Chapter 1

General Introduction and Overview of Lead Sulphide (PbS) and Bismuth Sulphide (Bi$_2$S$_3$) Thin Film

1.1 Introduction

Thin film is a two dimensional form of solid material, whose one dimension called thickness is much smaller than the other two dimensions. Thin film is formed by controlled condensation of the individual atom, molecule or ionic species on solid material (substrates) either by physical or chemical process. Thin film may cover a considerable thickness range, varying from a few nanometers to several micrometers depending upon the field of application. Thin film technology is the basic of amazing development in solid state electronics. Due to the production simplicity and economic feasibility, thin films have replaced the earlier crystal growth in solid state devices. The processing of materials into thin films allows easy integration into various types of devices. On the other hand, thin film technology contributes to the development of microelectronics by reducing the sizes of semiconductor devices to two dimensions. In addition to major contributions to variety of new and future scientifically based technology, the studies of thin films of different materials and their devices have directly or indirectly advanced new areas of research in different allied fields.

In the recent years, nanocrystalline (NCs) semiconductor thin films occupied an important place in research work due to their future applications in the diverse fields of science and technology. Nanocrystalline materials are single phase or multi-phase
polycrystalline materials with crystal sizes in the nanometer range less than 100 nm in at least one dimension [1-3]. Nanocrystalline semiconducting materials have opened a new chapter in the field of electronic applications, since the optical, electrical, magnetic and chemical properties of the material change significantly by changing the grain size and thickness of the film [4, 5]. The unusual properties of the nanocrystalline semiconductor thin films can be assigned to two effects: quantum confinement effect and surface effect [6]. The quantum confinement effect arises due to the confinement of electrons and holes when the size of the particle is comparable or smaller than the Bohr exciton radius and consequently changes the band structure. Due to diminishing size, a significant volume of atoms resides at the surface of the nanocrystalline thin films leading to a large volume fraction of surface atoms and these surface atoms drastically enhance or modify the physical and chemical properties of nanocrystalline thin films. The quantum size effect in NCs and resulting wide tunable band gap allow for light harvesting spanning a broad range of the solar spectrum, including the near infrared. Recent advances in the synthesis and characterization of semiconductor nanocrystals (NCs) have greatly improved the ability to tailor their electronic and optical properties making them suitable for several applications [7]. Thin film based on nanocrystalline solar cells have generally received a lot of attention in recent times and have been considered the most widespread alternative to bulk crystalline solar cell. This interest is based on the low material consumption, the relatively low cost and large area deposition possibilities at relatively low temperature [8-10]. It is known that greater the band gap of a solar cell semiconductor, greater is the output voltage provided towards electricity generation. Both high current and voltages are desired for efficient solar electric conversion. Thus, there exists an optimum band gap that corresponds to the highest
possible solar-electric energy conversion [11]. One of the main factors driving the current interest for semiconducting nanocrystalline thin film is due to the fact that optimization of devices such as solar cells, supercapacitors, photocatalytic coatings and electrochromic windows requires control of the physical and chemical properties of the employed materials [12-14]. Nanocrystalline thin films of semiconductor compounds such as CdS, CdTe, CdSe, ZnSe, ZnS, SnO₂, Cu₂S, ZnO, TiO₂, NiO, PbS, PbSe, Bi₂S₃ prepared by chemical bath deposition (CBD) method have been extensively used in sensors, light emitting diodes (LED), electroluminescence devices, lasers, optical amplifiers, photo detectors, lux meters and optical coatings [16-34].

Nanocrystalline thin films have been synthesized by different techniques such as chemical bath deposition, electro-deposition, spray pyrolysis, SILAR, physical vapour deposition, inert gas condensation, laser ablation, chemical vapour deposition, etc. [15] Among them chemical bath deposition method, which is suitable and most economic for the deposition of nanocrystalline thin film is used in the work presented in this thesis.

The studies of Schottky junction and heterojunction are a good example in which the impetus and motivation as well as the framework for the formulation of most of the research problems are provided by a desire to advance device technology. The utilization of more and more semiconducting materials for the fabrication of devices during the past decade has led to numerous basic and applied investigations and their interpretation in this field. The use of thin film technology in making Schottky junction and heterojunction have revolutionised in the semiconductor technology. The asymmetric nature of electrical conduction between metal-semiconductor was first reported by Braun in 1874 [35]. In 1938, the theory of metal-semiconductor contacts was developed by Walter Schottky [36], which is later name as Schottky-barrier contact.
In the same year, Mott also devised an appropriate theoretical model for swept-out metal semiconductor contact [37], which is known as the Mott barrier. Schottky barrier junction has a rectification capacity 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. The basic theory and historical development of rectifying metal-semiconductor contacts have been summarized by Henisch [38] and the properties and application of Schottky barriers have been reviewed by Atalla [39]. Metal-semiconductor junctions are used as rectifiers, microwave diodes, photo sensors and solar cells etc. [40-46].

