrangement.](image)

1.3.3.4 Volume Defects (3D)

The crystal may contain regions that are amorphous or may contain voids. Other volume defects are cracks, and inclusions. Volume defects can be produced if the crystal growth process is poor but in most epitaxial techniques used in modern optoelectronics; these defects are not a problem. However, the developments of new material systems such as diamond (C) or SiC are hampered by such defects. It should be emphasized that one of the major objectives of the applications of semiconductors in various electronic devices is to control the influence of surfaces, interfaces, and
grain boundaries on the properties of semiconductors and electronic devices. For example, great effort is directed towards processing steps that lead to the passivation of these defects [20]. Generally, some of these defects will be discussed in subsequent chapters.

1.4 An Overview of Transition Metal Chalcogenides (TMCs)

The transition elements are located in groups IB to VIIIB of the periodic table. Because they possess the properties of metals, the transition elements are also known as the transition metals. These elements are very hard, with high melting points and boiling points. Moving from left to right across the periodic table, the five $d$ orbitals become more filled. The $d$ electrons are loosely bound, which contributes to the high electrical conductivity and malleability of the transition elements. The transition elements have low ionization energies. They exhibit a wide range of oxidation states or positively charged forms. The positive oxidation states allow transition elements to form many different ionic and partially ionic compounds. The chalcogen elements belong to the VI-A subgroup of the periodic table.

These elements are: sulfur, selenium and tellurium. The chalcogens are the basic elements of the chalcogenides compounds. The chalcogenides are compounds of sulfur, selenium or tellurium with electropositive elements. These semiconductors are based on one atomic element from group II and one atomic element from group VI, each type being bonded to four nearest neighbors of the other type as shown in figure 1.8. The increased amount of charge from group VI to group II atoms tends to cause the bonding to be more ionic than in the case of III-V semiconductors [27]. Metal chalcogenides (sulfide, selenide and telluride) have been intensively studied over the past sixty years in the field of optoelectronics, holographic recording systems, electronic switching, infrared production, detection lubrication, gas sensors, catalysts and other optical devices etc. [28-33]. The Zn and Cd-chalcogenides (i.e., compounds with O, S, Se, and Te) are covering a wide range of electronic and optical properties due to the wide variations in their energy gap. These compounds are also relatively easily miscible, which allows a continuous “tuning” of various properties. However, the preparation of high quality materials and the processing technologies are not sufficiently developed in comparison with those related to Si and some III–V compounds.
Figure 1.8: Compound II-VI semiconductor such as CdS.

1.5 Literature Survey in TMCs Properties

1.5.1 Structural Properties of TMCs

All the 12 mono-chalcogenides of the IIB metals crystallize in the tetrahedral zinc blende (ZB) or wurtzite (W) structures, as shown in the table 1 below, with the exception of HgS that exists also in a distorted rock salt (RS) form. The II-VI or III-V compounds crystallize in zinc blende structure and show semiconducting behavior. Definitely, these compound semiconductors have both advantages and disadvantages over silicon. The main disadvantage of silicon is that it is an indirect band gap semiconductor. Hence radiative transition probability reduces significantly compared to direct band gap semiconductors, and make it unsuitable or inefficient in many applications particularly in optoelectronic applications. So, synthesizing semiconducting materials, both known and new type, of desired quality and studying their properties for possible technological applications is one of the most important fields of research in material science [2].

Some group III–V semiconductor compounds (e.g., GaAs, InP, and InAs) and group II–VI compounds (e.g., ZnS, ZnSe, and CdTe) crystallize in the zincblende structure. Some semiconductors can crystallize in several different structures depending on temperature or pressure, leading to polymorphism and the existence of
different polytypes. For example, ZnS can exist in several different structural forms, such as a cubic (zincblende) structure, or as a hexagonal (wurtzite) structure, or as various polytypes. Some of the important physical properties of group II – VI compounds are briefly summarized in table 1.1.

Ionic compounds, such as group IV–VI compounds (e.g., PbS, PbSe, and PbTe) crystallize in the rock salt structure (NaCl structure), which can be viewed as a cubic structure consisting of two interpenetrating FCC lattices displaced from each other by one-half of a cube diagonal [1].

Normally, zinc and cadmium chalcogenides exist with several modifications in structure, the major ones being the sphalerite structure and the wurtzite where the classified of crystal structures for II – VI compounds listed in table 1. 1 [34,35]. In the majority of the II – VI compounds, the interatomic distance in the tetrahedral of both modifications are very similar. In view of the two structures, zinc and cadmium chalcogenides prepared from the gaseous phase crystallizes not only in the three - layer (cubic) or two - layer (hexagonal) forms, but they can also have structures in which the sequence of layers is different. This would give rise to multilayer polytypic forms, similar to those observed for silicon carbide.

