Chapter I

Introduction to thin films, transparent conducting oxides and chalcogenide semiconducting thin films

1.1 Introduction to thin films

Thin film coatings are used to modify and increase the functionality of a bulk material. Thin films science and technology plays a vital role in high tech industries because the material cost of thin film is less as compared to the corresponding bulk material. Thin film technology has been developed for the need of the integrated circuit industry. The morphology, physical structure and chemical nature of thin films are different from the corresponding bulk materials because thin films as a two dimensional system have a large surface to volume ratio. Some of the important applications of thin films are including microelectronics, optoelectronics, communication, sensors and catalysis. Chopra [1] et al., define a thin film as a material created ab initio by the random nucleation and growth processes of individually condensing/ reacting atomic/ ionic/ molecular species on a substrate. The structural, chemical, metallurgical and physical properties of such a material are strongly dependent on a large number of deposition parameters and may also be thickness dependent. Thin film may be arbitrarily defined as a solid layer having a thickness varying from a few Angstrom (Å) to about 10 µm [2]. Thin film fabrications are generally carried out by depositing the required material in the atomistic deposition (atom by atom) over the required substrate, which may result in either single crystalline, polycrystalline, or amorphous structure depending on the deposition conditions. Advantages of thin film technologies such as low material consumption, shorter energy payback period, monolithic integration, large area modules, tunable material properties, low temperature processes and transparent modules, bring down the module cost and make thin film solar cell technology potential [3].
1.2 Transparent conducting oxides

Materials, like metals, are highly conductive, will not transmit visible light, and while highly transparent media like oxide glasses behave as insulators [4]. Transparent Conducting Oxides (TCOs) are a unique class of materials that exhibit both transparency and electrical conductivity simultaneously [5]. The first realization of a TCO material occurred a century ago when a thin film of sputter deposited cadmium metal underwent incomplete thermal oxidation upon post-deposition heating in air [6]. Since then, TCO films have been widely used as an important part of many optoelectronic devices. TCOs in general are n-type degenerate semiconductors with good electrical conductivity and high transparency in the visible spectrum. Thus, a low-resistance contact to the device and transmission of the most of the incident light to the absorber layer is ensured for the application of solar cell. The conductivity of a TCO depends on the carrier concentration and mobility. An increase in the carrier concentration may result in enhanced free carrier absorption, which reduces the transparency of the TCO in the higher-wavelength region. Hence increasing the mobility by improving crystalline properties is considered to be the pathway for a good TCO. A large number of TCO materials have been studied over the years such as In$_2$O$_3$, SnO$_2$, ZnO, and CdO as well as their doped oxides. All of the mentioned TCO materials are n-type semiconductors. However, there have been some studies on fabricating p-type TCO films, such as CuGaO$_2$ [7] and CuAlO$_2$ [8] and nitrogen and phosphorus doped ZnO [9, 10]. In n-type semiconductors where defects such as oxygen vacancies, impurity substitutions and interstitials donate electrons to the conduction band providing charge carriers for the flow of electric current. However, hole doping by ionised cation vacancies, impurity acceptor ion substitutions and/or oxygen interstitials act as electron acceptors and lead to p-type TCO materials [11]. Although p-type TCO materials have been reported, the commonly applied are n-type TCO binary (indium oxide, tin oxide, zinc oxide and cadmium oxide) and ternary (zinc stannate, zinc indate, cadmium stannate, cadmium zinc oxide and cadmium indate) semiconducting materials. Indium tin oxide is the most commonly used TCO for applications because of its high transmittance in the visible region and low resistivity. However, high cost and scarce resources of indium limit its usage for applications. Hence it is highly desirable to explore alternative material to replace ITO. Cadmium
stannate (Cd$_2$SnO$_4$) is an n-type defect semiconductor in which oxygen vacancies act as donor states. Cd$_2$SnO$_4$ exhibits high transmission in the visible range of light, high reflectivity in the IR region, mobility of $\sim$100 cm$^2$/Vs and electrical resistivity in the order of $10^{-4}$ $\Omega$ cm with good thermal stability which make it suitable TCO for several applications.