In 1951, Shockley first proposed the abrupt heterojunction to be used as an efficient emitter based junction in bipolar transistor [47]. In the same year, Gubanov published theoretical papers on heterojunction [48], Kroemer later analysed a similar although graded, heterojunction as a wide gap emitter [49]. Since then, heterojunctions have been extensively studied, and many important applications such as room temperature injection laser, light emitter diode, photodiode and solar cell etc. have been made. The heterojunction have been reviewed by Milnes and Feucht [50] and Sharma and Purohit [51].

At present, the sceneries of research and development in the field of electronics and the semiconductor-devices are so changing, it is therefore important for us to understand the fundamental physical processes and to equip ourselves with sufficient background on physics and mathematics to digest, appreciate, and meet the challenges of these dynamic fields.
### 1.2 Aims and objectives of the present work

The studies of semiconductor thin films and their junctions such as metal-semiconductor junctions and heterojunctions have received much attention due to their various applications in electronic devices. Different semiconducting materials are employed to study their suitability in different solid state devices depending on their band gaps and properties. Bi$_2$S$_3$ is a wide band gap material and suitable candidate for the solar energy conversion devices as its forbidden energy gap lies between 1.25 eV to 1.9 eV [52]. PbS is an interesting narrow band gap semiconductor which shows strong quantum confinement properties [53]. The band gap energy of PbS (0.41eV bulk form) can be increased to higher values by decreasing the size of the grains into the nanoregime. This property makes it capable of absorbing a major portion of solar energy and hence provides ample scope for the fabrication of solar cells. Thus, Bi$_2$S$_3$ is used as window material and PbS is used as absorber material for the heterojunctions. The primary function of a window layer in a heterojunction is to form a junction with the absorber layer and at the same time admitting maximum amount of light to the junction region and absorber layer.

In the present work, structural, optical and electrical properties of the nanocrystalline PbS and Bi$_2$S$_3$ are studied. Schottky junctions and heterojunctions based on nanocrystalline PbS and Bi$_2$S$_3$ are fabricated and studied their electrical characteristics with the aim of their possible uses in photovoltaic devices.

In brief, following are the aims and objectives of the present works:

i. To prepare nanocrystalline PbS and Bi$_2$S$_3$ thin films by chemical bath deposition (CBD) method.

ii. To study the structural, optical and electrical properties of the nanocrystalline PbS
and Bi$_2$S$_3$ thin films at different deposition parameters.

iii. To fabricate the Schottky barrier junctions based on nanocrystalline PbS and Bi$_2$S$_3$ thin films.

iv. To fabricate heterojunctions based on nanocrystalline PbS and Bi$_2$S$_3$ thin films with (p)Si and (n)Si wafers.

v. To study the current-voltage (I-V) and C-V characteristics of the Schottky junctions and heterojunctions and their photovoltaic effect.

vi. To calculate the various junction parameters from the I-V and C-V characteristics.

1.3 Overview of works on Lead Sulphide (PbS) and junctions based on Lead Sulphide (PbS)

1.3.1 Characteristics of Lead Sulphide (PbS)

Lead sulphide (PbS) is a IV-VI group of semiconductor having cubic crystal structure and a narrow band gap of 0.41eV at 300K in its bulk phase. Its crystal structure has been shown in Fig.1.01. It is a direct band gap ($E_g$) semiconductor having optical absorption coefficient greater than $10^5$ cm$^{-1}$ [54-58]. PbS exhibits large excitonic Bohr radius of 18 nm [32] which results in strong quantum confinement of both electrons and holes in nano-sized structure, so that the value of the band gap can be controlled by modifying particle size according to the effective mass model [59]. These unique properties make PbS very suitable for infrared detection applications and attractive for new applications such as solar cells [60, 61]. Both p-type and n-type can be made by doping. PbS has been also recommended as an earth-abundant sustainable affordable photovoltaic material [62]. PbS has wide applications in the fields of infrared photography, diode laser, humidity and temperature sensors, solar control coating, solar cells, optoelectronic devices and more recently as infra-red emitters [63-68].
1.3.2 Works on Lead Sulphide (PbS) film