**Table 1.1** Data collection of Physical Properties for some II–VI compound semiconductors.

<table>
<thead>
<tr>
<th>Material Property</th>
<th>CdS</th>
<th>CdSe</th>
<th>CdTe</th>
<th>ZnS</th>
<th>ZnSe</th>
<th>ZnTe</th>
</tr>
</thead>
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<tr>
<td><strong>Stable phase(s) at 300K</strong></td>
<td>ZB &amp; WZ</td>
<td>ZB &amp; WZ</td>
<td>ZB</td>
<td>ZB &amp; WZ</td>
<td>ZB</td>
<td>ZB</td>
</tr>
<tr>
<td><strong>Symmetry ZB/WZ</strong></td>
<td>C6me/F43m</td>
<td>C6me/F43m</td>
<td>–/–</td>
<td>C6me/F43m</td>
<td>–/F43m</td>
<td>–</td>
</tr>
<tr>
<td><strong>WZ density at 300K (gm/cm³)</strong></td>
<td>4.87</td>
<td>5.655</td>
<td>5.86</td>
<td>4.11</td>
<td>5.26</td>
<td>5.65</td>
</tr>
<tr>
<td><strong>Melting point (°C)</strong></td>
<td>1475</td>
<td>1239</td>
<td>1092</td>
<td>1830</td>
<td>1520</td>
<td>1295</td>
</tr>
<tr>
<td><strong>Sublimation temperature [°C]</strong></td>
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<td>700</td>
<td>1100</td>
<td>1100</td>
<td>1000</td>
<td>1000</td>
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<tr>
<td><strong>Elastic Stiffness Constants</strong></td>
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<tr>
<td>$C_{11}$ (GPa)</td>
<td>8.31</td>
<td>7.41</td>
<td>5.33</td>
<td>9.81</td>
<td>9.009</td>
<td>7.13</td>
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<tr>
<td>$C_{12}$ (GPa)</td>
<td>5.04</td>
<td>4.52</td>
<td>3.65</td>
<td>6.27</td>
<td>5.34</td>
<td>4.07</td>
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<tr>
<td>Lattice constant (WZ)</td>
<td>(a_0)</td>
<td>(b_0)</td>
<td>(c_0)</td>
<td>(c_0/a_0)</td>
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<td></td>
<td>0.4135</td>
<td>0.430</td>
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<td></td>
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<td>1.636</td>
<td>1.641</td>
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<tr>
<td></td>
<td>1.632</td>
<td>1.633</td>
<td>1.636</td>
<td>1.637</td>
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<tr>
<td>Thermal conductivity (W/Kcm)</td>
<td>0.2</td>
<td>0.09</td>
<td>0.01</td>
<td>0.27</td>
<td>0.19</td>
<td>0.18</td>
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<td>Dielectric constant</td>
<td>(\varepsilon_0/\varepsilon_\infty)</td>
<td>8.6/5.3</td>
<td>9.5/6.2</td>
<td>2.27/-</td>
<td>8.6/5.2</td>
<td>9.2/5.8</td>
</tr>
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<td>Specific Heat CL</td>
<td>0.33</td>
<td>0.255</td>
<td>0.205</td>
<td>0.47</td>
<td>0.339</td>
<td>0.264</td>
</tr>
<tr>
<td>Linear expansion coefficient ((10^{-6})\ K^{-1})</td>
<td>3.0/4.5</td>
<td>3.0/7.3</td>
<td>5.1/-</td>
<td>-/6.9</td>
<td>7.6/-</td>
<td>8.0/-</td>
</tr>
<tr>
<td>ZB/WZ</td>
<td>30.5</td>
<td>15</td>
<td>12</td>
<td>36</td>
<td>21</td>
<td>10</td>
</tr>
<tr>
<td>Exciton binding energy(meV)</td>
<td>(\lambda=10.6\mu m) ((\text{cm}^{-1}))</td>
<td>(\leq 0.007)</td>
<td>(\leq 0.0015)</td>
<td>(\leq 0.003)</td>
<td>(\leq 0.15)</td>
<td>1.2\times10^{-3}</td>
</tr>
<tr>
<td>Poission ratio</td>
<td>--</td>
<td>--</td>
<td>0.41</td>
<td>0.27</td>
<td>0.28</td>
<td>--</td>
</tr>
</tbody>
</table>

Note: the data adapted from various sources [36-51].

