CHAPTER 2

THEORETICAL INVESTIGATIONS OF ALLOY FORMATION

2.1 INTRODUCTION

In the second generation solar cells such as CdTe/CdS, CdTe play a vital role. CdTe photovoltaic technology has reached the technological maturity and it is one of the best selling product among thin film solar cells (Andrei Salavei et al. 2013). Its efficiency is about 8% for commercial 55W modules (Xavier Mathew et al. 2004). Closed space sublimation technique is the fast deposition method which is potentially cheap and cost effective. At the same time the development of flexible CdTe solar cells on polymer is difficult in the closed space sublimation because of high substrate temperature encountered during the sublimation process (Khrypunov et al. 2006).

2.2 CADMIUM TELLURIDE

CdTe is the II–VI compound semiconductor. CdTe is one of the low cost poly crystalline material and a leading candidate for photovoltaic applications due to optimum band gap for the efficient photo conversion and robustness with good scalability fit for industrial production with a variety of film preparation methods. The work on CdTe thin film solar cell started in 1970s but the progress in R &D got real impetus in 1980s with various techniques such as electro deposition, metal oxide chemical vapor deposition, sputtering, screen printing, vacuum evaporation, closed space sublimation (CSS). Among all these methods, closed space deposition is a productive method to deposit CdTe thin films at high rate of deposition, more efficient
and economic method. The efficiency of commercial CdTe module is about 8\% for 55W modules (Xavier Mathew et al. 2004). CdTe photovoltaic technology has finally reached the technological maturity and is now one of the best selling types of product among thin film solar cells (Andrei Salavei et al. 2013). A few microns thickness of CdTe thin film solar cells is sufficient to absorb 90\% of photons with energy greater than 1.45 eV. CdTe grows in to P type with a carrier concentration $10^{14}$/cm$^3$ which is suitable to form good partner with n type materials. CdTe grows polycrystalline with large grain size (2-10\(\mu\)m) (Romeo et al. 2010). The band gap of CdTe is most ideal match for solar spectrum making it suitable for use as absorber layer (Mahesha et al. 2009). Highest efficiency of CdTe solar cells is 16.5\% which is deposited by CSS. CdTe technology on glass substrate has progressed to a high level of production (Perrenoud et al. 2011).

Glass is a suitable substrate to deposit CdTe thin films. Distinct advantage of CdTe is the fast rate of deposition by closed space sublimation. If thin films produced in such a manner, solar electricity generated from CdTe would be potentially cheap and cost effective. CdTe is a stable compound that environmental and health issues of CdTe photovoltaics are insignificant which was investigated by Brookhaven national laboratory and national renewable energy laboratory (Fthenakis et al 2005). Development of flexible CdTe solar cells on polymer substrate is difficult with CSS process because of high substrate temperature encountered during sublimation process (Khrypunov et al. 2006). Glass is a comfortable and eco friendly material to deposit CdTe thin films. The two key properties of CdTe material are its near ideal band gap and its high optical coefficient (Ferekides et al. 2004). CdTe has high absorption coefficient $>5 \times 10^5$/cm. Cadmium telluride (CdTe) has been well recognized as a very attractive photovoltaic material because of the high potentiality of its several properties.
2.2.1 Properties Of Cadmium Telluride

The various properties of cadmium telluride found from the literature survey are mentioned below.

1. Lattice constant: 6.48 Å
2. Space group: F43m
3. Crystal structure: Zinc blende
4. Band gap: 1.5 eV – direct band gap
5. Density: 5.86 g/cm³
6. Melting point: 1041 °C
7. Boiling point: 1,050 °C
8. Solubility: Insoluble in water and other solvents
9. Refractive index: 2.91
10. Young's modulus: 52 GPa
11. Thermal conductivity: 6.2 W·m/m²·K at 293 K
12. Specific heat capacity: 210 J/kg·K at 293 K
13. Thermal expansion coefficient: 5.9×10⁻⁶/K at 293 K
14. Electron mobility: 1200 cm²/Vs
15. Hole mobility: 100 cm²/Vs

2.2.2 Deposition of Cadmium Telluride

The state of deposition influences the growth of CdTe thin films in closed space sublimation (Falco et al. 2006). Thin films deposited by closed space sublimation have good micro structure and uniformity. The deposition of CdTe in closed space method at high temperature is a reversible process as shown in equation below.
CdTe $\leftrightarrow$ Cd + $\frac{1}{2}$Te$_2$

In closed space sublimation method, the glass substrate was taken above the open end of the quartz ampoule at a distance of about 5mm. The quartz ampoule contains CdTe was placed in a boat. The ampoule tube was heated by tungsten boat using 220 V AC power supply with variable output current. The temperature of the source and substrates were measured and controlled by chromel-alumel thermocouple with an accuracy of 1°C.

2.3 TIN TELLURIDE

It is a new nano crystalline IV-VI semiconductor material. K.A Campbell et.al (2007) prepared and investigated polycrystalline SnTe thin films by thermal evaporation method at high pressure using the highly pure elements of tin and tellurium (99.999% purity) (Kristy et al. 2007). Research trends on the study of SnTe are progressing in order to increase the efficiency of solar cells (Saidur et al. 2012). SnTe exhibits three different crystal structures such as orthorhombic, cubic (NaCl-rock salt) crystal structure and rhombohedral structure (Matthias Batzill and Ulrike Diebold 2005).