There are several reports on the preparation, characterization and applications of nanocrystalline PbS thin films. Osherov et al. [69] investigated the optical properties of the chemically deposited PbS thin films on GaAs (100) coated substrates using infrared transmission and photoluminescence spectroscopy. The blue shifts in both absorbance and emission peaks of the nano-structured layers are obtained due to quantum size effects. Valenzuela et al. [70] reported optical properties of chemically deposited PbS films at temperature ranges 283-303K and established values of dielectric constant (ε) that were attributed to the empty spaces between the aggregates. The AFM analysis showed a mixture of PbS and voids but the structure was similar to the one reported by Seghaeir et al. [71]. Choudhury and Sarma [72] characterized nanocrystalline PbS thin films sensitised by CBD and reported crystal sizes of 2 nm-2.4 nm with a band gap...
range of 1.9 eV-2.6 eV. Sashchiuk et al. [73] reported the optical and electrical properties of various sizes of the PbS NCs in ZrO$_2$ sol gel films. Absorption and PL results provided strong evidence for carriers’ confinement. The electrical measurement of the films showed the electrical conductivity to be dependent on the PbS NCs properties and was attributed to an inter-NCs coupling and thermally activated carriers hopping from one NCs to the other by low electric fields and space charge limited current via Zirconia film in high electric fields. Gaiduk et al. [74] investigated and compared the characteristics of nanocrystals PbS layers deposited chemically on Ge, GaAs and Si. The investigations show that the morphology and the thickness of the layers strongly depend on the chemical nature of the substrates. That is, the layer of PbS deposited on Ge and GaAs are thicker than those deposited on Si but have a relatively small grain size. Hui Wang et al. [75] characterized nanocrystal PbS prepared in an oil-in-water microemulsion by a Sonochemical method and reported average crystal size to be 11nm. Saraidarov and Reisfeld [76] reported the optical and electrical properties of various sizes and concentrations of PbS nanocrystals (NCs) in hybrid thin films prepared by the Sol-gel process. TEM and absorption measurements showed that the average diameter of the PbS NCs varied between 2 nm and 8 nm with an increase in the temperature treatment and with an increase of the concentration of di-Urethane-Silica (DURS) and the PbS volume fraction (5-30 mole %). I-V characteristics were found to depend on the DURS concentration. Osuwa et al. [77] reported that the presence of cadmium ions on PbS thin films to enhance the crystallites, which in turn modified the absorption edges of the films resulting in the increase in band gap. Das and Kumar [78] reported that the crystal structure and optical properties of the PbS films influenced on growth parameters, doping and annealing. The crystallite size of nanocrystalline PbS
was calculated as 40.4 nm, which reduced to 31.9 nm after annealing. With increasing Sn doping concentration, FWHM, strain value and dislocation density decrease whereas crystallite size increases. Obadiah et al. [79] investigated the effect of deposition time on structural and microstructural as well as optical and electrical properties. Patil et al. [80] investigated the structural, surface morphological and electrical properties of nanocrystalline PbS films deposited at room temperature. From the investigation, it is found that the film is smooth, homogeneous and well covered to the glass substrate. Acharya and Bose [81] used lead acetate and thiourea to grow polycrystalline PbS thin films at 303K. Bo Zhang et al. [82] reported a new method of preparing size-controlled and well-dispersed PbS nanocrystals using water/C\textsubscript{12}E\textsubscript{8}/cyclohexane microemulsions as the nano-reactors. The sizes and morphologies of the cubic PbS nanocrystal can be modified by controlling the concentration of ions, the volume ratio of water surfactant and the reaction temperature. Amusan et al. [83] reported the influence of deposition time on the transmissivity of PbS thin film. The transmissivity initially increases with deposition time up to an optimum point beyond which it decreases with increasing deposition time. Popa et al. [84] reported an absorption band in the infrared range [1250 - 2400 nm] to be of 1.23 eV – 1.28 eV from absorption measurements and a 0.93 eV – 1.0 eV from photocurrent measurement. Oriaku and Osuwa [85] reported that the annealing temperature appreciably affected both the microstructures and crystallites sizes of the films. Gutman et al. [86] reported on the fabrication of composite PCs made of macroporous silicon and thin films of lead sulphide (PbS) NCs. Kang et al. [87] reported that quantum dots of PbS embedded in a TiO\textsubscript{2}-glycerol matrix can serve as passive mode locks and high speed photonics switches operating at fairly low power threshold. Mukherjee et al. [88] prepared nano-sized particles of PbS with average