1.5.2 Optical Properties of TMCs

Since all the II–VI compound semiconductors have direct energy gaps, efficient emission or absorption of electromagnetic radiation can be expected in these materials. Thus, these semiconductors are important mainly for their optical properties. Semiconductor technology has continuously progressed from the use of elemental semiconductors such as silicon and germanium to the use of binary, ternary and higher order alloys, particularly of III-V and II-VI compounds.

The interest in these semiconductor alloys stems from the desire to control the energy band gap, which ultimately dictates the spectral range over which the optical detectors and sources and other optoelectronic devices operate, and also to engineer the lattice parameter of the substrate to match that of the epitaxial layer [52, 53]. The band gap energy of II–VI compounds are given in table 1.2 at T=0 K and T=300 K with some related parameters.
II-VI semiconductor technology has been steadily progressing for the past sixty years. Earlier studies focused on luminescence in the zinc and cadmium sulfide and selenides, with basic studies on bulk II-VI crystals continuing into the 50’s and 60’s. In the 70’s and 80’s and part of the 90’s the focus of II-VI technology was dominated by mercury cadmium telluride (MCT) for infrared detection and, as epitaxy of MCT evolved, bulk CdTe and CdZnTe crystal growth advanced to provide lattice matched substrates with low defect density [54-56]. From the 90’s through now, II-VI materials found wider applications which include crystals for optoelectronics, electro-optics, nonlinear optics, gamma- and X-ray detectors, and terahertz sources and sensors [53, 57-59]. Interest II-VI materials stems from three main factors:

- Direct band gap, useful for both light sources and detectors;
- Band gaps spanning from semi-metallic to a wide band gap of 4 eV;
- Possibility of tailoring lattice parameters and band gap via ternaries and quaternaries.

Despite tremendous advances in epitaxial growth technologies in II-VI semiconductors, bulk crystal growth technology remains equally important to produce II-VI materials for the applications which require larger interaction length with electromagnetic radiations.
Table 1.2: Data collection of the band gap energy for some TMCs with some related parameters at $T = 0K \& 300 K$.

<table>
<thead>
<tr>
<th>Material</th>
<th>Property</th>
<th>Energy gap $E_g$ (eV) at 0K</th>
<th>Energy gap $E_g$ (eV) at 300K</th>
<th>Electron affinity $\chi_0$ (eV)</th>
<th>Transmittance range [μm]</th>
<th>Refractive index</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS(Γ)</td>
<td></td>
<td>2.583</td>
<td>2.42</td>
<td>4.87 / 4.50</td>
<td>0.5 - &gt;14</td>
<td>2.50 at 550 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.26 at 10 μm</td>
</tr>
<tr>
<td>CdSe(Γ)</td>
<td></td>
<td>1.846</td>
<td>1.75</td>
<td>4.95</td>
<td>0.7 - 25</td>
<td>2.5 at 550 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.4 at 10 μm</td>
</tr>
<tr>
<td>CdTe(Γ)</td>
<td></td>
<td>1.606</td>
<td>1.43</td>
<td>4.28</td>
<td>0.9 - 25</td>
<td>3.10 at 3 μm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.60 at 10 μm</td>
</tr>
<tr>
<td>ZnS(Γ)</td>
<td></td>
<td>3.841</td>
<td>3.68</td>
<td>3.9</td>
<td>0.4 - 15</td>
<td>2.30 at 550 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2 at 10 μm</td>
</tr>
<tr>
<td>ZnSe(Γ)</td>
<td></td>
<td>2.825</td>
<td>2.71</td>
<td>4.09</td>
<td>0.6 - &gt;15</td>
<td>2.60 at 633 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.20 at 10 μm</td>
</tr>
<tr>
<td>ZnTe(Γ)</td>
<td></td>
<td>2.394</td>
<td>2.26</td>
<td>3.53</td>
<td>0.7 - 20</td>
<td>2.80 at 1 μm</td>
</tr>
</tbody>
</table>

Note: the data adapted from various sources [36-51].

1.5.3 Electrical Properties of TMCs

The TMCs having good electrical properties and increased of capability in obtaining p- or n-type conductivity by doping [60]. The II–VI compounds are typically $n$-type as grown, except ZnTe, which is $p$-type. Others, such as ZnSe, ZnS and CdS, can be doped to produce a small majority of holes. For device applications, it is possible (i) to form heterojunctions in which the $n$- and $p$-sides of the junction are of different II–VI compound semiconductors and (ii) to use metal–semiconductor and metal–insulator–semiconductor structures for carrier-injection device applications. The challenges in growing II–VI crystals stem, to a large extent, from the highly ionic nature of bondings between anions and cations [61]. Table 1. 3 show the electrical parameter of the selected compound of II–VI group.
Table 1.3: II-VI compounds with their Resistivity, Mobility, Effective Masses $m_e$ and $m_h$, Effective Densities of States $N_c$ and $N_v$, and Intrinsic Carrier Concentration $n_i$ at Room Temperature.

