CHAPTER I

INTRODUCTION
1.1. Introduction

The II-VI compound semiconductors arouse great practical interest owing to their unique properties including their high photosensitivity to electromagnetic and particulate radiation, high absorption coefficient and direct band gap corresponding to a wide spectrum from near ultra violet to the far infrared. This makes them very much useful in a wide variety of electronic and opto-electronic devices. By virtue of their ability to form solid solution it is possible to vary systematically the band gap energy, as for example Zn/Cd-Te/Se system from 1.45 to 2.7 eV and hence the spectral range of photosensitivity, emission characteristics etc. However, the utilization of the II-VI based devices on a commercial scale has been hampered, so far, by difficulties in obtaining single crystals of these compounds with controlled and reproducible properties. But, recently, thin films of cadmium chalcogenides have received much more attention for their applications in electro-optic devices, photoconductors, thin film transistors and photoelectrochemical (PEC) solar cells. Even though CdTe has an optimum band gap for solar cell applications, it is very unstable in PEC cells, which use polysulphide electrolytes, while CdSe is more stable than CdTe but its efficiency is limited by its band gap. The ternary alloys like CdZnTe and CdSeTe over come this difficulty. II-VI semiconductor compounds can be prepared in the form of thin films on large area substrates, developing desired solid solutions with suitable dopants for device applications. Cd$_{1-x}$Zn$_x$Te is a ternary IIB-VIA compound semiconductor, which is having promising applications in a variety of solid-state devices, such as, solar cells, photo detectors and light emitting diodes, as the band gap is expected to be direct and tunable in the region between 1.45 and 2.35 eV (for $x = 0$ and $x = 1$ respectively) [1-4].

A thin material created ab-initio by an atom / molecule / ion clusters of species by condensation process is defined as thin solid films. A thin film is two dimensional in its macroscopic appearance as its thickness is negligibly small. The two dimensional aspect (where the surface to volume ratio is large) makes it altogether different from the bulk
counter part (where volume to surface ratio is large). It is possible to prepare thin films with required properties like, electrical, optical and structural properties which are found to determine by the parameters, such as, rate of deposition, substrate temperature, purity of the charge, thickness of the film, addition of impurities, ambient temperature and pressure and on residual gases. Thin film science and technology finds applications in many fields like optical coatings, superconductors, memory devices, tribology, space applications, biomedical sensors, strain gauges, etc. Though materials have been prepared in the form of thin films almost a century, the technology for specific applications available only for last three decades.

By the introduction of selective dopant elements into the semiconductor compounds the physical properties can be tailored, as we desire, which is the most appreciable one for the use of the material in electronic industry. Ion implantation is becoming an increasingly important technique for introducing one material into the near surface regions of another material and it has several advantages over the more conventional techniques [5]. Ion implantation provides an alternative method of introducing dopant atoms into the lattice. A vital aspect of the application of ion implantation to semiconductor technology, in contrast to diffusion process, is that the number of implanted ions can be controlled by the external system, rather than by the physical properties of the substrate. For example, dopants can be implanted at temperatures at which normal diffusion is completely negligible. Also, the dopant concentration is not limited by ordinary solubility considerations, and so a much wider variety of dopant elements may be used. Thus, one predominant application of ion implantation is that it might allow the investigation of the properties of species, which can not be introduced into semiconductor materials by conventional methods. In general, the properties of semiconductor compounds are much sensitive to the presence of lattice defects and impurities in controlled manner. Ion implantation into compound semiconductors has been investigated with increasing frequency in recent years [6]. Even though much works has been done on ion implantation into II-VI semiconductors, to the author’s best knowledge no report is available on ion implantation into CdZnTe both in thin film and bulk form.
Surface passivation is a key technology to improve the performance of the Hg$_{1-y}$Cd$_y$Te (MCT) infrared detectors. For the past two decades much work has been performed on passivation layers [7,8]. It begins with native oxide and native sulfide layers, and in the last decade CdTe was tremendously used for surface passivation due to its nearly lattice matching property with the MCT substrate. To get the exact lattice matching and better interfacial properties of the system Cd$_{0.96}$Zn$_{0.04}$Te is now being used. It gives the exact lattice matching with Hg$_{1-y}$Cd$_y$Te for all values of ‘y’.