diameters ranging from 9.9 nm to 18 nm within a polyacrylamide matrix. The estimated band gap for these nanosized particles is found to be much higher than that of bulk PbS in the range 1.03 eV-1.49 eV and the conductivity at temperature lower than 340K is controlled by an electron tunnelling mechanism. Kumar et al. [89] prepared the nanocrystalline PbS at different deposition temperatures and time and the samples were characterized by XRD, FTIR, SEM and UV-vis. The reported crystallite size was 40 nm and bandgap was 2 eV which was higher than the bulk due to quantum confinement. FTIR study of PbS nanoparticles showed the presence of different functional groups and presence of PbS. Reiche et al. [90] investigated photoemission properties of PbS-SiO$_2$ composite samples. Capoen et al. [91] reported PbS nanoparticles are found to have very different optical properties when they were mixed with sol-gel solutions. Lobo et al. [92] studied the surface structure of organically capped PbS nanocrystals using synchrotron radiation excited core–level photoelectron spectroscopy. The results indicated that the trioctylphosphine ligands passivate only the surface S sites while oleic acid ligands appear to bind mainly to Pb sites. Remadevi and Preetha [93] investigated the comparative studies on structural, optoelectronic and electrical properties of SILAR grown PbS thin films from acidic, neutral and alkaline cationic reaction bath and reported that the films prepared in alkaline medium obtained larger grain size. Ubale et al. [94] prepared the nanocrystalline PbS thin films by CBD method and reported that the structural, electrical and optical properties of the PbS films are dependent on film thickness. The crystallite size and conductivity increases with increase in film thickness. Pentia et al. [95] reported the comparative studies between two types of PbS films “Standard” and “nanocrystalline” prepared by CBD method. Kaci et al. [96] reported the deposition of the nanocrystalline PbS on p-type Si (100) and on corning glass slides
substrates by CBD method. The average film thickness of the samples grown on (100) silicon substrates were found to be up to 20% less than that grown on glass substrates. Dhlamini et al. [97] reported growth of lead sulphide nanoparticles embedded in an amorphous silica (SiO$_2$) host on Si(100) substrates at different temperatures by the pulsed laser deposition (PLD) technique. The red-shift increased slightly with an increase in deposition temperature, which suggests that there has been a relative growth in particles sizes during the pulsed laser deposition (PLD) of the films at the higher temperatures. Ezugwu et al. [98] prepared the nanocrystalline PbS thin films by CBD at room temperature within the self-organized pores of PVA and reported their structural, morphological and optical properties. Mulik et al. [99] reports on investigations of structural, morphological electrical and optical properties of nanocrystalline PbS by sol gel spin coating technique. Barote et al. [100] reported synthesize of polycrystalline n type PbS thin films in alkaline medium and their structural, optical, electrical and photo electrochemical properties. Sadovnikov et al. [101] studied the microstructural lead sulphide nanocrystalline powders and nanostructured films. The average size of PbS particles varies in the nano-powder and nano-films from 8 nm to 20 nm and 40 nm to 80 nm respectively. Obaid et al. [102] investigated the structural and optical properties of the nanocrystalline PbS thin film deposited on Si (100) substrate by solid-vapour deposition method. Preetha and Remadevi [103] reported the effect of doping on the structural, morphological, optoelectronic and transport properties of PbS thin films as a function of Al$^{3+}$ concentration. Doping improved surface morphology to a great extent. The crystalline sizes were found to increase from 19 nm to 32 nm whereas the band gap decrease from 2.41 to 1.34 eV with increasing Al$^{3+}$ doping concentration. Hamid S. Al-Jumaili et al. [104] reported the structural and optical properties of Pb$_{1-x}$Cd$_x$S
nanostructure films obtained by CBD method at various doping concentrations. The crystallite sizes were found to decrease and optical band gap vary from 2.1 eV to 3.95 eV with increasing Cd doping concentration. Moreno et al. [105] reported the growth of Ni$^{2+}$ doped PbS films by CBD. The average crystallite size decreased while the band gap increased from 2.4 eV to 3.8 eV with increasing doping concentration. Moreno et al. [106] reported the Cd doped PbS thin film. The optical band gap of films varied from 2.1 eV-4.0 eV with increase Cd$^{2+}$ doping concentration. Joshi et al. [107] synthesised nano films of Pb$_{1-x}$Fe$_x$S from an acidic chemical bath with Ethylenediaminetetraacetic acid (EDTA) as complexing agent and reported the optical band gap of films to vary from 1.65 eV to 1.42 eV with increase in iron concentration from $x=0.25$ to 0.75 in the films. Palomino-Merino et al.[108] prepared Hg$^{2+}$ doped nanocrystalline PbS thin films by CBD method. The crystallites size decreased with increasing doping concentration. Nanda and Sahu [109] studied the Raman scattering in PbS nanocrystalline semiconductors of different crystalline sizes prepared by an electrochemical route and compared with the results of PbS samples obtained by a chemical route. Nordin et al. [110] studied the comprehensive optical characterization of PbS NCs that included detailed temperature dependent absorption, photoluminescence (PL) and photoluminescence (PL) lifetime measurements covering a temperature range of 3-300K on the same PbS NCs system. Kumar et al. [111] deposited nanocrystalline (Pb$_{1-x}$Bi$_x$)S thin films using the CBD method and investigated the structural properties of these films.
1.3.3 Works on junctions based on Lead Sulphide (PbS)