1.3 Chalcogenide semiconducting thin films

Chalcogenide is a chemical compound consisting of at least one chalcogen anion and at least one more electropositive element. The three heaviest elements of the sulfur sub-group, namely selenium, tellurium, and polonium, are collectively referred to as the “chalcogens”. Sulfur, selenium and tellurium with metals and semimetals are collectively called as metal chalcogenides. Metal chalcogenide semiconductor thin films have attracted significant research attention during the past few decades because of their exciting photoelectrical characteristics. Chalcogenide thin films are of particular interest for the fabrication of large area photo diode arrays, solar cells, photoconductors and sensors. Binary, ternary and quaternary chalcogenide thin films are potentially useful in a range of areas, including solar control coatings, solar energy conversion, electronic and low-temperature gas sensor applications. Copper selenide a binary chalcogenide semiconductor find diverse applications in the photothermal therapy of cancer [12,13] and in electronic and optoelectronic devices like solar cells [14, 15], optical filters [16], thermoelectric converters [17], and super ionic conductors [18, 19]. Okimura and Matsumae [20] investigated the junction properties of Cu$_{2-x}$Se thin films deposited by vacuum evaporation method on n-type silicon and their suitability as a window material for solar cells. Chen et al. [18] used copper selenide as an absorbing layer and reported a Cu$_{2-x}$Se/CdS heterojunction solar cell with an efficiency of 5.38 % under simulated Am1 illumination.

Copper telluride is a I-VI compound semiconductor. They have attracted considerable research interest because of their potential applications in various fields such as back contact material in CdS/CdTe solar cells, anodes in lithium ion batteries, memory devices, photodetectors, gas sensing, and in photothermal therapy [21-26]. Gallium chalcogenides are layer-type binary semiconductors. The materials are of interest on account of their properties related to semiconductivity, photoconductivity,
and luminescence [27]. GaTe is useful in photoelectronic devices, radiation detectors [28,29], field-effect transistors and phototransistors [30]. Similarly CdS and CdTe are the leading and interesting materials for thin film solar cell applications. Lead and cadmium chalcogenide compounds are also have a significant number of investigations. But the toxicity of cadmium finds practical and industrial limitations that eventually open the era of other alternates. Ternary and quaternary metal chalcogenide thin films are taking an important place in the search for cadmium and lead free materials of narrow band gap semiconductors. More recently, ternary copper chalcogenides, such as copper indium selenide (CIS) and copper indium gallium selenide (CIGS) are used in solar technology. Recently, Cu (In,Ga) Se₂ - based thin film solar cells have achieved efficiencies as high as 21.7% in the lab scale [31]. However scarcity and high cost of In and Ga limits their application. Hence the quest for new absorber semiconducting materials of inexpensive, eco-friendly and earth abundant elements becomes important. Recently copper zinc tin sulfide (CZTS) has received considerable attention as the absorber material due to its optical properties such as direct band gap energy of 1.5 eV and large absorption coefficient of $\sim 10^4$ cm$^{-1}$. Moreover CZTS contains inexpensive elements like Cu, Zn, Sn and S. However there are still challenges with this system related to the structural polymorphism and multivalence of Sn. To solve this issue, it is necessary to develop alternative light absorbing materials which are composed of relatively earth abundant elements. In recent years, copper bismuth sulfide has emerged as one of the promising candidates for thin film solar cells. Copper bismuth sulfide is a ternary p-type semiconducting material [32-34] with optical band gap energy in the range of 1.24 to 1.8 eV and high absorption coefficient of $\sim 10^5$ cm$^{-1}$ [32,35-38]. Copper bismuth sulfide can be a potential candidate for the application of solar cell. In order to obtain chalcogenide materials with excellent performances, the properties of thin films should be optimized through research activities. Hence we report on the preparation of copper selenide, copper telluride, gallium telluride and copper bismuth sulfide thin films by electron beam evaporation method and their characterization.
1.4 Review of literature