The present thesis aims at studying the physical properties of vacuum evaporated Cd$_{0.96}$Zn$_{0.04}$Te thin films. The prepared Cd$_{0.96}$Zn$_{0.04}$Te thin films are characterized using variety of techniques to determine their structural, optical, electrical and opto-electronic properties. The effects of boron ion implantation on the structural and optical properties of the films are also analyzed. The current-voltage and capacitance-voltage properties of the Cd$_{0.96}$Zn$_{0.04}$Te passivated Hg$_{0.78}$Cd$_{0.22}$Te MIS structures are also carried out in the present investigation.

1.2. Cd$_{1-x}$Zn$_x$Te thin films

Cd$_{1-x}$Zn$_x$Te is a ternary II-B-VIA compound semiconductor, which is having promising applications in a variety of solid-state devices, such as, solar cells, photo detectors and light emitting diodes, as the band gap is expected to be direct and tunable in the region between 1.45 and 2.35 eV (for x = 0 and x = 1 respectively) [1-4]. Cd$_{1-x}$Zn$_x$Te is used in optical memory devices, X-ray and gamma ray detectors [9-13]. Cd$_{1-x}$Zn$_x$Te material with a band gap of 1.65 – 1.75 eV is especially attractive for use in high efficient tandem solar cell structures [14-19]. This material is also attractive for non-linear optical devices [20]. Though much work has been published on the properties of bulk Cd$_{1-x}$Zn$_x$Te, very limited information is available on Cd$_{1-x}$Zn$_x$Te thin films [21-24]. Cd$_{1-x}$Zn$_x$Te thin films have a very good transmittance in the IR region [25]. Normally the as prepared Cd$_{1-x}$Zn$_x$Te films are p-type with a typical carrier concentration in the range of $10^{16}$ to $10^{17}$ cm$^{-3}$ and have a mobility of 100 cm$^2$V$^{-1}$s$^{-1}$ [26]. Thin film solar cells based on Cd$_{1-x}$Zn$_x$Te have received much attention due to economic reasons and ease of fabrication of large area thin film devices.
Cd_{1-x}Zn_{x}Te thin films have been deposited by employing various techniques, such as, two source vacuum evaporation (TSVE) [27], two stage vacuum evaporation [28,29], closed space vapour transport (CSVT) [30], hot wall epitaxy (HWE) [31], metalorganic chemical vapour deposition (MOCVD) [32], molecular beam epitaxy (MBE) [16] pulsed laser deposition (PLD) [33,34] and vacuum evaporation [35-38]. Each technique produces thin films with different properties, which would be optimized for the particular application of the thin film. Among the various techniques mentioned above, vacuum evaporation is a well-established technique and is very much suitable for preparing large area thin films. It is possible to prepare uniform films with good adherence to the substrate surface and reproducibility by this technique. The films can be deposited with uniform stoichiometry. The simple method of deposition, good reproducibility and good electro-optical properties makes this technique particularly suitable for the low temperature deposition of Cd_{1-x}Zn_{x}Te thin films for use as windows in heterojunction solar cells or photodetectors. The development of low cost solar based on Cd_{1-x}Zn_{x}Te depends on the exploitation of thin films and thus Cd_{1-x}Zn_{x}Te thin films obtained under various conditions, requires comprehensive structural, optical, electrical and opto-electronic characterization. There are only limited reports available on the properties of Cd_{1-x}Zn_{x}Te thin films deposited by single source vacuum evaporation and also consistent results have not been arrived. In particular, not much work has been done for the Cd_{0.96}Zn_{0.04}Te thin films, which is having more technological applications.

