Chapter-1

1.1 Introduction

Thin film is a two dimensional form of solid material created by random nucleation and growth processes of individually condensing / reacting atomic / ionic / molecular species on a substrate [1], whose one dimension, called the thickness is much smaller than the other two dimensions. In technical terms, the thickness of the film must be limited to the order of mean free path of the carriers participating in the particular electronic transport process for which the film has been fabricated. Thin films may encompass a considerable thickness range, varying from a few nanometers to several micrometers depending upon the field of application [2].

Thin films are of great importance to many practical problems. The common and important use of thin films is in the field of microelectronics. Smaller, faster and cost-effective is the technological imperative of present times and thin films play an important role in fulfilling these needs due to which thin films have replaced the earlier crystal growth in solid state devices. The use of thin films in making active and passive components made it possible to produce VLSI (very large scale integration) and microcomputers. The thin-film technology has also been used in fields such as optics, space science, aircraft, superconductivity, photovoltaic effect etc. The investigation on thin-films have led to the development of new kind of active devices and passive components, different types of sensors [3, 4], magnetic memories [5], superconducting films [6], optical image storing devices [7,8], electromechanical devices like strain gauge [9], gas detecting transducers [10], interference filters [11], reflecting and
antireflecting coatings [12] and many others [13-15]. Therefore, research on thin-films has been occupying an important place for its contributions to the development of modern science and technology by tailoring and engineering new properties of the materials in thin-film form.

1.2 Schottky barrier junctions and heterojunctions

One of the main applications of the thin film technology in electronics is the formation of junctions. The use of thin film technology in making metal-semiconductor Schottky barrier junctions and semiconductor-semiconductor heterojunctions have revolutionised in semiconductor technology along with optoelectronics. The junction devices developed by intimate contact of metal and semiconductor, exhibiting rectifying behaviour is known as Schottky barrier junction. This asymmetric nature of electrical conduction between metal-semiconductor contacts was first reported by Braun in 1874 [16]. The metal-semiconductor rectifying junction is the oldest solid state device used in electronics. In 1938, the theory of metal-semiconductor barrier layers was developed by Walter Schottky [17]. In the same year, Neville Mott also devised an appropriate theoretical model for swept-out metal-semiconductor contacts that is known as the Mott barrier [18]. Schottky barrier or Schottky diode has a rectifying capability with a large current in forward bias and very low leakage current in reverse bias. Because of their importance in direct current and microwave applications and as tools in the analysis of other fundamental physical parameters, metal-semiconductor contacts have been studied extensively. The basic theory and historical development of rectifying metal-semiconductor contacts have been summarised by Henisch [19] and the properties and
applications of Schottky barriers have been reviewed by Atalla [20]. The metal semiconductor junctions are much used as rectifiers, microwave diodes, UV detectors, switching diodes, photo sensors and solar cells [21-27]. Due to its fast switching effect, it is widely used in digital circuits and radar applications [25-28].

Junctions formed by two semiconductors of different band gap energies are known as heterojunctions. The $p$-$n$ heterojunction was discovered by Ohl in 1940 when he observed the photovoltaic effect, when light was flashed onto a silicon rod [29, 30]. The theory of $p$-$n$ junction diode was developed by Shockley in 1949 [31]. The theory was subsequently refined by Sah et' al [32] and Moll [33]. The study of semiconductor heterojunctions is a most desired field of research for development of active devices and passive components. In 1951, Schottky first proposed the abrupt heterojunction to be used as an emitter based junction in bipolar transistor [34]. In the same year, Gubanov published theoretical papers on heterojunctions [35]. Kroemer later analysed a similar although graded, heterojunction as a wide gap emitter [36]. Since then, heterojunctions have been extensively studied, and many important devices, such as room temperature injection laser, light emitting diode, photodiode, veristor, varactor, solar cell etc. have been made. In addition, by forming periodic layered heterojunctions with layer thickness of the order of 100 Å, the so called super lattice structures have been produced [37]. The heterojunctions have been reviewed by Milnes and Feucht [38] and Sharma and Purohit [39].

