Chapter I

Preface
1.1 Motivation

The necessity for a novel technique to achieve microelectronic system of high complexity has stimulated the emergence of new branch of material science known as thin solid films. The use of the multitechnical approaches for the growth and characterization of thin films has led to the exploitation of thin films of materials in the design of integrated circuits and now moved the thin film physics into the forefront of current solid state research and nano-technology. Thin films of pure metals, alloys, semiconductors and organic compounds have become indispensable in industry and science because of their varied and needful properties. With the development of sophisticated methods of production and examination, the reproducibility of results on thin film system as well as the understanding of their basic characteristics has been greatly improved. All the physical properties of thin films such as optical, structural, electrical and electronic etc., play a vital role in the expanding sphere of industrial, scientific, technical and defence applications.

For most semiconductor devices, the formation of a low-resistance, a metal-based, ohmic contact requires the establishment of a heavily doped region directly beneath the metal contact. If the surface layer is doped sufficiently high, current transport across the interface proceeds principally via tunneling at the Fermi level. In the case of p-CdTe, it has not yet been demonstrated that p-type doping levels sufficient to establish tunneling from the metal contact to the semiconductor can be produced [1-3]. For this reason, the formation of ohmic contacts continues to merit serious consideration in devices such as CdTe thin-film solar cells. In addition, the stability of various metal contacts is still unproved, even though they may initially demonstrate sufficiently low values of specific contact resistance.

Although the research aimed at providing a more complete understanding of p-type dopant incorporation into p-CdTe continues, several other avenues of producing ohmic contacts are also being actively investigated. One of these involves in the ohmic behavior of a p-CdTe contact could be greatly assisted by the use of an interface layer of heavily doped ZnTe. In this scheme, the close alignment of the
valence bands permits hole transport between the CdTe and the ZnTe, while transport between the heavily doped ZnTe and the metal can proceed via tunneling [4,5]. In addition, it has been demonstrated the relatively high optical band gap of ZnTe (2.26 eV) makes it a promising material for use as an optically transparent contact / interconnect for a mechanically stacked, multiple-junction solar cell [6]. Although these and other uses make p-ZnTe a potentially useful material, many issues regarding the physical properties of p-ZnTe remain unresolved. For example, it has not yet been determined if thin film ZnTe can be readily produced with doping levels sufficient to allow tunneling from the adjacent contact metal (i.e., \( \geq 1 \times 10^{19} \text{ cm}^{-3} \)) [7]. The doping level required for tunneling will be minimized if the whole effective mass in the ZnTe is found to be low. Likewise, even if these doping levels can be achieved, relatively little is known about the stability of typical ZnTe dopants. Regarding the ZnTe/metal interface, interfacial reactions have been observed during metal deposition on in vacuo cleaved, crystalline ZnTe [8]. However, the potential effects of these reactions on contact formation and/or stability have not been determined. Finally, regarding the case of thin film solar cells, very little information exists concerning which of the observations noted in crystalline ZnTe will apply to thin film (polycrystalline) devices.

1.2 Introduction

Semiconductor thin films play an important role in industry because of their varied properties. The semiconducting properties of thin films allow them to be used in the recently developing microelectronics field. The advancement of thin film optical system has been so tremendous that the optical devices such as reflecting, antireflecting and filters find innumerable applications in various fields of science. The reflectance and the transmittance of semiconductors can provide useful information about the electronic band structure and density of free carriers in a material under study.

A semiconductor compound is a substance containing two or more elemental semiconductors in a fixed ratio. The most useful types of binary compounds are those averaging four valence electrons per atom. These can usually be obtained from one-to-one combination of Group III elements of the periodic table like gallium, and
Group V elements like arsenic. The Group II and Group VI elements combination is also possible. However, there are a much larger number of semiconductors available today, and more and more III-V and II-VI compound semiconductors are applied.

II-VI compounds typically exhibit a larger degree of ionic bonding than III-V compounds, since the respective elements differ more in the electron affinity due to their location in the periodic table.

The wide spectral ranges, the high probability of radiative transitions and the relatively high mobility of the carriers of wide-band II-VI semiconductors have naturally attracted the attention of many researchers wishing to develop optoelectronic devices. It is well known that the electrical properties of these materials are greatly affected by the relative variation of the two components during the growth.

In order to establish a foundation for more detailed studies of ZnTe related interfaces, it is vital to acquire a general understanding of the thin film ZnTe material itself. Because of the relatively high vapor pressure of Zn compared to Te, it is likely that films deposited from nominally stoichiometric sources will be Zn deficient. Although this situation would be detrimental for the case of undoped ZnTe, because the aim here is to produce p-type material, with substitutional Cu on Zn sites, it may be possible to use the state of Zn deficiency advantageously. With this in mind, the following study has been designed to indicate not only the extent of Zn deficiency but to identify process parameters of film thickness and substrate temperature that could be used to control it. In this work, both pure and copper layered ZnTe thin films were produced by vacuum evaporation. The effect of these parameters were studied using compositional, structural, optical, electrical and photoconduction analysis.