It is known that the vacuum evaporated Cd_{1-x}Zn_{x}Te thin films are polycrystalline and exhibit zinc blende structure [36,38,39]. Also the band gap of the alloy system varies with the zinc composition in the alloy. The band gap of the Cd_{1-x}Zn_{x}Te thin films can be varied from 1.45 eV (CdTe) to 2.35 eV (ZnTe), by varying the 'x' value.

Prasada Rao et al. [40] have determined the structural and optical parameters of the two source vacuum evaporated Cd_{1-x}Zn_{x}Te thin films. They found that the lattice parameters, such as, lattice constant, grain size, etc., are varying with the Zn composition in the films. Also they demonstrated the variation of the structural and optical parameters with annealing temperature and observed the direct allowed band gap as 1.51 eV for Cd_{1-x}Zn_{x}Te (x = 0.04) thin films.
Samantha et al. [41] studied the structural and optical parameters of the vacuum evaporated Cd\(_{1-x}\)Zn\(_x\)Te (0 < x < 1) thin films by X-ray diffraction and optical transmittance measurements and they have also mentioned the preparation method for the Cd\(_{1-x}\)Zn\(_x\)Te alloy system. They studied the variation of the structural and optical properties of the Cd\(_{1-x}\)Zn\(_x\)Te thin films with thickness of the films and with substrate temperature. Also they checked for the stoichiometry of the films with substrate temperature. The optical band gaps of the Cd\(_{0.25}\)Zn\(_{0.75}\)Te thin films vary between 1.46 eV to 1.52 eV with substrate temperature and demonstrated the wavelength dependence of refractive index ‘n’. The refractive index value was found to decrease with increase in wavelength.

Guptha et al. [42] studied the electrical and optical properties of undoped and copper-doped Cd\(_{1-x}\)Zn\(_x\)Te thin films prepared by two-zone hot-wall technique. Copper doped films showed an indirect transition at ~ 1.54 eV. It was observed that the grain-boundary scattering played an important role on the electron transport properties of the films. Increased doping dose culminated in segregation of dopant at the grain boundaries. The grains were partially depleted with filled traps and the trap states lay below the Fermi level.

Samantha et al. [35] studied the mechanism of anomalous photovoltage in Cd\(_{0.8}\)Zn\(_{0.2}\)Te thin films and explained on the basis of the formation of junctions at the grain boundaries and the surface band bending. The role of atmospheric oxygen on the surface space charge and indirectly on photovoltage was demonstrated. The change of polarity with ambient temperature was explained, as was the combined effect of the two models.

Chatopadhyay et al. [28] have studied the optical properties of two stage vacuum evaporated Cd\(_{1-x}\)Zn\(_x\)Te (0.1 < x < 0.7) thin films. They reported the variation of refractive index and the extinction coefficient for the films with composition and photon energy. They observed the non-linear behaviour of band gap with zinc content.

Shao et al. [43] prepared the Cd\(_{1-x}\)Zn\(_x\)Te thin films by simultaneous evaporation method. They evaporated CdTe and ZnTe simultaneously to get the desired solid solution and found that the structural and optical parameters are varying with the Zn composition.
Samantha et al. [44] explained the anomalous photovoltage in polycrystalline Cd$_{0.25}$Zn$_{0.75}$Te thin films prepared by vacuum evaporation. The effect was explained as a combined effect of mainly p-p$^+$ junctions at the grain boundaries and surface band bending apart from other factors. Also they developed a new method to enhance the photovoltage by placing a fine mesh in front of the substrate during the film deposition and explained the enhancement of photovoltage with the help of a trap-induced space-charge model.

Franc et al. [45] have studied the diffusion lengths of minority carriers in Cd$_{1-x}$Zn$_x$Te (x ~ 0.04) single crystals produced by the vertical gradient freezing method. Electron beam induced current (EBIC) images in the scanning electron microscope were used for the evaluation of minority carrier diffusion lengths at 300 K in different samples.