1.3 Background of the present work

Modern technology in electronics and optoelectronics favours long lasting, low
cost, light weight, compact, flexible and fast responding devices. Thin film devices posses most of the qualities mentioned above which have been enhancing the research activities for the development of various thin film devices such as heterojunction diodes and Schottky barrier diodes since last forty years. These Schottky barrier diodes and heterojunction diodes are being used in various electronics and optoelectronics devices including solar cells. The knowledge of electrical properties such as conductivity, type of conductivity, carrier concentration, photo conductivity, band gap etc. and optical properties such as transmittance, reflectance, absorbance, absorption co-efficient, refractive index, extinction co-efficient, optical energy gap etc. of semiconductor thin films are very essential for the fabrication of thin film heterojunction diodes and Schottky barrier diodes. Due to limitation of conventional energy resources people are trying to use nonconventional energy resources such as solar energy, wind energy, tide energy etc. Out of these resources, solar energy seems to be a promising one to replace the conventional energy resources. Solar cells directly convert light energy into electricity. Therefore, in this modern age, research of solar cell is finding an important place and scientists are investigating for new low cost and echo-friendly materials for possible use as solar cell.

In the present investigation, studies were carried out on electrical and optical properties of Bi$_2$S$_3$ and Bi$_2$O$_3$ thin films and their Schottky barrier junctions and heterojunctions with an aim for their possible use as photovoltaic devices. The compound semiconductors of the fifth-sixth (V-VI) group of the periodic table possess suitable energy gaps to be used for optoelectronics device fabrication. Among the compounds, Bismuth sulphide (Bi$_2$S$_3$) with suitable energy gap and high absorption
coefficient seems to be one of the most promising semiconductors for photovoltaic devices. 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 [40]. The transparent electronics employ wide band gap semiconductors, which are transparent in the visible portion of the electromagnetic spectrum, as window layer for fabrication of electronic devices and circuits. The metallic semiconductor, Bi$_2$O$_3$ of group (V-VI), with wide energy gap and highly transparent in thin film form has been creating interest for its possible use as window material in heterojunction photovoltaic devices. It was proposed in the present work to study different electrical and optical properties of these compounds and their junctions in the form of thin film.

The thermal evaporation in vacuum has been occupying an important place in thin film technology, due to its ability to produce high quality, pure compound films for most thin film applications. Thin films of Bi$_2$S$_3$ and Bi$_2$O$_3$ were proposed to prepare by vacuum evaporation technique from Bi$_2$S$_3$ and Bi$_2$O$_3$ powder compounds respectively. Proper doping was carried out to increase the carrier concentration hence to enhance the electrical conductivity and to convert the semiconductor to $p$-type and $n$-type.

The thin film Schottky barrier junctions proposed to be prepared were Bi$_2$S$_3$ based Schottky barrier junction and the thin film heterojunction proposed to prepare was between Bi$_2$S$_3$ and Bi$_2$O$_3$ thin films.

The main objectives of the present study are to develop Bismuth based thin film Schottky barrier junctions and heterojunctions that possess photovoltaic effect.
The thin films to be prepared were proposed to be studied for their different properties such as electrical conductivity, photoconductivity, effect of temperature on films, carrier life time, transmittance, reflectance, absorbance, refractive index, extinction coefficient, dielectric constant, absorption coefficient, energy gap etc. Proposed investigation on junctions are $C-V$ characteristic, $I-V$ characteristic in dark and under illumination and to determine different junction parameters such as barrier height, ideality factor, saturation current, series resistance, carrier concentration, Richardson's constant, short-circuit current, open-circuit voltage, fill factor, efficiency etc.

In brief, following are the aims and objectives of the present work

(i) Preparation of thin films of Bi$_2$S$_3$ and Bi$_2$O$_3$,
(ii) Heat treatment of Bi$_2$S$_3$ and Bi$_2$O$_3$ films,
(iii) Doping of Bi$_2$S$_3$ and Bi$_2$O$_3$ thin films,
(iv) Preparation of Schottky barrier junctions from bismuth based compound: Bi$_2$S$_3$.