1.4.1 Cadmium stannate thin films

Cadmium stannate (Cd$_2$SnO$_4$) thin film is n-type semiconductor material exhibiting promising properties such as low electrical resistivity and high transmission (>90%) in the visible range and high reflectivity in the IR region. Cadmium stannate is a ternary oxide known since 1970 and Nozik [39] first demonstrated the potential of this material as a transparent conductor when he prepared amorphous films with conductivities exceeding 1300 S/cm, optical band gap of 2.85 eV and mobility as high as 100 cm$^2$/Vs. Haacke et al. [40] prepared thin films that were primarily crystalline spinel Cd$_2$SnO$_4$ thin films and reported higher conductivities (6700 S/cm) that was reported by Nozik. Wu et al. [41] prepared high quality fully crystalline spinel Cd$_2$SnO$_4$ thin films with conductivities as high as 8300 S/cm. Literature survey shows that several techniques were utilized for the preparation of Cd$_2$SnO$_4$ thin films and only few reports are available on the preparation of pure and doped Cd$_2$SnO$_4$ thin films by spray pyrolysis method. Haacke et al. [42] was the first to report the preparation of Cd$_2$SnO$_4$ thin films by spray pyrolysis method. Ortiz [43] prepared Cd$_2$SnO$_4$ thin films on pyrex glass at various substrate temperature (370 – 450 °C) by spray pyrolysis method using aqueous solution of CdCl$_2$ and SnCl$_4$. Arbitus et al. [44] deposited Cd$_2$SnO$_4$ thin films by spray pyrolysis method using Cd(thd)$_2$(TMEDA) and Bu$_2$Sn(AcAc)$_2$ as precursor materials and monoglyme as a solvent. Potlog et al. [45] reported on the preparation of Cd$_2$SnO$_4$ thin films at lower deposition substrate temperature by spray pyrolysis technique and investigated the effect of Sn/Cd ratio (1:1 and 1:3) on optical and structural properties. Krishnakumar et al. [46] prepared Cd$_2$SnO$_4$ thin films by spray pyrolysis method at substrate temperature of 450 and 500 °C using aqueous solution of cadmium acetate and tin (II) chloride in different molecular weight ratios of 2:1, 4:1, 6:1, 8:1 and 10:1 and they attained minimum resistivity of 3.56 × 10$^{-3}$ Ω cm (Cd/Sn ratio in the solution is 6:1). Kumaravel et al. [47] prepared Cd$_2$SnO$_4$ thin films by spray pyrolysis method on the Corning substrate at substrate temperature of 525 °C using aqueous solution of cadmium acetate and tin (II) chloride precursors in 8:1 mole ratio and they reported lowest resistivity of 2.66 ×10$^{-3}$ Ω cm. Further Kumaravel et al. studied the annealing effect [47], indium doping [48] and 120 MeV swift Ag$^{9+}$ ions irradiation [49] on Cd$_2$SnO$_4$ thin films. They reported that Cd$_2$SnO$_4$ thin films annealed
in vacuum at 600 °C for 30 min acquires resistivity in the $2.66 \times 10^{-3}$ - $9.24 \times 10^{-4}$ Ω cm range. They obtained minimum resistivity of $1.76 \times 10^{-3}$ Ω cm for 1 wt. % indium doping in cadmium stannate thin films. Ag$^{9+}$ ion irradiation decreases the transmittance and increases the resistivity ($5.57 \times 10^{-3}$ Ω cm) of pure Cd$_2$SnO$_4$ thin films. The electrical properties of Cd$_2$SnO$_4$ thin films obtained from previous reports were presented in Table 1. Thin films of Cd$_2$SnO$_4$ combine the characteristics of both cadmium oxide (CdO) and tin oxide (SnO$_2$) and exhibit good electrical and optical properties. Further characteristics of Cd$_2$SnO$_4$ thin films can be tailored by suitable dopants for the required application. Deokate et al. [69] prepared fluorine doped (0–10 at.%) cadmium oxide (F: CdO) thin films by spray pyrolysis method and reported that the electrical resistivity of F: CdO (4 at.%) thin film is reduced to $2.6 \times 10^{-4}$ Ω cm from $5.6 \times 10^{-4}$ Ω cm of CdO. Thus fluorine doping causes reduction in resistivity by more than half the value of CdO thin films. Elangovan and Ramamurthi [70] prepared fluorine doped tin oxide (F: SnO$_2$) thin films by spray pyrolysis method and showed that the resistivity of SnO$_2$ thin films reduces from $46.3 \times 10^{-4}$ Ω cm to $2.1 \times 10^{-4}$ Ω cm for 15 wt. % fluorine doping in the solution. Similarly several authors [71-74] prepared F: CdO and F: SnO$_2$ thin films and reported that fluorine doping has reduced the resistivity significantly. This has motivated us to prepare fluorine doped cadmium stannate (F: Cd$_2$SnO$_4$) thin films for various doping concentration of ammonium fluoride in the spray solution. Undoped and F: Cd$_2$SnO$_4$ thin films were prepared by spray pyrolysis method and the effect of fluorine doping on the structural, optical and electrical properties of Cd$_2$SnO$_4$ thin films were studied.