<table>
<thead>
<tr>
<th>Material Property</th>
<th>Resistivity ($\Omega \text{.cm}$)</th>
<th>Electron Hall mobility ($\text{cm}^2/\text{vsec}$)</th>
<th>Hole Hall mobility ($\text{cm}^2/\text{vsec}$)</th>
<th>$m_e$ ($m_0$)</th>
<th>$m_h$ ($m_0$)</th>
<th>$N_c$ ($10^{18}$ cm$^{-3}$)</th>
<th>$N_v$ ($10^{18}$ cm$^{-3}$)</th>
<th>$n_i$ ($\text{cm}^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CdS(}\Gamma\text{)}$</td>
<td>$10^8 - 10^{12}$</td>
<td>340</td>
<td>340</td>
<td>0.2</td>
<td>1</td>
<td>2.41</td>
<td>25.7</td>
<td>0.012</td>
</tr>
<tr>
<td>$\text{CdSe(}\Gamma\text{)}$</td>
<td>$\sim 10^8$ (n-type)</td>
<td>650</td>
<td>-</td>
<td>0.112</td>
<td>1.51</td>
<td>0.94</td>
<td>46.5</td>
<td>$1\times10^4$</td>
</tr>
<tr>
<td>$\text{CdTe(}\Gamma\text{)}$</td>
<td>$10^2 - 10^3$</td>
<td>1050</td>
<td>100</td>
<td>0.096</td>
<td>0.76</td>
<td>0.75</td>
<td>16.5</td>
<td>$3\times10^6$</td>
</tr>
<tr>
<td>$\text{ZnS(}\Gamma\text{)}$</td>
<td>$10^8 - 10^{10}$</td>
<td>165</td>
<td>5</td>
<td>0.34</td>
<td>1.79</td>
<td>4.97</td>
<td>60.3</td>
<td>$2\times10^{-12}$</td>
</tr>
<tr>
<td>$\text{ZnSe(}\Gamma\text{)}$</td>
<td>$\sim 10^8$ (p-type)</td>
<td>500</td>
<td>30</td>
<td>0.16</td>
<td>0.65</td>
<td>1.61</td>
<td>13.1</td>
<td>$8\times10^{-5}$</td>
</tr>
<tr>
<td>$\text{ZnTe(}\Gamma\text{)}$</td>
<td>$10^8 - 10^7$</td>
<td>340</td>
<td>100</td>
<td>--</td>
<td>--</td>
<td>2.2</td>
<td>0.78</td>
<td>--</td>
</tr>
</tbody>
</table>

Note: the data adapted from various sources [30-35].

The materials have poor thermal conductivity at growth temperatures, poorer than fused silica commonly used as crucible material. The occurrence of both zinc-blende and wurtzite structures in most II-VI compounds leads easily to the formation of stacking faults/twins. In addition, formation of the high concentration of vacancies and defect complexes complicates the control of electrical properties of these materials.

1.5.4 Some Important Applications of TMCs

All zinc chalcogenides are important materials in the fabrication of heteroepitaxial solid-state devices, like those involving ZnSe/GaAs, ZnSe/Ge, ZnS/GaP, ZnS/Si, ZnTe/InAs, and ZnTe/GaSb interfaces. In fact, ZnSe is rather the most extensively investigated wide-gap II–VI compound in heteroepitaxy, in terms of interface chemistry, growth mechanism, and defect generation in epilayers. It also constitutes one of the basic materials for the construction of heterojunction devices under lattice matching conditions by adopting suitable alloy systems of other II–VI compounds. Generally, the semiconductor is used for electronic device due to:
1. Their material characteristics can be changed significantly through the process known as “doping”. Doping is a process of adding impurity to semiconductor material. That material can be changed from poor conductor to a good conductor of electricity.

2. Their characteristics can be altered significantly through the application of heat or light- an important consideration in the development of heat- and light-sensitive devices.