Bakr [37] studied the effect of annealing on Zinc diffused CdTe thin films prepared by vacuum evaporation technique. He showed that during thermal annealing process at 100$^\circ$ C and after 30 min, a thin layer of CdZnTe mixed structure have been formed on the top of CdTe films with variable band gap between 1.74 and 2.05 eV. The formation of the mixed structure was attributed to the diffusion process of Zn atom to the top surface of CdTe films.

Ashour et al. [46] have studied the thermal effect on structural properties of evaporated CdTe films during and after deposition. CdTe films have been deposited by vacuum evaporation at different substrate temperature and annealed at 300$^\circ$ C for 2 hours. They observed a decrease in FWHM of the (111) peak with both substrate temperature and annealing. Also the grain size of the films and the internal microstrain were found to increase with increase in substrate temperature.

The optical properties of vacuum evaporated CdTe and ZnTe thin films have been studied by many workers [47-49]. From the reports we can found that the band gap value of CdTe and ZnTe were 1.45 eV and 2.35 eV respectively.

The influence of crystalline quality on the thermal, optical and structural properties of Cd$_{1-x}$Zn$_x$Te for low zinc concentration was reported by Rodriguez et al. [50]. They studied the XRD and PL studies on Cd$_{1-x}$Zn$_x$Te single crystals with low ‘x’ values (x = 0.08).
Tobenas et al. [51] reported the growth of Cd$_{1-x}$Zn$_x$Te epitaxial layers by isothermal closed space sublimation (ICSS). They confirmed the epitaxial quality of the films by X-ray and transmission electron diffraction patterns. The influence of growth parameters on the composition and the thickness of the films were discussed.

Cardona [52] studied the fundamental reflectivity spectrum of several II-VI semiconductors (like CeTe, ZnTe, HgTe, HgSe and ZnSe) and compared the reflectivity spectrum of the group VI semiconductors. A general feature of these spectra was the presence of two peaks within the fundamental absorption region. The lower energy peak, which corresponds to a maximum in the refractive index, can be splitted into a doublet. This peak was probably due to direct transition between the valence band extrema in the (111) direction at the edge of the Brillouin zone (L point) and the corresponding conduction band minima. The splitting of this peak corresponds to the spin orbit splitting of the valence band extrema (L$_3$). The second peak corresponds to a maximum in the combined density of states for the transitions.

Spectroscopic ellipsometry has been widely used to determine the optical constants of II-VI semiconductors. Optical constants of Zn$_{1-x}$Cd$_x$Te ternary alloys have been studied by Adachi and Kimura [53]. The pseudodielectric-function spectra of the Zn$_{1-x}$Cd$_x$Te crystals have been recorded by a spectroscopic ellipsometer in the 1.1 - 5.6 eV photon energy range at room temperature. They observed E$_0$, E$_0$+$\Delta_0$, E$_1$, E$_1$+$\Delta_1$ and E$_2$ critical points which arose due to the interband transitions.

The optical constants of the Cd$_{1-x}$Zn$_x$Te (0 < x < 1) films were studied by Prasada Rao et al. [39,40]. They observed that the films exhibited polycrystalline nature with zinc blende structure and the lattice constant ‘a’ varied between 6.484 – 6.104 Å. The SE spectra for the optical constants showed three peaks corresponding to E$_1$, E$_1$+$\Delta_1$ and E$_2$ structures of the interband transition.

Sadao Adachi and co-workers have studied the numerical derivative analysis of the pseudodielectric-function of CdTe and ZnTe [54,55]. They observed E$_0$, E$_0$+$\Delta_0$, E$_1$, E$_1$+$\Delta_1$ and E$_2$ critical points for the CdTe crystals and E$_0$, E$_1$, E$_1$+$\Delta_1$ and E$_2$ critical points for the ZnTe crystals. Even though many reports are available on the structural and
optical properties of the Cd$_{1-x}$Zn$_x$Te ($0 < x < 1$) thin films, not many reports are available on the Cd$_{0.96}$Zn$_{0.04}$Te thin films prepared by vacuum evaporation.