Table 1

<table>
<thead>
<tr>
<th>Technique</th>
<th>$T_s$ (°C)</th>
<th>Doping</th>
<th>$\rho$(Ωcm)</th>
<th>$n$(cm$^{-3}$)</th>
<th>$\mu$(cm$^2$/Vs)</th>
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<tr>
<td>Spray pyrolysis</td>
<td>700-750</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1-5</td>
<td>[42]</td>
</tr>
<tr>
<td>Spray pyrolysis</td>
<td>430</td>
<td>-</td>
<td>$-10^2$</td>
<td>2.9x10$^{19}$</td>
<td>$\sim$ 10</td>
<td>[43]</td>
</tr>
<tr>
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<td>500</td>
<td>-</td>
<td>3.5x10$^3$</td>
<td>9x10$^{19}$</td>
<td>40</td>
<td>[46]</td>
</tr>
<tr>
<td>Spray pyrolysis</td>
<td>525</td>
<td>-</td>
<td>2.7x10$^3$</td>
<td>7.9x10$^{19}$</td>
<td>31.5</td>
<td>[47]</td>
</tr>
<tr>
<td>Spray pyrolysis</td>
<td>525</td>
<td>Indium (1 wt. %)</td>
<td>1.8x10$^3$</td>
<td>9.8x10$^{19}$</td>
<td>36.1</td>
<td>[48]</td>
</tr>
<tr>
<td>Spray pyrolysis</td>
<td>400</td>
<td>-</td>
<td>2x10$^3$</td>
<td>-</td>
<td>-</td>
<td>[50]</td>
</tr>
<tr>
<td>Dip coating</td>
<td>fired at 600, annealed at 680</td>
<td>-</td>
<td>3.3x10$^4$</td>
<td>15.5x10$^{20}$</td>
<td>12</td>
<td>[51]</td>
</tr>
<tr>
<td>Chemical Bath</td>
<td>Annealed at 400</td>
<td>-</td>
<td>1.01x10$^2$</td>
<td>1.7x10$^{20}$</td>
<td>3.62</td>
<td>[52]</td>
</tr>
<tr>
<td>Sol gel</td>
<td>Annealing at 550</td>
<td>-</td>
<td>2x10$^3$</td>
<td>-</td>
<td>-</td>
<td>[53]</td>
</tr>
<tr>
<td>Pulsed laser deposition</td>
<td>270</td>
<td>-</td>
<td>-</td>
<td>6x10$^6$</td>
<td>25</td>
<td>[54]</td>
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<td>RF sputtering</td>
<td>-</td>
<td>-</td>
<td>5x10$^4$</td>
<td>100</td>
<td>59.6</td>
<td>[41]</td>
</tr>
<tr>
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<td>Annealed at 580-700</td>
<td>-</td>
<td>1.5x10$^4$</td>
<td>7.2x10$^{20}$</td>
<td>-</td>
<td>[50]</td>
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1.4.2 Copper selenide thin films