Many researchers are interested towards the exploration of novel approaches for fabrication of high efficient and low cost solar cells. Tang et al. [112] reported 2% efficient PbS/Al Schottky barrier solar cell using PbS colloidal quantum dot (QD). PbS nanocrystal solar cell with nearly 4% efficiency and 60% fill factor on a device active area 4 mm$^2$ has been reported by Szendrei et al. [113]. The photoactive layers (140 nm) were made from PbS nanocrystals (NCs) of 3.5 nm and 4.3 nm corresponding to band gap of 1.3 eV and 1.1 eV respectively. Nanocrystalline films were deposited by spin coating, LBL from suspension containing PbS NCs. 5.2% efficient PbS nanocrystal Schottky solar cells have been reported by Piliego et al. [114]. The detailed measurements of the physical parameters of the Schottky barrier formed at the interface of a semiconducting colloidal quantum dot film and a metal contact and the ideality factors 1.3 for the Al/PbS CQD Schottky devices were reported by Clifford et al. [115]. Debnath et al. [116] have reported a ITO/PbS CQD film/LIF/Metal Schottky device with fill factor 51% and 3.6% efficiency. Strasfeld et al. [117] fabricated planar PbS quantum dot devices with ohmic and Schottky type electrodes and investigated the vast difference between the local photocurrents that arise due to ohmic and Schottky contacts.