Raman scattering studies have been performed by several workers on the CdTe and CdZnTe alloy systems. Aydinli et al. [33] have studied the structural, optical and Raman scattering studies of the Cd$_{1-x}$Zn$_x$Te ($0 < x < 1$) thin films prepared by vacuum evaporation. They found that ~1Å/pulse deposition will give good stoichiometric films. In the Raman spectra of the films they have observed two-mode vibrations. Also the LO and TO peak positions were found to shift with zinc composition.

Olego et al. [56] used Raman scattering measurements to investigate the lattice-dynamic properties of Cd$_{1-x}$Zn$_x$Te grown by MBE on GaAs substrates. The first-order Raman spectra for the ternary samples show two sets of longitudinal- and transverse-optical (LO, TO) modes, which arise from CdTe- and ZnTe- like vibrations. They established empirical correlation between the behaviours of the line-shapes and the magnitude of LO-TO splitting. Such a correlation, which appears to be a general characteristic of two-mode alloy semiconductors, provides supportive experimental evidence for the discrete-continuum interaction model.

Perkowitz et al. [57] demonstrated the longitudinal-optic and transverse-optic (LO and TO) phonons in bulk Cd$_{1-x}$Zn$_x$Te ($x = 0.005 - 1$) at low temperature (20 K). They confirmed that, within a two-mode model, both the CdTe- and ZnTe like TO-mode frequencies increases with ‘x’, unlike any other II-VI ternary compound with known phonon modes. The ZnTe-like TO frequency at very low ‘x’ is near to the prediction from impurity-mode theory.

Oh et al. [58] grown lattice-mismatched Cd$_{1-x}$Zn$_x$Te epilayers with various Cd mole fractions on GaAs substrates by molecular beam epitaxy. The surface and stoichiometry of the Cd$_{1-x}$Zn$_x$Te films were investigated by X-ray photoelectron spectroscopy and Auger electron spectroscopy measurements. Raman spectra showed that the frequency of the longitudinal mode decreases and the Cd mole fraction increased, which was caused by the decrease of the mode oscillator strength. Photoluminescencence spectra showed that the FWHM corresponding to the bound exciton line increased as the Cd mole fraction increased, which originates from the alloy broadening due to the compositional fluctuations of the cations.
Levy et al. [59,60] studied the Raman scattering and photoluminescence studies of the Cd$_{1-x}$Zn$_x$Te ($0 < x < 1$) epilayers prepared by MOCVD. The Raman spectra of the samples recorded at 70 K exhibited LO and TO peaks. And in the PL spectrum they observed lines due to the recombination of free excitons in their ground state level, and no emissions associated with structural and/or deep impurity levels.

Cohen et al. [61] studied the Raman scattering and photoluminescence spectra of CdTe, Cd$_{0.97}$Zn$_{0.03}$Te. In the Raman spectra LO and TO mode vibrations have been observed. In the PL spectra the main spectral features are due to free excitons (polaritons), excitons bound to neutral donars ($D^0,X$), excitons bound to neutral acceptors ($A^0,X$) and a shallow bound-exciton band unidentified origin (S-band).

Olego et al. [62] studied the opto-electronic (PL) properties of the Cd$_{1-x}$Zn$_x$Te films grown by molecular beam epitaxy on GaAs substrates. A new equation to determine the optical band gap and the composition was developed. The PL line shapes pointed out the high quality of the novel ternary system.

Gonzales-Hernandez et al. [30] reported the PL, XRD and SEM analysis of Cd$_{1-x}$Zn$_x$Te solid solution films prepared by closed space vacuum transport method. They observed a good crystalline quality of the films from the emission lines of the PL spectrum.

Lee and Giles [63] analyzed the low temperature photoluminescence from bulk CdTe and Cd$_{0.967}$Zn$_{0.033}$Te. The energy difference between the X and X-1LO bands in CdTe was $20.7 \pm 0.01$ meV. The splitting between the transverse- and longitudinal-polariton components was $\sim 0.5$ meV in CdTe and $\sim 1.0$ meV in Cd$_{0.967}$Zn$_{0.033}$Te. Above-band-gap PL due to phonon-absorption processes was observed from the samples, which indicate that the PL was related to bound exciton-phonon quasi-particles. Emission above $E_g$ related to (e,h) transitions was observed.