Copper selenide has gained importance during the past decades because of its potential application in the fabrication of photovoltaic devices. Copper selenide is a p-type semiconductor. A variety of techniques has been employed for the preparation of copper selenide thin films. Okimura and Matsumae [20] deposited Cu$_{2-x}$Se thin films by vacuum evaporation method on n-type silicon to investigate the junction properties and their suitability as a window material for solar cells. They reported solar conversion efficiency of 8.8%. Chen et al. [18] used copper selenide as an absorbing layer and reported a Cu$_{2-x}$Se/CdS heterojunction solar cell with an efficiency of 5.38% under simulated AM1 illumination. Copper selenide Cu$_x$Se ($x \sim 2$) was examined by Hiramatsu et al. [75] as a hole injection layer for low-temperature organic devices and they reported that Cu$_x$Se film combined with copper phthalocyanine (CuPc) is a promising candidate for a low-voltage hole injection anode or a buffer layer in low-temperature devices such as organic light emitting diodes or thin film transistors.

By utilizing spray pyrolysis technique Yadav [76] prepared copper selenide thin films at different substrate temperature (300, 325, 350, 375 and 400 °C) and they reported that the prepared films are polycrystalline in nature with hexagonal crystal structure irrespective of the substrate temperature. C-V, I-V characteristics (in dark and under illumination) of the copper selenide thin films deposited on F: SnO$_2$ coated glass substrate at various substrate temperatures was also studied [77]. The surface properties