Luther et al. [118] reported a PbS/ZnO QD heterojunction solar cell with 3% efficiency. The PbS absorber layer (70nm), deposited layer-by-layer (LBL) from a suspension of 5.2nm QDs had a band gap of 1.3eV. Pattantyus-Abraham et al. [119] reported above 5% efficient cells using depleted-layer heterojunction between TiO$_2$ and PbS QD. Brown et al. [120] showed that the incorporation of a MoO$_3$ interfacial layer improves the efficiency of ZnO/PbS QD solar cell. They reported photo conversion
efficiency (PCE) of 3.5±0.4 % for ZnO/PbS/MoO$_3$/Au structure. Gao et al. [121] obtained ZnO/PbS/MoO$_x$/Au QD solar cell having PCE (power conversion efficiency) of 4.4%. The n-type MoO$_x$ layer served as a hole extraction layer. Mous et al. [122] prepared nano PbS/Si heterojunction by chemical bath deposition method and studied the electrical transport properties at room temperature. The ideality factor of the diode decreases with increasing deposition time. The photocurrent increases with increasing the bias voltage and decreases with increasing the deposition time. Nanda and Sahu et al. [123] prepared self-assembled heterojunction between electrodeposited PbS nanoparticles and indium tin oxide substrate and studied the current-voltage and capacitance-voltage characteristics of the junction. Patil et al. [124] prepared p-polyaniline/n-PbS heterojunction as a room temperature (300K) liquefied petroleum gas sensor. The maximum response upto 70% for 0.06 vol% of LPG was observed at a voltage of +1.4V. Hernandez-Borja et al. [125] prepared thin film solar cells of CdS/PbS by chemical bath deposition method. The solar cells are photosensitive in a large spectral range (all visible and near infrared regions); the cell with the area of 0.16 cm$^2$ without any special treatment has shown the values of open-circuit voltage $V_{oc}$ of 290 mV and short circuit current $J_{sc}$ of 14 mA/cm$^2$ with the efficiency 1.63% (fill factor is 0.36) under illumination intensity of 900 W/m$^2$. Rahnami and Zemel [126] prepared PbS/Si heterojunctions by depositing PbS films on silicon substrates using the method of Davis and Knorr. Current-voltage and capacitance–voltage characteristics indicate that there are no observable interface states in the PbS/Si heterojunctions. Watanabe and Mita [127] reported the electrical properties of the CdS/PbS heterojunctions. The photovoltaic effect in the infrared region was considered due to the photoemission of electrons from PbS to CdS. Bhandari et al [128] reported heterojunction solar cells
based on PbS-QDs and RF magnetron sputtered CdS thin films with efficiency 3.3%.

Stancu et al [129] studied the electrical and optical characteristics of the PbS/SiO$_2$/Si devices based on microcrystalline and nanocrystalline PbS. The hysteresis effects in C-V and G-V characteristics were found in nanocrystalline based heterostructure. Chemically prepared (n)Bi$_2$S$_3$/(p)PbS solar cells with a short-circuit current density ($J_{sc}$) 6 mA/cm$^2$, an open circuit voltage ($V_{oc}$) 280 mV and conversion efficiency of 0.5% under a 1000W/m$^2$ solar radiation have been reported by Moreno-Garcia et al. [130]. Rath et al. [131] presented the applicability of solution processed inorganic p-n junction based on p-type PbS QDs and n-type Bi$_2$S$_3$ NCs. The reported devices showed PCE of 1.6% for 860 nm PbS QDs and over 1% for 1300 nm PbS QDs.

1.4 Overview of works on Bismuth Sulphide (Bi$_2$S$_3$) and junctions based on Bi$_2$S$_3$

1.4.1 Characteristics of Bismuth Sulphide (Bi$_2$S$_3$)

Bismuth Sulphide is a member of V-VI semiconductor compounds whose band gap energy 1.7 eV, lies in the visible range of the solar energy spectrum which makes it very useful for solar energy conversion devices [132-134]. Bi$_2$S$_3$ has an orthorhombic crystal structure [135] with 4 molecules per unit cell as shown in Fig.1.02. Each molecule contains two bismuth atoms and 3 sulphur atoms which add up to 20 atoms per unit cell. Bohr excitonic radius of bulk Bi$_2$S$_3$ is 28.9 nm [136] which implies that significant quantum confinement effect can be observed at relatively large Bi$_2$S$_3$ nanoparticles. Bi$_2$S$_3$ is one of the earliest materials known to exhibit photoconducting properties [137]. Due to its significant thermoelectric effect, this material is important in view of its thermoelectric application as well [138]. It is widely used in optoelectronics,
photoelectrochemical devices, thermoelectric cooler, electrical switching, solar selective coatings, decorative coatings [29, 137]. Nanostructures of Bi$_2$S$_3$ have potential applications in electrochemical hydrogen storage, hydrogen sensors; X-ray computed tomography imaging, biomolecule detection and photoresponsive materials [139].