In addition, ZnTe is promising material for pure green light emitting diodes (LEDs), since it has the energy gap of 2.26 eV at room temperature and the band structure is of direct optical transition type. Hence a p-n junction diode structure (Al/ZnTe/CdSe/Al) has been fabricated and its characteristics have been studied.
1.3 About zinc telluride

Zinc telluride (ZnTe) is one of the II-VI compound semiconductors. It is usually a p-type semiconductor. Its crystal structure is cubic. Its lattice constant is 6.103 Å [9]. Its CAS number is 1315-11-3. Its melting point is 1238.5°C. ZnTe, being a wide and direct band gap (2.26 eV) [10] semiconducting material with low electronic affinity (3.53 eV) [11] it can absorb photons in the visible region without any phonon assisted mechanism that makes it useful in several electro-optic and optoelectronic applications [12]. The defects governing the electrical behaviour of the pure material are due to Zn vacancies, which can accept one or two electrons [13-16]. By the thermal vacuum evaporation techniques, Zn vacancies are created as a result of the higher Zn re-evaporation as compared to Te, because of the higher Zn vapour pressure at the same temperature. The as grown ZnTe films are highly resistive and their resistivity at room temperature is \( \sim 10^5 \Omega m \) [17].

p-type doping of crystalline ZnTe by substitutional Cu acceptors (on a Zn site) does not appear to demonstrate carrier compensation. It has also been observed that Cu is a more effective dopant in crystalline ZnTe than other Group 1B elements. Because of the successful use of Cu in crystalline ZnTe, early studies investigated using Cu to form p-type thin film material to fabricate low-resistivity thin films.

Zinc telluride has potential applications in a variety of solid-state devices such as solar cells, photodetectors and light emitting diodes. It has been extensively studied for applications as a purely green light emitting diode and as back contact for CdTe in CdTe/CdS heterojunction solar cells [18-21], since it is expected to have a small valance band discontinuity with CdTe and can be doped degenerately with copper [19-22], to obtain low resistance. ZnTe and its alloys may effectively be used as window materials in CdTe heterojunction solar cells. These thin films were also used in tandem solar cell structure, which utilizes CdZnTe as the absorber material, and for the fabrication of a CdZnTe/ZnTe quantum well structure. All these activities created a renewed interest in the studies of ZnTe films for device applications.
1.4 Survey of literature

A variety of methods have been used to prepare ZnTe thin films. Some examples are thermal vacuum evaporation [23], physical vapor transport [24], vapor phase epitaxy [10], molecular beam epitaxy [25], hot wall evaporation [26], metallorganic vapor phase epitaxy [27] and electrodeposition [28]. Because of its importance several workers [11,29-34] have made a detailed study of the crystal structure of ZnTe thin films. They have observed that these films deposited on glass substrates kept at room temperature have cubic zinc blende type structure. Pal et al [35] have carried out studies on the optical properties of ZnTe thin films and calculated the optical constants. Thutupalli and Tomlin [36] have measured the optical constants (n,k) of thin polycrystalline ZnTe films and evaluated the band gaps. A theoretical model has been proposed by Pawlikowski [37] for ZnTe films and he determined the absorption coefficient near the fundamental absorption edge at normal incidence. Mondal et al [30] have reported the dependence of refractive index, absorption and extinction coefficients on incident photon energy \((h\nu)\) for ZnTe films deposited on glass substrates by hot wall evaporation technique.

Semiconducting thin films have been extensively studied for a long time, because of their high technical value. In recent years, owing to a number of practical applications in the field of microelectronics and optoelectronics a great deal of interest has been shown in the study of the dielectric and conduction behaviour of various semiconducting materials [38-41]. Most of the experimental work carried out so far relates to d.c. which give information about the nature of transport processes. Studies on space charge and thermally stimulated currents in ZnTe thin films have been carried out by Taro Hino and Ken Yamashita [42]. Parakh and Garg [43] have studied the conduction mechanisms in vacuum evaporated ZnTe thin films and they found that the type of conduction is Poole-Frenkel. The current – voltage (I-V) characteristics of bulk crystal ZnTe devices are of the space-charge-limited type [44]. Shirakawa et al [45] have reported space-charge-limited currents in their Al/ZnTe/Al sandwich devices. Other authors interpreted the electrical conduction in ZnTe films in terms of a Poole-Frenkel or a Schottky mechanism [46]. Conduction mechanisms in the off state of ZnTe thin films have been studied by Marc Burgelman [47] using this aspect for the fabrication of switching devices.
Burgelman [47] has made an attempt to understand the conduction mechanism in high-resistivity evaporated ZnTe films. Senokosov et al [48] have prepared single-crystal ZnTe films of 10-30 μm thick and investigated their current transport characteristics. Low frequency current oscillation in ZnTe films have been reported by Matveeva et al [49]. A few other reports [50-52] are available about amorphous ZnTe films prepared in ultrahigh vacuum with reproducible properties. Atwal et al [53] reported the electrical resistivity of silver doped ZnTe film. Morris et al [54] reported the stoichiometry, resistivity, optical properties and morphology of films prepared at various substrate temperatures of pure and copper doped ZnTe films. He reported that the resistivities can be varied from about 10^6 Ω cm to about 10^2 Ω cm by appropriate doping. Gessert et al [55] reported the Zn composition dependence of electrical resistivity of Cu doped ZnTe films. The substrate temperature dependence on electrical properties of copper doped ZnTe films has been reported by Mondal et al [56]. Both copper concentration and substrate temperature dependence of resistivity of copper doped ZnTe films were also reported by Gessert et al [18].