<table>
<thead>
<tr>
<th>Technique</th>
<th>T (°C)</th>
<th>E (°C)</th>
<th>R (Ωcm$^{-2}$)</th>
<th>C (µF/cm$^2$)</th>
<th>I (W/cm$^2$)</th>
<th>Ref.</th>
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<td>300</td>
<td>-</td>
<td>3.15x10$^{-4}$</td>
<td>6.3x10$^{20}$</td>
<td>30.86</td>
<td>[55]</td>
</tr>
<tr>
<td>RF sputtering Annealed at 680</td>
<td>-</td>
<td>-</td>
<td>1.3x10$^{-4}$</td>
<td>8.9x10$^{20}$</td>
<td>54.5</td>
<td>[56]</td>
</tr>
<tr>
<td>RF sputtering Annealed at 600</td>
<td>-</td>
<td>-</td>
<td>2.1x10$^{-4}$</td>
<td>7.4x10$^{20}$</td>
<td>32.3</td>
<td>[57]</td>
</tr>
<tr>
<td>RF sputtering Annealed at 600-700</td>
<td>-</td>
<td>-</td>
<td>$\sim$2x10$^{21}$</td>
<td>$\sim$2x10$^{30}$</td>
<td>10-35</td>
<td>[58]</td>
</tr>
<tr>
<td>RF sputtering Annealed at 400</td>
<td>-</td>
<td>-</td>
<td>3.2x10$^{-4}$</td>
<td>4x10$^{22}$ - 5x10$^{28}$</td>
<td>10-35</td>
<td>[59]</td>
</tr>
<tr>
<td>RF sputtering Annealed at 680</td>
<td>-</td>
<td>-</td>
<td>1.3x10$^{-4}$</td>
<td>8x10$^{20}$</td>
<td>65</td>
<td>[60]</td>
</tr>
<tr>
<td>RF sputtering RT</td>
<td>-</td>
<td>-</td>
<td>4.3x10$^{-7}$</td>
<td>-</td>
<td>-</td>
<td>[61]</td>
</tr>
<tr>
<td>RF sputtering 200</td>
<td>-</td>
<td>-</td>
<td>6.5x10$^{-4}$</td>
<td>8.2x10$^{16}$ - 7.2x10$^{18}$</td>
<td>-</td>
<td>[62]</td>
</tr>
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<td>6.6x10$^{-4}$</td>
<td>$10.4x10^{20}$</td>
<td>9.1</td>
<td>[63]</td>
</tr>
<tr>
<td>Atom beam sputtering</td>
<td>65-170</td>
<td>-</td>
<td>$1x10^{-3}$</td>
<td>$\sim$10$^{30}$</td>
<td>24</td>
<td>[64]</td>
</tr>
<tr>
<td>DC sputtering</td>
<td>200</td>
<td>-</td>
<td>2x10$^{-4}$</td>
<td>2.8x10$^{14}$</td>
<td>-</td>
<td>[65]</td>
</tr>
<tr>
<td>DC magnetron sputtering</td>
<td>30±10</td>
<td>-</td>
<td>4.5x10$^{-4}$</td>
<td>5x10$^{16}$</td>
<td>40</td>
<td>[66]</td>
</tr>
<tr>
<td>DC reactive sputtering</td>
<td>Up to 120</td>
<td>-</td>
<td>-</td>
<td>2.7x10$^{20}$</td>
<td>13.6-20</td>
<td>[67]</td>
</tr>
<tr>
<td>Electroless</td>
<td>As deposited</td>
<td>-</td>
<td>-</td>
<td>4x10$^{-1}$</td>
<td>2.2x10$^{15}$</td>
<td>7</td>
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</table>
of Cu₈Se thin film deposited on (polyamide 6 – PA 6) polymer surface via adsorption/diffusion method was investigated by Ivanauskas [78]. Urmila et al. [79] analysed the photoluminescence of Cu₇Se₄ thin films deposited by reactive sputtering method. Li et al. [80] studied the effect of sputtering power on optical and electrical properties of copper telluride thin films deposited on glass substrate at room temperature by magnetron sputtering method. They reported that by adjusting the sputtering power the thickness of the film varied and the films shows high crystalline quality. Hankare et al. [81] studied the variation of thickness as a function of deposition temperature and deposition time. Liew et al. [82] reported that the root mean square and mean roughness value were decreased while the average grain size was increased as film thickness increased. The effect of non–stoichiometry on the copper telluride thin films was studied by Bari et al. [83] and they reported that band gap energy was increased with increase in at. % of copper in composition. They observed that the grain size increase with decrease of at. % of copper in composition. Xue et al. [84] prepared three kinds of copper selenide thin films (CuSe₂, CuSe, Cu₂Se) by pulsed laser deposition method in argon atmosphere and they reported that the selenium ratio in the target and substrate temperature is the decisive factor for the composition and structure of the as–deposited thin film. Copper selenide thin films were deposited on glass substrate between 300 and 450 °C employing aerosol- assisted chemical vapour deposition method by Hu et al. [85] and they reported that amorphous films were obtained under 300 °C and polycrystalline thin films were obtained at deposition temperature > 300 °C. Zainal et al. [86] reported polycrystalline copper selenide thin films with mixed phase. Dhanam et al. [87] prepared cubic Cu₂₋ₓSe and tetragonal Cu₃Se₂ thin films from the same reaction mixture at room temperature by slightly varying the pH. Cu₂₋ₓSe films are more conductive than Cu₃Se₂ films.

Kim et al. [88] thermally treated the as deposited copper selenide thin films under nitrogen atmosphere at various temperatures from 250 to 400 °C in order to study the effect of the annealing temperature on the optical band gap and surface morphology. Effect of annealing on vacuum evaporated copper selenide thin films was studied by Peranantham et al. [89] and they reported that the film annealed at 473 K shows a stoichiometric CuSe composition and the film annealed at 673 K tend to
become Cu$_2$Se. Ambade [90] deposited nanocrystalline copper selenide thin films on glass and tin doped – indium oxide substrates using chemical bath method and annealed at 200 °C for 1 h. Gracia et al. [91] reported that annealing of Cu$_{2-x}$Se and CuSe films at 400 °C in nitrogen leads conversion of Cu$_{2-x}$Se to Cu$_2$Se and CuSe to Cu$_{2-x}$Se. Literature survey shows that only a few reports are available on the effect of deposition and annealing temperature on the structural, optical and electrical properties of copper selenide thin films prepared by physical vapour deposition method. Hence further research is necessary to investigate the properties of copper selenide thin films deposited and annealed in vacuum at different substrate temperature.