Cadmium mono-chalcogenides, with their energy band gaps (CdS: 2.4 eV, CdSe: 1.7 eV, CdTe: 1.4 eV), have been thoroughly studied both theoretically, as model semiconductor materials, and technologically, for applications ranging from solar photocatalysis to solar photovoltaic (photoelectrochemical) conversion. Activated CdS and CdSe have also been used extensively as phosphors; their application, however, is now limited by the toxicities of cadmium and selenium, although they are still used in radar displays and high-resolution storage tubes.

CdSe and CdTe find application in solar cells, thin film transistors, memory as well as magneto-optical and optoelectronic devices, photoelectrochemical cells (CdSe), photoconductors, and γ-ray or infrared (CdTe) detectors [62-64]. Notably, CdTe has been recognized theoretically [65] as the semiconductor yielding the highest efficiency of photovoltaic solar energy conversion (ca. 24%, defined as the ratio of the maximum electrical power output to the solar power flux incident to the semiconductor surface [66].

### 1.6 Choice of Material (CdS) and Its Importance

#### 1.6.1 Cadmium (Cd) and Its Importance

Cadmium is a chemical element with the symbol Cd and atomic number 48. Its group name is a transition metal. It is main group metal in group 12 (CAS IIB) of the periodic table. Cadmium is a rare element and is derived exclusively from zinc ores. It is most often found in combination with other elements, such as oxygen (cadmium oxide), chlorine (cadmium chloride), or sulfur (cadmium sulfide). Cadmium is found throughout the environment from natural sources and processes such as the erosion and abrasion of rocks and soils, and from singular events such as forest fires and volcanic eruptions. Crystal structure of cadmium is hexagonal close packed. The main physical properties of cadmium are reported in table 1.4.
Most cadmium metals today are produced as a by-product of the extraction, smelting and refining of the nonferrous metals – zinc, lead and copper. Cadmium and its compounds are highly toxic. The harmful effects of cadmium to humans and the environment include: it is flammable in powder form, toxic by inhalation of dust or fume, and is a carcinogen. Soluble compounds of cadmium are highly toxic. By Long term-concentrates in the liver, kidneys, pancreas, and thyroid cause hypertension. Short term health effects include a flu-like illness with chills, headache, aching and/or fever. High exposures can cause rapid and serve lung damage, with shortness of breath, chest pain, cough and a buildup of fluid in the lungs. The main target organs for cadmium are the kidney and liver, with critical effects so the World Health Organization has recommended a maximum intake of 0.4-0.5 mg/week [67].

### 1.6.2 Sulfur (S) and Its Importance

Sulfur is a chemical element with the symbol S and atomic number 16. Its group name is chalcogen. It is main group metal in group 16 of the periodic table. It is a reactive element that given favorable circumstances combines with all other elements except gases, gold, and platinum. Sulfur appears in a number of different allotropic modifications: rhombic, monoclinic, polymeric, and others. The rhombic structure is the most commonly found sulfur forms. Sulfur is an odorless, tasteless, light yellow solid. The rhombic structure is the most commonly found sulfur forms. Each allotropic form differs in solubility, specific gravity, crystalline, crystalline arrangement, and other physical constants. These various allotropes also can exist together in equilibrium in definite proportions, depending on temperature and pressure. The major derivative of sulfur is sulfuric acid (H₂SO₄), one of the most important elements used as an industrial raw material. Sulfur is also used in batteries, detergents, fungicides, manufacture of fertilizers, gun power, matches and fireworks. The main physical properties of sulfur are reported in table 1.4.

Other applications are making corrosion-resistant concrete which has great strength and is foster resistant, for solvents and in a host of other products of the chemical and pharmaceutical industries. Sulfur can be found commonly in nature as sulfides. During several processes sulfur bonds are added to the environment that are damaging to animals, as well as humans. These damaging sulfur bonds are also shaped in nature during various reactions, mostly when substances that are not naturally present have already been added. They are unwanted because of their
unpleasant smells and are often highly toxic. Sulfur can be found in the air in many different forms. It can cause irritations of the eyes and the throat with animals, when the uptake takes place through inhalation of sulfur in the gaseous phase. Sulfur is applied in industries widely and emitted to air, due to the limited possibilities of destruction of the sulfur bonds that are applied [68, 69].