Thin film heterojunction: Bi$_2$S$_3$-Bi$_2$O$_3$.

(v) All samples were proposed to be prepared by evaporation technique.

(vi) Studies of optical properties of the Bi$_2$S$_3$ and Bi$_2$O$_3$ films: transmittance, reflectance, absorbance, refractive index, extinction coefficient, absorption coefficient, dielectric constant, energy gap.

(vii) Electrical properties of the Bi$_2$S$_3$ and Bi$_2$O$_3$ films: resistivity, conductivity, energy gap, photoconductivity, carrier life time etc.

(viii) Measurement of $C-V$ characteristics, $I-V$ characteristics of Schottky junctions and heterojunctions in dark and under illumination,
Determination different junction parameters: barrier height, ideality factor, saturation current density, carrier concentration, series resistance, Richardson’s constant, short-circuit current, open-circuit voltage, fill factor, efficiency etc.

Analyses of the data and conclusions.

1.4 An overview of works on Bi$_2$S$_3$ and Bi$_2$O$_3$

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

The Bismuth Sulphide (Bi$_2$S$_3$) is a V-VI binary compound. It is a layered semiconductor that crystallizes in the orthorhombic system (Pbnm space group) and is isostructural to antimony sulphide (Sb$_2$S$_3$) and antimony selenide (Sb$_2$Se$_3$) [41]. Fig.1 shows the structure of Bi$_2$S$_3$ [42]. The optical band gap of the semiconductor in crystalline form was reported by some authors as 1.3 eV [41-45]. The optical band gap ($E_g$) of Bi$_2$S$_3$ varies with the crystallinity and/or stoichiometry of the material [46]. Also, the variation of optical energy gap may be due to the interference by diffused reflectance within the material itself [47] and the anisotropy of the film formation process [48]. The value of $E_g$ of a natural Bi$_2$S$_3$ crystal was reported as 1.1eV and synthetic single crystals grown from the melt was reported as 1.1-1.3eV [49-51]. The Bi$_2$S$_3$ compound has a tendency to dissociate on heating as well as on condensation over a heated substrate leading to films that are non-stoichiometric in composition [52]. For polycrystalline Bi$_2$S$_3$ thin films, the value of optical band gap $E_g$ was reported as 1.3-1.7eV [53]. The complicated crystalline structure, non-stoichiometry in composition, presence of impurity etc. are the hindrances in the study of electronic structure of Bi$_2$S$_3$. 
The work function of a thermally evaporated Bi$_2$S$_3$ was reported as 5.3 eV [54]. Calculated work function of {010} crystalline plane of Bi$_2$S$_3$ nanobelt was reported as 5.13 eV [55]. Similarly, calculated work function of microbelt Bi$_2$S$_3$ for {001} crystalline planes was reported 4.93 eV, 5.11 eV for {100} crystalline planes and 5.13 eV for {010} planes [55]. The electronegativity (EN) and electron affinity ($\chi$) are two very important parameters to propose energy diagram of Bi$_2$S$_3$ based solar cell. The proposed value of $\chi$ for Bi$_2$S$_3$ was reported as 4.5 eV [46]. Bismuth sulphide in the thin film form is a challenging material for photovoltaic devices because of its midway band gap ($E_g$ = 1.7 eV), absorption coefficient of the order of $10^4$ to $10^5$ cm$^{-1}$ and reasonable conversion efficiency [56, 57]. The Bi$_2$S$_3$ compound is normally n-type [58-60], but, preparation of p-type Cu$_3$BiS$_3$ thin film have been reported [61].