1.4.3 Copper telluride thin films

Literature survey shows that copper telluride thin films were prepared by several methods. Reports are available on the deposition of copper telluride thin films on different substrates such as steel and ITO [92], glass microslides [93], corning glass [94], borosilicate glass [95] and mica [96]. Luo et al., [97] reported that efficient and stable cadmium telluride (CdTe) solar cells can be obtained with Cu$_{1.5}$Te as a back contact layer. Dhasade et al., [98] employed electron irradiation technique on electrodeposited copper telluride thin films to prepare copper telluride nanostructures. Neyvasagam et al., [99-101] studied the effect of thickness on the structural, optical and electrical properties of copper telluride thin film prepared by thermal evaporation method. Pathan et al., [93] prepared copper telluride thin films by modified chemical bath deposition method and they reported that the film consists of different phases of copper telluride. De Mour Flores et al., [94] studied the influence of substrate temperature (RT – 300 °C) on the properties of Cu$_x$Te thin films prepared by pulsed laser deposition method and they reported that mixed phases of copper telluride thin films were obtained for the film deposited at 100 °C and single phase hexagonal Cu$_2$Te thin films was obtained for the film deposited at 300 °C. Ferizovic and Munoz [95] prepared Cu$_2$Te thin films at room temperature by magnetron sputtering method and studied the dependence of annealing temperature (200 °C – 500 °C) on the structural, electrical and optical properties and they reported that copper telluride thin film deposited at room temperature yielded mixed stoichiometric and non-stoichiometric phases, annealing temperature above 400 °C yielded films with single phase Cu$_2$Te
which exhibits large absorption coefficient compared to non-stoichiometric films. Dawar et al. [96] prepared copper telluride thin films by vacuum evaporation technique at 350 °C on mica substrate and studied the effect of annealing at the same temperature in vacuum for ~ 2h. They reported that the films grown at substrate temperature below 573 K were amorphous and films grown at a substrate temperature of ~ 623 K contained the uncombined elemental constituents in addition to copper telluride, however annealing in vacuum for ~ 2h produced polycrystalline films composed of single phase of copper telluride. Park et al., [102] investigated the annealing effects of the evaporated Cu₂Te films on the photovoltaic properties of CdS/CdTe thin film solar cells. Literature survey reveals the importance of substrate temperature and annealing temperature to get single phase copper telluride thin films. Very few reports are available on the influence of substrate and annealing temperature on the copper telluride thin films. Hence further research is necessary to study the effect of substrate and annealing temperature on the structural, optical and electrical properties of copper telluride thin films.