Table 1.4: Some physical properties of cadmium and sulfur

<table>
<thead>
<tr>
<th>Element</th>
<th>Cd</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Crystal Structure</strong></td>
<td>Hexagonal close packed</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td><strong>Lattice Constant (Å)</strong></td>
<td>$A = 2.98; C = 5.620$</td>
<td>$a= 10.4646 , b= 12.8660 , c= 24.4860$</td>
</tr>
<tr>
<td><strong>Atomic Weight</strong></td>
<td>112.41</td>
<td>32.06</td>
</tr>
<tr>
<td><strong>Atomic Number</strong></td>
<td>48</td>
<td>16</td>
</tr>
<tr>
<td><strong>Electron Configuration</strong></td>
<td>$s^2 , 2s^2p^6 , 3s^2p^6d^{10} , 4s^2p^6d^{10} , 5s^2$</td>
<td>$1s^2 , 2s^2p^6 , 3s^2p^4$</td>
</tr>
<tr>
<td><strong>Density (20°C)</strong></td>
<td>8.65 g/cm³</td>
<td>2.07 g/cm³</td>
</tr>
<tr>
<td><strong>Melting Point (S.T.P)</strong></td>
<td>320.9 °C</td>
<td>113 °C</td>
</tr>
<tr>
<td><strong>Boiling Point (S.T.P)</strong></td>
<td>765 ± 2 °C</td>
<td>445 °C</td>
</tr>
</tbody>
</table>

1.6.3 Cadmium Sulfide (CdS) and Its Importance

CdS, being II-VI semiconducting compound, has some interesting properties which make it a beneficial material in optoelectronic devices [70]. It is yellow in color. CdS exists as two different polymorphs, hexagonal (wurtzite) form or cubic (zincblende) form, or mixture from them depending upon the thermodynamic parameters and growth techniques but wurtzite is the common form of CdS with a band gap of 2.4 eV CdS finds a place in the class of wide gap semiconductors [6,71,72]. The Cd-S bonds in the crystal have both ionic and covalent character. Bulk CdS usually has n-type conduction, which is due to the deficiency of S. Pure CdS crystals have a high resistivity about $10^{12} \, (\Omega \cdot \text{cm})$. CdS resistivity can be reduced by doping or by some growth techniques [73-78]. Cadmium sulfide (CdS), a wide energy gap semiconductor has emerged as an important material due to its applications in photovoltaic cell as window layers, optical filters and multilayer light emitting diodes, photo detectors, thin film field effect transistors, gas sensors, and transparent conducting semiconductor for optoelectronic devices [79-102].
Cadmium and its compounds is highly toxic, stable, with high melting points and volatility. Cadmium sulfide is obtained as a yellow precipitate by passing hydrogen sulfide into a dilute acid solution of a cadmium salt. It is soluble in dilute nitric acid and concentrated mineral acids and insoluble in yellow ammonium sulfide. CdS is an important yellow pigment, used in the paint, glass, rubber, paper, textile, and pyrotechnics industries. Cadmium sulfate is used in electroplating and as a starting material for pigments, stabilizers, and other cadmium compounds that can be precipitated from aqueous solution. It is used to produce fluorescent materials. Some basic properties of cadmium sulfide are listed in below table 1.5.

![CdS Crystal Structures](image)

**Figure 1.9:** The crystal structure of CdS (a) cubic (zinc-blend) (b) hexagonal (wurtzite).
Table 1.5: Important physical properties of cadmium sulfide (CdS)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal structure</td>
<td>Cubic; Hexagonal</td>
</tr>
<tr>
<td>Color</td>
<td>Yellow/Orange or Brown</td>
</tr>
<tr>
<td>Appearance</td>
<td>Yellow-orange solid.</td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>144.46 g/mole</td>
</tr>
<tr>
<td>Melting Point</td>
<td>980 °C</td>
</tr>
<tr>
<td>Boiling point</td>
<td>1750 °C</td>
</tr>
<tr>
<td>Density</td>
<td>4.82 g/cm³</td>
</tr>
<tr>
<td>Solubility</td>
<td>Insoluble in hot and cold water</td>
</tr>
<tr>
<td>Thermal conductivity (at 25 °C)</td>
<td>0.2 W/cmK</td>
</tr>
<tr>
<td>Refractive index (λ=10. 6 μm)</td>
<td>2.2</td>
</tr>
<tr>
<td>Specific Heat</td>
<td>0.47 J/gK</td>
</tr>
</tbody>
</table>