Band gap of SnTe is 0.18eV at 300K finds applications in photovoltaics. SnTe thin films could be prepared by thermal methods in vacuum which helps to achieve compound formation by controlling the reactants and substrate temperature. The optical absorption studies as a function of deposition time indicated that the band gap of the SnTe thin film increases as the deposition time decreases (Ivanov et al 2013). Band gap energy decreases with the increase in deposition time. But the band gap of SnTe increases with the increase in tin content. The band gaps of electrodeposited SnTe thin films for 10 and 30 minutes were found to be 0.32 and 0.20 eV, respectively (Ilkay Şişman & Hasan 2011). But Thickness of the
SnTe thin film also changes with the deposition time. It behaves like p-type material. The absorption coefficient of SnTe is very high. Thermal stability of SnTe is much poorer due to large ionicity of Sn-Te bonding (Meng-Jiao 2013). SnTe finds applications in photo detectors and thermo electric generators.

2.3.1 Properties of Tin Telluride

The various properties of SnTe observed from literature survey are mentioned below.

1. Lattice constant: 0.63 nm
2. Space group: Fm3m, No. 225
3. Crystal structure: Halite (cubic)
4. Band gap: 0.18 eV, narrow band gap
5. Density: 6.445 g/cm³
6. Melting point: 790 °C
7. Specific heat capacity: 185 J K⁻¹ kg⁻¹
8. Electron mobility: 500 m² V⁻¹ s⁻¹

2.4 CADMIUM TIN TELLURIDE

The author has chosen the material CdSnTe₂ since the material is new. Based on the following literature survey the author continued to prepare the CdSnTe₂ thin films by closed space deposition method. CdSnTe₂ is a ternary compound. Only a few literatures were available about the compound. K.Sakthivel et al. (2009) has reported that CdₓSn₁₋ₓTe has unique structure with narrow range of lattice constants and tunable band gap from visible to infra red by adjusting the composition of alloy ‘x’. Cd₀.₂₅Sn₀.₇₅Te and Cd₀.₂₅Te₀.₇₅Sn exhibited direct band gaps with rock salt structure (Sakthivel et al. 2009). Venkatachalam & Ganesan (2008) investigated the Cd₀.₄Sn₀.₆Te
thin films and found that the optical band gap decreased with the increase in the substrate temperature and the thickness of the films. CdZnTe compound was also considered as a model material for the preparation and characterization of CdSnTe₂ thin films. A pseudo potential density functional investigation done by Gomez et al. (2003) on CdₓSn₁₋ₓTe has shown rock salt structure (Gomez et al. 2003). Grosch et al. (1994) reported that CdₓSn₁₋ₓTe is a mixed crystal which makes a transition from ten (x=0) to eight electron system between IV-VI and II-VI compound.

CdZnTe is a ternary compound and an excellent II-VI semiconductor compound. Adding zinc with CdTe increases the band gap and is suitable for the maximum absorption of solar spectrum. II-VI, III-V binary and ternary semiconductors are useful in photovoltaics and optoelectronics (Aissat et al. 2013). CdZnTe is one of the promising materials which have wide applications and successfully used in the fabrication of solar cells. Researchers developed CdZnTe thin films by several methods such as thermal evaporation, chemical vapour deposition, sputtering, metal organic chemical vapour deposition, molecular beam epitaxy, etc. Among all these methods, closed space deposition has quick rate of deposition (Huang et al. 2012). The lifetime and mobility of CdZnTe semiconductors are more with band gap around 1.5 eV and also capable of operating at room temperature (Semendy et al. 2010). CdZnTe thin films have attracted more attention in solar cells due to its high absorption coefficient, operatability and good life time mobility. The range of band gap of CdZnTe is from 1.5 eV to 1.8 eV. This band gap can be varied from 1.5 to 2.25 eV by varying the composition of elements in the alloy. The nature of CdZnTe thin films found to be polycrystalline on annealing the thin films. The strain and crystalline size increases with the increase in annealing temperature (Vidhya et al. 2015). Preparation of CdZnTe by physical vapour deposition regulates the growth rate (de Melo et al. 2015). CdZnTe thin films deposited on glass substrate
have good morphology and adhesion (Arbaouia et al. 2006). Murali (2008) in his studies reported that vacuum evaporation is the most common technique in the preparation of CdZnTe thin films. Polycrystalline thin films with cubic zinc blende structure have been prepared by closed space deposition method. The films have tunable band gap from 1.5 eV to 2.3 eV. Closed space sublimation is the economic method to deposit CdZnTe thin films with good stoichiometry (Kosyak et al. 2016). CdZnTe thin films grown on glass substrates are sensitive to substrate temperature, annealing and gas pressure and also with tunable band gap from 1.5 eV to 2.25 eV. Based on the above literature survey, the author has selected CdSnTe for his study by closed space deposition method.

### 2.5 CONCLUSIONS

The properties, preparation and characterization of binary compounds such as CdTe, SnTe and ternary compounds (CdSnTe) have been investigated. This chapter has given a route for the preparation of thin films. There are various methods of preparation of thin films. Among those methods, closed space deposition method is a reliable, economic and harmless technique with fast rate of deposition. CdTe is a polycrystalline material exhibiting direct band gap of 1.5 eV with zinc blende structure and high absorption coefficient. The band gap of SnTe thin films ranges from 0.18 eV to 0.2 eV with rock salt structure. CdSnTe thin films exhibited face centered cubic structure and CdZnTe thin films has band gap 1.5 eV. All these thin films CdTe, SnTe, CdSnTe and CdZnTe thin films were prepared by closed space sublimation method. Therefore the author has selected a new material CdSnTe to prepare the thin films by closed space sublimation method. The structural properties are discussed in chapter 5, optical properties in chapter 6. The experimental results are compared with the theoretical values by *ab-initio* study which is elaborated in chapter 7.