The Bi$_2$S$_3$ with direct band gap 1.3 eV has been suggested to be useful material for photodiode arrays and photovoltaics. Moreover, Bi$_2$S$_3$ is used in many fields such as
optoelectronic devices, thermoelectric cooling, photoelectrochemical devices, electrical switching, solar selective coating, decorative coatings [62, 63]. In recent years, Bi$_2$S$_3$ semiconductor nanostructure has been attracting considerable attention due to its wide applications in television camera, thermoelectric devices, electronic and optoelectronic devices and IR spectroscopy [64].

Literature survey reveals that various techniques such as thermal evaporation [65], flash evaporation [66], chemical bath deposition [67-69], electrodeposition [70-72], spray pyrolysis [73, 74], successive ionic layer adsorption and reaction (SILAR) [75], hot wall chemical deposition [76], etc have been used to prepare Bi$_2$S$_3$ thin-films. In thermal evaporation technique Bi$_2$S$_3$ thin films are prepared either by thermal evaporation of Bi$_2$S$_3$ compound or by co-evaporation of individual bismuth and sulphur element. The reported data on the fabrication and analysis of Bi$_2$S$_3$ thin film prepared by vacuum evaporation is very poor. S. Mahmoud and several others prepared Bi$_2$S$_3$ thin films by co-evaporating bismuth and sulphur elements [77] and studied their optical, electrical and structural properties. Different characteristics such as crystalline size, absorption coefficient, optical energy gap, activation energy etc. at low and high temperature were determined on these films [78, 79]. The electrodeposited films were found to be polycrystalline in nature. Comparison study between Bi$_2$S$_3$ thin-film prepared by vacuum evaporation method and chemical bath deposition was made by M. E. Rincon et al [80]. Their study reveals that Bi$_2$S$_3$ thin films prepared by chemical bath deposition are more stoichiometric and less crystalline and posses lower electrical conductivity and higher optical band gap than Bi$_2$S$_3$ thin-film prepared by vacuum evaporation method. They also studied on the role of stoicheomitrity and amorphicity on
the electrical and optical properties of Bi$_2$S$_3$ thin films and found that excess Bi largely increases the electrical conduction of the films whereas amorphous films are less-conducting than crystalline one. On the other hand the optical properties are determined by the normal structural bonding (NSB), so the degree of amorphicity does not impact largely on the determination of optical constant vs photon energy. Literature survey reveals that most of the recent research works so far have been published [81, 82] are on chemically deposited Bi$_2$S$_3$ thin films. Structural characterisation of Bi$_2$S$_3$ thin films deposited on ITO substrates at room temperature through an environment friendly non-aqueous system has been reported [59]. The thin film prepared through this process was found to be amorphous in structure with spherical grains having rough surfaces and void space. Many researchers have fabricated nano Bi$_2$S$_3$ films and studied their structural, electrical, optical etc. properties. Preparation of Bi$_2$S$_3$ nanorods by microwave heating method and characterization by XRD, TEM and X-ray photoelectron spectra (XPS) have been reported [83], Synthesized of Bi$_2$S$_3$ nanowire by molten salt solvent method was reported [84]. The photo switchable conductivity of Bi$_2$S$_3$ nanowire films showed great potential applications in optoelectronic nanodevices. Preparation of uniform rod-like Bi$_2$S$_3$ nanostructures by hydrothermal process in a high yield and characterised by XRD and SEM have been reported [85], Preparation of Bi$_2$S$_3$ nanoflowers on an alumina template by photochemical synthesis and characterization by XRD, SEM and TEM have been reported [86]. Preparation of spherical Bi$_2$S$_3$ flowers by a facile environment friendly hydrothermal method have been reported [87]. Preparation of Rod-like and slice nanocrystalline Bi$_2$S$_3$ thin films by the asynchronous-pulse ultrasonic spray pyrolysis (APUSP) technique from Bi(NO$_3$)$_3$ and thiourea at relatively low
temperature without any complexing agent or stabilizing agent and characterization by XRD, XPS and SEM etc. have been reported recently [88].