*Note: The data adapted from various sources [103--105].*

1.7 An Overview of Metal-Semiconductor (Schottky Barrier) Junctions

Research work on metal/semiconductor interfaces goes back to the 1930's and the first model on this subject was introduced by Schottky in 1939 [106]. Since then, over the past five decades active research has taken place due to rapid advances in characterization techniques and in the microelectronic devices used in various applications such as computing and telecommunication. Research laboratories throughout the world have been involved in metal/semiconductor interface research and there are now over five different models to describe the formation of Schottky barriers at metal/semiconductor interfaces [107,109]. Scientists have seriously considered a range of possible mechanisms of Schottky barrier formation at these interfaces, and undoubtedly one or more of these mechanisms will dominate for a given system. It is therefore vital to identify and understand the Schottky barrier formation at a particular family of metal/semiconductor interfaces in order to design and develop practical devices [110]. The metal-semiconductor junctions are much used as rectifiers in high power applications circuits, microwave diodes, UV detectors, switching diodes, photo sensors and solar cells. Due to its fast switching effect, it is widely used in digital circuits and communications and radar applications also.
Schottky diodes are often used as ant saturation clamps on transistors as they are used in radio frequency applications as mixer (or) detector diode and also Schottky barrier diodes are used in stand-alone photo voltaic systems. Most of the electronic devices require reliable ohmic contacts for electrical signals to flow into and out of the device, and highly stable metal/semiconductor rectifying contacts as the active region. In both cases it is desirable to know how to fabricate reliable and efficient metal contacts with high yield and stability. It is therefore essential to gain a good understanding of the interfaces metal/CdTe, metal/CdS and metal/ZnSe for development of the above mentioned devices and other possible electronic devices based on II-VI semiconductor materials [111-119]. The following section contains a summary of earlier and recent work on the subject and reviews some of the work in the literature.

A Schottky contact refers to the contact between a metal and a semiconductor that hinders the flow of carriers in and out of the semiconductor. When negative charges (electrons) are brought near the metal surface, positive charges are induced in the metal. When the applied electric field is coupled with the force induced to carry an electron into vacuum, the effective work function is somewhat reduced. Such lowering of the barrier is referred to as Schottky effect and the rectifying contacts are referred to as Schottky barrier diodes. The major differences between a Schottky barrier and a p-n junction diode are its typically lower junction voltage, and decreased (almost nonexistent) depletion width in the metal.

MS diode electrostatics and the general shape of the MS diode I-V characteristics are similar to p-n junction diodes, but the details of current flow are different. In a p-n junction diode dominant current mechanisms:

i. arise from recombination in the depletion layer under small forward bias.

ii. arise from hole injection 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 1.10).
Figure: 1.10: Current transport mechanisms in p-n junction diode and MS Schottky diode.

When $\Phi_m > \Phi_s$, the n-type semiconductor fermi level is initially higher than that of the metal before contact is made as shown in the figure 1.11, the fermi levels on both sides line up and relative to the fermi level in the metal, the fermi level in the semiconductor is lowered by an amount equal to the difference between the two work functions. In order to align the fermi levels, the electrostatic potential of the semiconductor must be raised relative to that of metal. In the figure 1.11, after a contact has been made, a depletion region $W$ is formed near the junction on the n-type semiconductor side. The positive charge on the n- type side due to uncompensated donor ions within $W$ equals the net negative charge accumulated on the metal.

At equilibrium, a contact potential of $V_b$ is formed at the junction. This potential prevents further electron diffusion from the semiconductor conduction band into the metal. The contact potential is given by the difference in the work function potentials $\Phi_m - \Phi_s$. The potential barrier height, $\Phi_B$ for electron injection from the metal into the semiconductor conduction band is $\Phi_m - \chi$, where $q\chi$ is the electron affinity measured from the vacuum level to the semiconductor conduction band edge. By applying either forward or reverse-bias voltage, the equilibrium potential difference $V_b$ can be decreased or increased as in the p-n junction.
Figure 1.11: Schottky barrier junction between a metal and n-type semiconductor with $\Phi_m > \Phi_s$ for a band diagram before and after joining of the junction [120].

Figure 1.12 describes the energy band diagram for a Schottky barrier on a metal - p-type semiconductor with $\Phi_m < \Phi_s$. In this case the fermi level of the metal is higher than that of p-type semiconductor before the contact has been made. Aligning fermi levels at equilibrium requires a positive charge on the metal side and a negative charge on the p-type semiconductor side of the junction. In the p-type semiconductor of the figure, a depletion width of $W$ is formed near the junction after the contact has been made. The negative charge due to ionized acceptors within $W$ matches the positive charge on the metal. The potential barrier $V_b$ prevents further hole diffusion from the semiconductor into the metal and is equal to the difference in the work function of the semiconductor and metal ($\Phi_s - \Phi_m$). The potential can be raised or
lowered by applying voltage across the junction just like in the metal - n type semiconductor junction.

Figure 1.12: Schottky barrier between a metal and p-type semiconductor with $\Phi_m < \Phi_s$ for band diagrams before and after joining the junction [120].