Figure 1.02: Crystal structure of bismuth sulphide (Bi$_2$S$_3$).

1.4.2 Works on Bismuth Sulphide (Bi$_2$S$_3$) films

Many researchers have been carried out on the preparation, characterization and applications of Bi$_2$S$_3$ thin films by employing several deposition techniques such as chemical deposition [5, 28, 140-145], vacuum evaporation [146-149], cathodic electrodeposition [150], anodic electrodeposition [151], hot-wall method [152], solution gas interface [153], spray deposition [29, 154-157], ultrasonic methods [158, 159], microwave irradiation [160,161], hydrothermal synthesis [162-164], solvothermal decomposition [165] etc.
Chemical bath deposition (CBD) of Bi$_2$S$_3$ thin films have been reported earlier by using different bismuth ion releasing sources such as bismuth nitrate, bismuth chloride and sulphur ion sources such as thiosulfate, thiourea and thioacetamide. Lokhande et al. [166] investigated the nanocrystalline Bi$_2$S$_3$ thin films deposited by CBD method at low temperature and characterized by XRD, SEM, AFM, RBS, HRTEM and EDAX. He showed the film to be stoichiometric with some inclusion of oxygen. Mane et al. [167] reported nanocrystalline Bi$_2$S$_3$ thin films deposited onto fluorine doped tin oxide (FTO) coated glass substrates with different thicknesses at deposition temperature of 279K and studied the photoelectrochemical (PEC) properties using polysulphide electrolyte. Ahire and Sharma [147] reported the preparation of Bi$_2$S$_3$ thin films by modified chemical bath deposition method onto fluorine doped tin oxide (FTO) coated glass substrates and photoelectrochemical characterization was carried out using Bi$_2$S$_3$ films as a photoelectrode and carbon as a counter electrode. Mane et al. [148] prepared nanocrystalline Bi$_2$S$_3$ thin films for different thicknesses using ethylenediamine tetra-acetic acid (EDTA) as complexing agent and reported their structural characterization. The crystallites size was found to increase from 6.85 nm to 33.86 nm whereas the electrical resistivity decrease from $2.4043 \times 10^6 \ \Omega \text{cm}$ to $0.7250 \times 10^6 \ \Omega \text{cm}$ with increasing film thickness. Mane et al. [168] reported the structural characterization of Bi$_2$S$_3$ thin films prepared from non-aqueous bath on ITO substrates and also studied photo-electrochemical performance. Yan et al. [169] deposited Bi$_2$S$_3$ nano-thin films on indium tin oxide (ITO) glass using Bi(NO$_3$)$_3$ and Na$_2$S$_2$O$_3$ as precursors at room temperature by cathodic electrodeposition process and investigated the influence of precursor on structural properties of the Bi$_2$S$_3$ films. Zhang et al. [170] reported low temperature hydrothermal synthesis of Bi$_2$S$_3$ nanorods in the temperature
range of 373K-443K. Variano et al. [171] prepared the colloidal suspension of bismuth sulphide in aqueous solution at room temperature, with a solution of Bi(NO$_3$)$_3$ and Na$_2$S.9H$_2$O as the starting materials, using hexametaphosphate as complex agent of Bi$^{3+}$, however, the product was colloidal particles only. Benramdane et al. [172] prepared Bi$_2$S$_3$ thin films by spray-pyrolysis method from a bismuth chloride solution and studied their structural and optical characterization. Killedar et al. [29] reported the preparation and characterization of Bi$_2$S$_3$ thin films by spray deposition from non-aqueous media. Chemical deposition of Bi$_2$S$_3$ films was carried out by Pramanik and Bhattacharya [173], using thiourea as a sulphide ion source and triethanolamine (TEA) as a complexing agent in an alkaline bath (pH value 8). The films were reported to be amorphous with a band energy (indirect) 1.47 eV. Acharya et al. [174] fabricated amorphous Bi$_2$S$_3$ thin films by chemical deposition and reported that annealing at 473K does not have any influence on the amorphous nature. Biswas et al. [175] prepared Bi$_2$S$_3$ thin films using TEA and thioacetamide as complexing agent and sulphide ion source respectively in an alkaline bath. The films were amorphous with an optical band gap of 1.7 eV and resistivity of $10^5$-$10^7$ Ω cm. Lokhande and Co-workers [176-178] obtained amorphous Bi$_2$S$_3$ thin films from acidic as well as alkaline baths using the disodium salt of ethylenediaminetetraacatic acid (EDTA) as a complexing agent and Na$_2$S$_2$O$_3$ thiourea as the sulphide ion source. The band gap energy was reported to be 1.54 eV (indirect) and 1.7eV (direct). Palyakav et al. [179] formed a layer of Bi$_2$S$_3$ on bismuth by reactive vacuum diffusion in sulphur vapour. Krishnamurthy and Shiv Kumar [157] deposited Bi$_2$S$_3$ films by the hot wall chemical deposition technique. Miller and Heller [180] deposited Bi$_2$S$_3$ films onto bismuth substrates anodically. Pawar et al. [158,181,182] prepared amorphous Bi$_2$S$_3$, Sb$_2$S$_3$, As$_2$S$_3$ and Sb$_{2-x}$Bi$_x$S$_3$
films by the solution gas interface method. Lokhande and Bhosale [155] prepared polycrystalline Bi$_2$S$_3$ thin films by electrodeposition. Desai and Lokhande et al. [54] reported the films deposited chemically from non-aqueous baths to be amorphous in nature. Gadakh and Bhosale [183] deposited Bi$_2$S$_3$ thin films by spray pyrolysis using EDTA as complexing agent and investigated the effect of concentration of complexing agent on the structural, electrical and optical properties of the films. Yesugade et al. [184] deposited Bi$_2$S$_3$ films by electrodeposition with EDTA as complexing agent. The films were polycrystalline having band gap energy of 1.58 eV. Cantarero et al. [185] reported the resistivity and Hall-effect measurements in oriented single crystals of Bi$_2$S$_3$ between 30K and 500K and thermo power measurements at room temperature. Pejova and Grozdanov [5] reported the chemically deposited Bi$_2$S$_3$ thin film and studied their structural and optical properties of the prepared film. Subramanian et al [186] investigated the effect of electron irradiation on the structural and optical properties of Bi$_2$S$_3$ thin films. Gao et al. [187] prepared Bi$_2$S$_3$ films by CBD in which ammonium citrate was used as the chelating reagent, and two reagents thioacetamide (TAM) and sodium thiosulfate (Na$_2$S$_2$O$_3$) were used as the sulphur source. The structure, morphologies, optical properties and photocurrent response of the Bi$_2$S$_3$ films were studied. Mahmoud [188] investigated the structural, surface topography, optical and electrical properties of Bi$_2$S$_3$ thin films prepared by the spray pyrolysis technique onto glass substrates. Balasubramanian et al. [189] described a chemical method for deposition of Bi$_2$S$_3$ thin films using thiosulfate as a sulphide ion source. The thickness of the film was varied by changing the bath temperature to see its effect on the structural parameters. Medles et al. [190] reported the optical and electrical properties of Bi$_2$S$_3$ thin films deposited by spray pyrolysis. Balasubramanian et al. [191] reported the
optical properties and quantum confinement effect on Bi$_2$S$_3$ thin films prepared by chemical method. Mageshwari and Sathyamoorthy [153] prepared nanocrystalline bismuth sulphide thin films by thermal evaporation using the bismuth sulphide nanoparticles synthesized by surfactant-assisted solvothermal technique as the source material. Influences of substrate temperature on the structural, optical and electrical properties of the prepared films were investigated. Mageshwari et al. [154] prepared nanostructured bismuth sulphide thin films using as-synthesized 1D Bi$_2$S$_3$ flower like powder as a source material and studied the structural and optical properties. Lokhande et al. [149] reported the thickness dependent properties of chemically deposited Bi$_2$S$_3$ thin films. Desai and Lokhande [150] reported room temperature preparation of Bi$_2$S$_3$ thin films from an aqueous acidic bath using thioacetamide (TAM) as sulphide ion source. Ubale et al. [192] have prepared Bi$_2$S$_3$ thin films by modified chemical bath deposition at room temperature and reported their electrical and optical properties. Ubale [144] described how the growth process of Bi$_2$S$_3$ got affected in the presence of the complexing agent EDTA and studied its impact on the structural, electrical and optical properties. Balasubramanian et al. [193] described a chemical method for deposition of Bi$_2$S$_3$ thin films from an acidic aqueous medium using sodium thiosulphate as S$^{2-}$ ion source and studied the effect of annealing on structural and optical properties. Song et al. [194] prepared Se-doped nanocrystalline bismuth sulphides by a hydrothermal process using Na$_2$SeSO$_3$ as the selenium source. Lukose and Pradeep [195] reported the preparation of polycrystalline stoichiometric Bi$_2$S$_3$ thin films by reactive evaporation at substrate temperatures ranging from 423 K to 473 K. Liao et al. [196] reported for the preparation of Bi$_2$S$_3$ nano-rods by microwave radiation. Deshmukh et al. [197] studied electrical and optical properties of the films
obtained from aqueous alkaline bath using thiourea as a source of sulphur ions and TEA as a complexing reagent. The films were n-type polycrystalline having direct band gap of 1.7 eV. Zhou et al. [198] reported the synthesis of bismuth sulphide nano-rods in an acidic media at room temperature, employing bismuth nitrate and sodium sulphide as bismuth and sulphur sources in the presence of sodium dodecyl sulphate. Hussain et al. [199] prepared Bi$_2$S$_3$ thin films in PVA matrix using Na$_2$S as the sulphide ion source. Begum et al. [200] reported preparation bromine doped Bi$_2$S$_3$ thin films in PVA matrix using Na$_2$S as the sulphide ion source.