Photoelectrochemical properties have been studied on Bi$_2$S$_3$ thin films prepared by combining chemical bath deposition with self-assembled monolayers (SAMs) and suggested that patterned Bi$_2$S$_3$ thin films are attractive systems for surface tailoring and also provide a novel approach to effectively control the photoelectrochemical properties of nanostructured Bi$_2$S$_3$ thin films with promising applications in microsystem devices for solar energy conversion [89]. Fabrication of flower-like nanostructures of Sb$_{2-x}$Bi$_x$S$_3$ (x = 0.4, 1.0) by a facile and mild solvothermal method have been reported [90]. Preparation of Bi$_2$S$_3$ single crystal and its electronic transport properties have been reported [91]. R. S. Mane and other studied photovoltaic properties of chemically deposited Bi$_2$S$_3$ thin-film photoelectrochemical solar cells [92, 93]. Photoconductive properties of Bi$_2$S$_3$ thin film was studied by M. T. S. Nair and others [94, 95]. Literature survey reveals that photoconductive properties are largely dependent on post deposition treatment of the films. Proper annealing increases the photoconductivity of the as deposited film. The amorphous to crystalline transition, change in micro-crystallinity including modification of intergrain boundaries, change in stoichiometry, oxygen incorporation, etc. of Bi$_2$S$_3$ thin film upon annealing may be the cause of variation of photo and dark conductivities of the film. K. Yao et-al successfully fabricated H$_2$ and LPG sensors with high sensitivity, using individual Bi$_2$S$_3$ nanomaterial [96, 97]. The photocatalytic behaviour of Bi$_2$S$_3$ was investigated by several workers. Literature survey shows that Bi$_2$S$_3$/TiO$_2$, CdS/TiO$_2$ [98]; Olive-shaped Bi$_2$S$_3$/BuVO$_4$ microspheres [99]; Bi$_2$S$_3$/Cd [100], etc. are few photocatalyste. KBi$_{6.33}$S$_{16}$ and K$_2$Bi$_8$S$_{13}$ were
synthesized by the direct combination of $K_2S/Bi_2S_3$ at high temperature (>700 °C) [101]. Baoxing Chen and Ctirad Uher studied transport properties (resistivity, Hall effect, thermopower, and thermal conductivity) of $Bi_2S_3$ and two new ternary bismuth sulfides, $KBi_6.33S_{10}$ and $K_2Bi_8S_{13}$, to explore their potential for thermoelectric applications [102]. Investigation on as-prepared $Bi_2S_3$ nanostructures by Raman scattering experiment in which 33, 38, 46, and 53 cm$^{-1}$ phonon modes were observed have been reported [103].

Fig. 2: Structural diagram of $Bi_2O_3$.

1.4.2 Review of $Bi_2O_3$

Fig. 2 gives the structure of $Bi_2O_3$ [42]. There are five main $Bi_2O_3$ modifications, which are denoted by $\alpha$, $\beta$, $\gamma$, $\delta$ and $\omega$ [104]. It possesses various physical and chemical properties due to its modifications. The $Bi_2O_3$ thin film possesses significant values of band gap, refractive index and dielectric permittivity and shows remarkable (UV)
photosensitivity and photoluminescence [105-109]. The physical properties of Bi$_2$O$_3$ thin films are strongly dependent on deposition technology and characterisation process. Due to variation of phase composition in Bi$_2$O$_3$ samples the optical band gap has been observed to vary from about 2eV to 3.96eV [105, 106, 109-113]. The optical properties of Bi$_2$O$_3$ thin film have been reported by many authors [110, 111, 114-121]. The modifications of Bi$_2$O$_3$ are characterised by distinct crystalline structures and optical properties.

The bismuth trioxide thin-film have attracted the interest of many researchers both experimentally and theoretically due to some important applications of it such as antireflecting coating, transparent ceramic, catalysts, sensors, fuel cells, optoelectronic devices, varistor, varactor, parent substance for some high-TC superconductors etc. [122-124]. It has been reported that Bi$_2$O$_3$ proved to be a potential candidate for blue laser CD and/or DVD recording [125].