1.8 Brief Review of Research Works on Metal / II-VI Semiconductor

In this section is an attempt to present recent developments and progress in electrical contacts to II-VI semiconductors. Experimental evidence shows that a large number of metals are interact with II-VI semiconductors, when the electrical contact is made. Careful examination of the large body of literature on metal/II-VI semiconductors shows a wide variation in reported results and contradictory conclusions. Results appear to vary from research lab to lab for the same metal/semiconductor system and therefore the relevant industrial development program find it hard to select an appropriate device fabrication procedure. As demonstrated in table1.6 and table 1.7 the entire selected metals/II-VI semiconductor
shows the reported studies on Schottky-Barrier Heights at room temperature. Additionally, the values of Schottky parameters i.e. barrier heights, ideality factor, series resistance and saturation current in Al/ n-CdS thin films at 300 K were summarized in table 1.7.

**Table 1.6:** Earlier work of measured Schottky-Barrier Heights on metals/ ZnS, metals/ ZnSe and metals/ ZnTe at 300 K.

<table>
<thead>
<tr>
<th>Metal /Semiconductors</th>
<th>ZnS</th>
<th>ZnSe</th>
<th>ZnTe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>1.65-1.81</td>
<td>1.21</td>
<td>0.94-1.06</td>
</tr>
<tr>
<td>Al</td>
<td>0.8</td>
<td>0.58-0.76</td>
<td>0.76</td>
</tr>
<tr>
<td>Au</td>
<td>2.00-2.19</td>
<td>1.36-1.55</td>
<td>0.51-0.64</td>
</tr>
<tr>
<td>Cu</td>
<td>1.75</td>
<td>1.1</td>
<td>0.80-0.84</td>
</tr>
<tr>
<td>Mg</td>
<td>0.82</td>
<td>0.70</td>
<td>--</td>
</tr>
<tr>
<td>In</td>
<td>1.5</td>
<td>0.9</td>
<td>0.99-1.13</td>
</tr>
</tbody>
</table>

*Note: The data adapted from various sources [40,104,115,121-123].*

**Table 1.7:** Earlier work of measured Schottky-Barrier Heights on metals/ CdS, metals/ CdSe and metals/ CdTe at 300 K.

<table>
<thead>
<tr>
<th>Metal /Semiconductors</th>
<th>CdS</th>
<th>CdSe</th>
<th>CdTe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>0.56</td>
<td>0.43</td>
<td>0.8</td>
</tr>
<tr>
<td>Al</td>
<td>--</td>
<td>--</td>
<td>0.76</td>
</tr>
<tr>
<td>Au</td>
<td>0.68-0.84</td>
<td>0.49-0.7</td>
<td>0.59-1.0</td>
</tr>
<tr>
<td>Cu</td>
<td>0.5</td>
<td>0.33</td>
<td>0.82</td>
</tr>
<tr>
<td>Mg</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>In</td>
<td>--</td>
<td>--</td>
<td>0.69</td>
</tr>
</tbody>
</table>

*Note: The data adapted from various sources [40,104,115,121-123].*
Table 1.8: Summary of recent developments of Schottky parameters in Al/ n-CdS thin films at 300 K.

<table>
<thead>
<tr>
<th>Barrier Heights $\phi_p$</th>
<th>Ideality factor (n)</th>
<th>Series resistance (Ω)</th>
<th>Saturation current (A)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.76</td>
<td>3.4</td>
<td>840</td>
<td>$3.25 \times 10^{-7}$</td>
<td>[14]</td>
</tr>
<tr>
<td>0.74</td>
<td>1.54</td>
<td>130</td>
<td>$4.14 \times 10^{-7}$</td>
<td>[15]</td>
</tr>
<tr>
<td>0.68</td>
<td>1.24</td>
<td>55.56</td>
<td>$4.43 \times 10^{-5}$</td>
<td>[8]</td>
</tr>
</tbody>
</table>

Summary

This chapter is an introduction of the current study and it include the goals of the study also includes a brief review of some of the physical properties and electrical properties and optical properties of some II–VI compound in general and cadmium sulfide in particular. Also, it includes a review of the crystal structure and the defects that may occur to it, which may benefit to the current study. In addition, a quick look to earlier work of measured Schottky-Barrier Heights on metals/some II–VI compounds and the recent development of Schottky parameters in Al/ n-CdS.

References

[53] Mool Chand Gupta and John Ballato (Eds.), Handbook of Photonics (Taylor & Francis, 2006).
[72] Palik, Edward D., “Cadmium Sulfide”, in Handbook of Optical Constant of