### 1.4.4 Gallium telluride thin films

Gallium telluride (GaTe), a binary p-type semiconductor, belongs to III – VI metal chalcogen family. Gallium telluride compounds exist in different phases and their structures depend on the phase composition [103]. It has direct band gap. Layered GaTe has high potential applications in various optoelectronic devices, radiation detectors and solar cells due to the optimum band gap as a solar window material [104]. The GaTe crystal has layered structure (lamellar) and each mono layer consists of Te-Ga-Ga-Te sheets. The chemical bonding within the layer is covalent bonding and between the layers exist Van der Waals forces [105]. Zhu et al. [106] deposited Ga₂Te₃ thin films on Si and quartz substrate at room temperature by pulsed laser deposition technique. They annealed the films at 450 °C in vacuum chamber for 20 min in order to get crystallization. Gillan and Barron [107] prepared gallium telluride thin films on Si (100) substrate at 285-310 °C by low pressure metal organic chemical vapor deposition method. Bekheet et al. [108] deposited Ga₂Te₃ thin films on highly polished pyrographite and glass substrates at different thickness ranged from 250 – 611 nm by thermal evaporation method. From the I-V characteristics Bekheet et al. [108] reported
that Ga$_2$Te$_3$ thin films are typical for a memory switch. Cinar et al. [109] electrochemically prepared GaTe thin films on p-type Si substrate in order to produce a Schottky device and they studied the current voltage characteristics of the Sn/GaTe Schottky device as a function of temperature. They have calculated the band gap energy of GaTe thin films as 1.67 eV from the absorption measurements. Sen and Bose [103] prepared Ga$_2$Te thin films on glass, mica and alumina substrate at 300 and 525 K by electron beam evaporation method. They reported that for all substrates with increasing substrate temperature the carrier concentration and mobility are increased. George et al. [110] prepared Ga$_2$Te$_3$ thin films by low pressure chemical vapor deposition method and they reported that Ga$_2$Te$_3$ is a p-type semiconductor with a resistivity of $195\pm10$ Ω cm and hole mobility in the range of 10 - 40 cm$^2$/Vs. Literature review shows that only a few reports are available on gallium telluride thin films. Few reports are available on the deposition of gallium telluride thin films on different substrates and thickness but no report is available on the effect of substrate temperature (200 – 500 °C) on gallium telluride thin films. Hence gallium telluride thin films were prepared by electron beam evaporation method at different substrate temperature (200 – 500 °C) and the structural, morphological and optical properties were studied.

1.4.5 Copper bismuth sulfide thin films

The compound Cu$_3$BiS$_3$ (CBS) is a bismuth sulfosalt of copper and it is found in nature as the mineral wittichenite from the wittichen mines, Baden, Germany [111]. Its structure is orthorhombic. The compound is stable at room temperature and is among 13 compounds identified in the Bi-Cu-S ternary alloy system [112]. I-V-VI ternary copper based sulfides are expected to become promising absorber material for photovoltaics. It is a semiconducting material with band gap energy in the range of 1.24 - 1.8 eV which shows good thermal stability (> 573 K), possesses high – optical absorbance in the visible region and also has potential application in hetrojunction solar cells. Copper bismuth sulfide thin films were prepared by several methods such as sulfurization [113], sputtering [114], spray pyrolysis [32], and chemical bath deposition method [37]. More reports are available on the preparation of copper bismuth sulfide thin films by two step method [33-36,113,115-117]. Only few reports are available on single step method for the preparation of CBS thin films [32,37,38,114,118].
Gerein and Haber et al. [117] reported that Cu$_3$BiS$_3$ thin films prepared by two-step process contain voids and pockets between the film and substrate even when optimized processing conditions were employed making them unsuitable for use in thin film photovoltaics. To overcome these problems Gerein and Haber [114] prepared Cu$_3$BiS$_3$ thin films on fused silica substrates in a single step process by reactive sputtering deposition of Cu-S and Bi on hot substrate and reported that the films are crystalline, phase–pure, dense, smooth and continuous. Influence of copper mass ratio on the grain size and electrical conductivity of Cu$_3$BiS$_3$ samples were investigated by Dussan et al. [115]. The band bending of the Cu$_3$BiS$_3$/In$_2$S$_3$ structure was studied by Mesa et al. [118]. Characterization of Al/ Cu$_3$BiS$_3$/Buffer/ZnO systems with buffer layers In$_2$S$_3$ or ZnS by TEM was reported by Mesa et al. [119]. The influence of substrate temperature (250 – 400 °C) on the structural and optical properties is studied by Liu et al. [32] by spray pyrolysis method. The deposition temperature strongly influences the properties of thin films [120]. Literature review reveals the requirement of more studies on the effect of substrate temperature on Cu$_3$BiS$_3$ thin films prepared by single step process. Hence we report the work in this thesis.
References