The Bi$_2$O$_3$ thin films have been prepared by various methods such as spray pyrolysis [126], anodic oxidation [127], flash evaporation [128], thermal oxidation of Bismuth thin films by using furnace [129, 130], pulse laser deposition[131], reactive magnetron sputtering [132] etc. Synthesis of Bi$_2$O$_3$ nano particles and characterization of the same by XRD and SEM has been reported [133]. I. Ardelen et al. investigated on the influence of manganese ions content on the structure of 2Bi$_2$O$_3$-B$_2$O$_3$ glass matrix by means of FT-IR and Raman spectroscope [134]. The change in optical properties of LiF-B$_2$O$_3$ glass with stepwise replacement of LiF by Bi$_2$O$_3$ and on annealing was studied by S. Arora et al. [135]. Their study reveals that with the increase of Bi$_2$O$_3$ concentration in Bi$_2$O$_3$- LiF-B$_2$O$_3$ glass the optical band gap of the sample decreases and the optical energy gap of the sample also decreases when annealed at different
temperature. Bismuth glass containing ZnO and Li2O was prepared by conventional melt-quench technique and its physical and spectroscopic properties were studied and analyzed. The impact of variation of the concentration of ZnO and Li2O on various physical, thermal conductivity and electrical conductivity properties of bismuth glass have been studied and analysed by S. Bale et al. [136]. Bismuth oxide (Bi2O3) nanowires have been synthesized by X. Shen et al on Au-coated Si substrates by atmospheric pressure chemical vapour deposition (APCVD) approach, using Bi(S2CNEt2)(3) as a precursor in the presence of oxygen [137]. Preparation of stabilized δ-Bi2O3 thin films by electrodeposition on different conductor substrates has been reported by K. Laurent et al. Their study reveals that the electrodeposited thin films have a good quality with an excellent adhesion to the substrates. The films have been characterised by XRD and TEM and found to be nanocrystalline [138]. Deposition of Bi2O3 thin films on dense Yttria Stabilized Zirconia (YSZ) substrates by CVD method under atmospheric pressure for intermediate temperature SOFC (solid oxide fuel cell) applications have been reported by T. Takeyama et al. [139]. The films prepared at different temperatures were investigated by XRD and SEM. The XRD investigation confirms that above 700°C δ-Bi2O3 films with a cubic structure is formed. Synthesization of Bismuth trioxide (Bi2O3) ultrathin films on silicon substrates by means of atomic layer deposition (ALD) using Bi(thd)3 (thd: 2,2,6,6-tetramethyl-3,5-heptanedionato) and H2O as precursors have been reported [140]. Magnetic and structural properties of iron-containing bismuth borate glasses, whose composition is denoted as xFe2O3·(80.0−x)Bi2O3·20.0B2O3, in mol% (18.2≤x≤40.0), have been explored and the effect of variation of Fe2O3 content on the magnetic properties of the glass was studied [141]. The Bi2O3 based compounds are finding applications as
photocatalyst. Photocatalytic behaviour of Bi$_2$O$_3$ doped with different amount of La$^{3+}$ were reported. 3% La-Bi$_2$O$_3$ was found to exhibit best photocatalytic activity [142]. Preparation of heterojunction semiconductors Bi$_2$O$_3$/BaTiO$_3$ by milling-annealing method and characterization of the same by XRD, TEM, energy dispersion X-ray spectroscopy (EDS) and UV-vis diffusion reflectance spectroscopy have been reported [143]. The photocatalytic activities of Bi$_2$O$_3$/BaTiO$_3$ was studied by degrading methyl orange and methylene blue. The optical properties of δ-Bi$_2$O$_3$ thin films grown on Si and quartz substrates under different oxygen flow ratios (OFR) by radio frequency reactive magnetron sputtering [144] have been investigated by using spectroscopic ellipsometry and optical absorption spectrum. A novel and simple citrate-assisted solution approach has been developed for the shape-selective synthesis of Bi$_2$O$_3$ nanostructures with controllable band gaps and morphologies at a relatively low temperature of 40°C by Hongbing Lu et al. Different distinctive morphologies, including nanorods, nanoplates, plate-built cylinders, nanoplates with holes, and nanorings, are created due to the selective adsorption of the citrate molecules on certain faces during crystal growth. The distinctive nanostructures extend the family of Bi$_2$O$_3$ nanostructures, and they also provide new opportunities for exploring the potential applications of Bi$_2$O$_3$ in a number of fields including photocatalysis, gas sensors, and photoelectrochemistry [145]. Doping of ZnO with Bi$_2$O$_3$ and TiO$_2$ at different sintering temperature for fabrication of ZnO-Bi$_2$O$_3$-TiO$_2$ veristor ceramics has been reported [146]. The samples were studied with XRD and UV-visible spectrometer. Preparation of Bi/Bi$_2$O$_3$ structure and study of hydrogen evolution activity of the structure by splitting water has been reported [147]. Ye Yu Guseinov et al and others studied I-V characteristics of Bi/Bi$_2$O$_3$/Bi sandwiched structure and found negative resistance of the
structure [148, 149]. Influence of CeO$_2$ on the microstructure and electrical behaviour of ZnO-Bi$_2$O$_3$ based varistors have been studied by M. Lei et al. [150]