Cu doped ZnTe films have been prepared by various methods, including thermal evaporation of ZnTe and Cu from two sources [21], RF and dc sputtering [20, 57], electro-deposition [58], hot wall evaporation [53] and thermal evaporation [59].

Feng [21] et al has been observed an abnormal conductivity behavior with temperature in Cu doped ZnTe polycrystalline films. Maqsood et al [60] prepared Cu doped ZnTe thin films by immersion in Cu(NO_3)_2-H_2O solution. He showed a decrease of transmission with an increase of immersion time, and a slight shift in the optical band gap. He also observed that the sheet resistance of as-deposited films was very high, while the resistivity of the films immerse in Cu solution reduced to less than 1 Ω cm after annealing at 400°C in vacuum for one hour. Aqili [61] has been obtained a drastic decrease of sheet resistance in copper doped ZnTe. Kobayashi [62] have studied the electrical and optical properties of Cu doped high conductivity ZnTe thin films.

Kimmerle et al [63] have been fabricated p-n junction based on wide bandgap II-VI compounds by vacuum evaporation and have been characterized by I-V, C-V and spectral response measurements. Spear et al [64] and Carlson and Wronkski [65] have reported an amorphous p-n junction fabricated from doped amorphous silicon.
Moore et al [66] have shown that a rectifying junction can be formed between ZnTe and ZnSe and they were unable to identify the current mechanisms involved at that time. Gasin et al [67] and Pal et al [68] were fabricated ZnTe/CdTe heterojunctions by hot wall method and studied the direct and reverse currents and the photoelectrical properties. Kuo et al [69] were studied optical properties of ZnTe/CdSe superlattice. Kemner et al [70] studied atomic rearrangement at ZnTe/CdSe interfaces by X-ray diffraction, X-ray absorption fine-structure spectroscopy and transmission electron microscopy.

1.5 Scope of the present work

Despite the extensive studies carried out on several properties of pure and copper doped ZnTe thin films, there is still, need information concerning the microstructure, electrical, optical, dielectric properties and the effect of film thickness, substrate temperature and copper composition on these properties of these films. Therefore, systematic and detailed study of various properties of pure and copper layered ZnTe thin film seems to be required. Hence, the present investigation is focused on the preparation of pure and copper layered ZnTe thin films and study of their physical properties viz., structure, surface morphology, composition, optical, dielectric, conduction, transport, and photoconduction studies. Also the heterojunction i.e., p-n junction diode in the form of Al/ p-ZnTe/ n-CdSe/Al structure have been fabricated and studied.

1.6 Organization of the thesis

The first chapter is of introductory nature. A brief review about the ZnTe semiconductor and survey of literature is given in this chapter. Selection of substrates, the procedure used to clean the substrates and the coating techniques used in the present investigations are briefly explained in the second chapter. Chapter III deals about the structural characterization of the ZnTe thin films prepared by thermal evaporation technique. The dependences of the structure of the ZnTe thin films on film thickness, substrate temperature and copper composition have been discussed. Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and Energy Dispersive Analysis by X-rays techniques used to analyze the thickness dependence
on surface morphology and composition of the ZnTe thin films are also described in this chapter III. The optical transmittance and absorption spectra were recorded to study the optical properties like optical transition, optical band gap, optical constants etc. The dependence of the optical properties of the ZnTe thin films on film thickness, substrate temperature and copper composition have been discussed in chapter IV.

Chapter V deals with the dielectric properties of ZnTe films. The dielectric parameters and the thickness dependence of the dielectric constant have been studied in detail. Dependence of capacitance and loss on frequency and temperature ranges specified therein have been examined. The results are interpreted on evaluating the temperature co-efficient of capacitance. Chapter VI outlines the electrical conduction properties of ZnTe films where the identification of mechanisms in the films under a.c. and d.c. fields have been made. The thickness dependence of activation energies involved in each of the phenomenon has been presented. The resistivity analysis of copper layered ZnTe thin films are reported in chapter VII.

The photoconduction phenomenon in ZnTe films of various thicknesses in the visible region using suitable masks is presented in the chapter VIII. Formation and characterization of p-n heterojunction diode are dealt in the chapter IX. The last chapter summarizes the important conclusions drawn from the various investigations carried out on pure and copper layered ZnTe thin films.

Relevant references are given at the end of each chapter.
References