Recently, extensive researches have been carried out on the synthesis of one dimensional (1D), two dimensional (2D) and three dimensional (3D) microstructures of Bi$_2$S$_3$ [201]. Depending on the growth condition, different structures such as nanotubes [202-205], nanowares [206-208], nanoflowers [209, 210] and nanoribbons [211] of Bi$_2$S$_3$ have been reported to be synthesized by different research groups using hydrothermal and solvothermal processes. There are several reports [153, 212, 213] on the photoelectrochemical characterizations of Bi$_2$S$_3$ thin films and various microstructures.

### 1.4.3 Works on junctions based on Bi$_2$S$_3$

There are limited literature pertaining to the preparation and characterization of Schottky junctions and heterojunctions based on Bi$_2$S$_3$. Pineda et al. [214] fabricated hybrid solar cells of the configuration ITO/Bi$_2$S$_3$/P3OT/Au [(P3OT) is poly3-octylthiophene polymer]. They investigated the photovoltaic performance of the solar cell and reported that the cell using a Bi$_2$S$_3$ film of thickness 50 nm had the highest open-circuit voltage of 440 mV and short-circuit current density of 0.022 mA/cm$^2$. 


Recently, Martinez et al. [215] fabricated hybrid heterojunctions by using Bi$_2$S$_3$, NCs and P3HT poly (3-hexylthiophene) polymer with a power conversion efficiency of 1%. Becerra et al. [216] have analysed the feasibility of combining p-Si with an n-Bi$_2$S$_3$ thin film to form thin film solar cell using evaporated (n)Bi$_2$S$_3$ on (p)Si. They reported short-circuit current density of 3 mA/cm$^2$; open-circuit voltage of 360 mV; and efficiency of 0.5%; which improved to 7.2 mA/cm$^2$, 485 mV and 1.7%, respectively, after heating the cell in forming gas. Moreno-Garchia et al. [130] have fabricated (n)Bi$_2$S$_3$/(p)PbS solar cell by chemical CBD method. They carried out an extensive study to explore the relevance of each thin film component and suggested ways to improve the cell parameters. Their best (n)Bi$_2$S$_3$/(p)PbS solar cell junctions produced open-circuit voltage of 280 mV and short-circuit current density of 6 mA/cm$^2$ and energy conversion efficiency of 0.5%. The same research group [217] extended their work on (n)Bi$_2$S$_3$/(p)PbS solar cells by introducing CdS and ZnS window layers in their solar cell structure and reported an improvement of the various junction parameters. Kachari et al. [218] reported the fabrication of Al/(p)Bi$_2$S$_3$ Schottky barrier junction by vacuum evaporation method. They have evaluated the various junction parameters from the I-V characteristics of the junction. Further, they investigated the photovoltaic performance of the junction. Bao et al. [206] reported the formation of Schottky contact between Bi$_2$S$_3$ nanowires and gold (Au) electrode. The photo-switchable conductivity of individual Bi$_2$S$_3$ nanowires was studied, indicating possible applications in optoelectronic nano-devices. Bessekhouad et al. [219] prepared (n)Bi$_2$S$_3$/(n)TiO$_2$ heterojunctions by direct mixture of both constituents and by precipitation of the Bi$_2$S$_3$ with commercial TiO$_2$ at different concentrations. They have analysed (n)Bi$_2$S$_3$/(n)TiO$_2$ junction by UV-Vis spectroscopy and established that the junctions were able to absorb
the light up to 800 nm. Moreno-García et al. [220] fabricated CdS/(n)Bi$_2$S$_3$/(p)PbS solar cell and reported open-circuit voltage of 250 mV and short-circuit current density of 3.45 mA/cm$^2$. Bi$_2$S$_3$ film was introduced basically to secure stability for the CdS/PbS junction. Wang et al. [221] synthesized Bi$_2$S$_3$ nanorods and nanowires. Further they fabricated bulk hybrid heterojunction solar cells by blending the Bi$_2$S$_3$ nanorods or nanowires with MDMO-PPV polymer [(abbreviation MDMO-PPV is Poly [2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene]]. Ladhe et al. [222] have chemically prepared (n)Bi$_2$S$_3$ and (p)CuSCN layers to fabricate (n)Bi$_2$S$_3$/(p)CuSCN heterojunction on fluorine doped tin oxide (FTO) coated glass substrates. They successfully employed the heterojunction as an LPG sensor at room temperature. Rath et al. [223] reported the first solution-processed heterojunction solar cells based on p-type PbS quantum dots and n-type Bi$_2$S$_3$ nanocrystals. In this solar cell nanostructured n-type Bi$_2$S$_3$ was used as electron acceptor. They reported a power conversion efficiency of 1.6% for 860 nm PbS QDs and over 1% for 1300 nm PbS QDs.
References