1.4.3 Brief review of research works on Bi$_2$S$_3$ based Schottky barriers junctions

Up to our knowledge no data have been reported on solid state Schottky barrier junction or heterojunction of Bi$_2$S$_3$ thin films prepared by thermal evaporation method. However, there are a few reports on junctions of Bi$_2$S$_3$ thin films prepared by chemical deposition technique. The formation of photoelectrochemical (PEC) solar cell with the configuration Bi$_2$S$_3$/(NaOH-Na$_2$S-S/C) was reported in the literature [93, 151, 152]. In this case, nanocrystalline Bi$_2$S$_3$ thin film was chemically deposited onto FTO (fluorine doped tin oxide) glass substrate. In the two electrode system solar cell, chemically deposited nanocrystalline Bi$_2$S$_3$ films on FTO coated glass functions as electrode and graphite as counter electrode and 0.25M polysulphide (NaOH-Na$_2$S=S) was used as an electrolyte. The cathodic behaviour of Bi$_2$S$_3$ confirms n-type conductivity of the Bi$_2$S$_3$.

Different parameters of the PEC solar cell such as junction ideality factor, shunt resistance, series resistance, fill factor, conversion efficiency (%), flat band potential, decay constant; energy band gap, spectral response etc. have been reported in the literature [151,152]. Arup K. Rath et al. theoretically showed the applicability of nanostructured n-type Bi$_2$S$_3$ and p-type PbS colloidal quantum dots for preparation of p-n junction solar cell [153]. In this solar cell nanostructured n-type Bi$_2$S$_3$ was used as electron acceptor. The fabrication and characterisation of all-chemically deposited Bi$_2$S$_3$/PbS solar cells have been reported [154]. The Schottky contact between Bi$_2$S$_3$ nanowire and gold (Au) electrode has been reported [155]. As the light source was...
switched on and off, the nanowire could be reversibly switched between low and high conductivity, indicating its potential applications in optoelectronic nanodevices. The theoretical feasibility of combining p-type crystallities Si with n-type Bi$_2$S$_3$ thin film to form thin film solar cell have been reported by D. Becerra et al [156]. The fabrication of Bi/Bi$_2$S$_3$ heterostructure through an in-situ electrochemical route has been reported [157]. $I$-$V$ characteristics of the junctions were found to have non linear behaviour and show M-S-M type junction characteristics. Preparation detail of ITO/Bi$_2$S$_3$/P3OT/Au structure was reported by Edwin et al. 2011, where the thickness of poly3-octylthiophene (P3OT) polymer film used was about 900 nm thick, the hybrid structure showed photovoltaic effect. The effect of thickness of Bi$_2$S$_3$ on the photovoltaic performance of ITO/Bi$_2$S$_3$/P3OT/Au solar cells was examined and found to behave as an electron acceptor in the hybrid solar cell with poly3-octylthiophene as electron donor [46]. Preparation of W/ Bi$_2$S$_3$/W, Ag/Bi$_2$S$_3$/W and Cu/ Bi$_2$S$_3$/W (W-tungsten substrate) structure and their non-linear $I$-$V$ characteristics have been reported [158]. Fabrication of PEC cell with the configuration (CdS)$_x$(Bi$_2$S$_3$)$_{1-x}$/(NaOH-S-Na$_2$S)/C (where x possess different numerical values) and its nonlinear behaviour of $I$-$V$ characteristics at room temperature have been reported [159]. Preparation of (n)Bi$_2$S$_3$//(p)CuSCN heterojunction by simple chemical rout and its use as LPG sensor at room temperature have been reported [160]. Z. Zhang et al. described a metal-semiconductor- metal model to study $I$-$V$ characteristics of Bi$_2$S$_3$ nanowire transistor [161]. Preparation of Bi$_2$S$_3$ nanowire and fabrication of field-effect transistors (FETs) from it has been reported [162]. Fabrication of individual Bi$_2$S$_3$ nanowire-Based Room-Temperature H$_2$ sensor has been reported. In this case Platinum electrode was found to behave as an ohmic contact with n-type Bi$_2$S$_3$ nano tubes. Single nanowire devices were used to detect
H₂ (in N₂) at room temperature with a sensitivity of 22% at 10 ppm (corresponds to 4.0 \times 10^{-7} \text{mol/L}) \[163\]. Fabrication of photoresponse device by sandwiching an as-deposited Bi₂S₃ thin film on FTO on a blank FTO glass substrate with a device configuration of FTO/Bi₂S₃/FTO have been reported [164]. Applications of Bi₂S₃ nanorods and nanowires, for fabrication of the structure of ITO/PEDOT:PSS/MDMO-PPV:Bi₂S₃/Al [(abbreviation of PEDOT:PSS is Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) and MDMO-PPV is Poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene)] solar cell have been reported [165]. The exhibition of nonlinear current-voltage (I-V) characteristics with excellent photoresponse by as-prepared Bi₂S₃ nanowire has been reported. Fredy Mesa et al. prepared Cu₃BiS₅/CdS, Cu₃BiS₅/ZnS and Cu₃BiS₅/In₂S₃ structures and studied Cu₃BiS₅ as absorber layer for photovoltaic performance [166].

1.4.4 Brief review of research works on Schottky barriers and heterojunctions based on Bi₂O₃

The literature survey shows that the report of Schottky barriers and heterojunctions formed with Bi₂O₃ is very few. Fabrication of n-Bi₂O₃/n-Si heterojunction and its characterisation [167] for dark and illuminated I-V, C-V, and spectral responsivity of the heterojunction has been reported. The ideality factor of the junction was reported to be around 4.8. The optoelectronic properties of the heterojunction suggest that it can be used as a visible-enhanced photodetectors, Current-voltage characteristics of ZnO-Bi₂O₃ heterojunction have been reported by L. F. Lou [168]. The immittance response of the SnO₂–Bi₂O₃ based thick-films was studied by Mohammad A. Alima, et al [169]. Sulfurization of the surface of metal oxide electrodes
is a very simple and useful technique for designing semiconductor hetero structures or multicomponent semiconductor electrodes. The formation of microcrystals of Bi$_2$S$_3$ on sintered Bi$_2$O$_3$ pellet by sulfurizing them in H$_2$S atmosphere have been reported [170]. The Bi$_2$S$_3$|Bi$_2$O$_3$ electrodes exhibited rapid decay in photocurrent under intense light probably due to rapid recombination of electrons and holes and/or photocorrosion of Bi$_2$S$_3$. This photocurrent decay limits the practical application of Bi$_2$S$_3$|Bi$_2$O$_3$ electrodes in solar cell.
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