Gonzalaez-Hernandez et al. [64] prepared high resistivity intrinsic Cd$_{1-x}$Zn$_x$Te single crystals and studied the PL properties. The resistivity of the Cd$_{1-x}$Zn$_x$Te was found to be of the order of $10^8 \, \Omega \, \text{cm}$. The PL spectra indicate a high crystalline perfection for the samples in the compositional range investigated. As a result of that, the PL spectra showed lines due to free excitons in their ground and first excited state levels, and no emission associated with structural and/or deep impurity levels.
From the literature survey, it is clear that not much work has been done on the Cd$_{0.96}$Zn$_{0.04}$Te thin films. Hence our present work aims at characterization of Cd$_{0.96}$Zn$_{0.04}$Te thin films prepared by vacuum evaporation.

1.3. Ion implantation

Ion implantation is a technique used to introduce impurities into solids in a uniform and reliable manner [5]. This technique makes use of ions with energy in the range of keV to a few MeV, which bombard the target. The ions slow down due to the interaction with the solid target and finally come to rest at a depth normally referred to as the "Range" ($R_p$). The concentration and penetration depth of the implanted impurities can be controlled by controlling the beam current, time of implantation and energy of the ion beam. Being a non-equilibrium process, there are no solubility constraints and we can implant any type of ion species into any target. Ion implantation technology is mainly used in semiconductor technology, though it also finds applications in several other areas like surface modifications for improvement of hardness, wear and corrosion resistance etc. It is a key technology for the fabrication of doped layers in semiconductor microelectronic devices, which has several advantages over the conventional doping methods such as reproducibility, uniformity and good dopant profile control. The depth to which the ions penetrate into the semiconductor is mainly determined by the energy of the ion beam. This means that the junction depth can be accurately specified and easily reproduced by controlling the energy of the incident ions.

In general, ion implantation introduces considerable lattice disorder, which has a significant influence on the structural, optical, electrical and opto-electronic properties of the semiconductors. The defects produced during implantation are normally annealed out by suitable thermal treatments. Though radiation damage is often considered as an undesirable consequence of ion implantation process, there are situations where defects are deliberately introduced into semiconductors to tailor the electrical and optical properties.

The major features governing the successful exploitation of ion implantation are the range distribution of the implanted species, the amount and nature of the lattice disorder created, the location of the implanted species within the unit cell of the crystal.
and the electrical characteristics that result from the ion implantation and subsequent thermal annealing. Fig. 1.1 represents the ion implantation process.

**Fig. 1.1. Schematic representation of the ion implantation process**

One of the most important factors in ion implantation is the range (depth) of the implanted species. In recent years, a large amount of theoretical and experimental work has been devoted to the task of understanding the loss of energy process that governs the range distribution and it is now possible to predict accurately most of the factors involved. There are several computer simulations available to determine the range and stragglng of ions and the most popular among them being the transport of ions in matter (TRIM) program [65]. Other problems inherent in the use of implantation techniques arise
from the lattice disorder and radiation damage effects produced by the incident ion species. The radiation damage produced during implantation has a strong influence on the properties of the material. Increased optical absorption and shift of the absorption edge to lower energies and reduction in the sharpness of the absorption edge are normally observed during the implantation with energetic ions, which are caused by the lattice damage. The resistivity, carrier concentration, the mobility and the type of carriers are influenced by the implantation-induced damages. Ion implantation is used to convert the type of the carriers (n-type to p-type or vice-versa) in semiconductor materials like ZnSe, CdS and CuInSe$_2$. Post implantation annealing of the samples will remove the defects produced during implantation. The annealing involves rising the temperature of the material in order to provide thermal energy to assist the recovery of the damaged material.

1.4. Ion implantation in compound semiconductors

Ion implantation is a technically qualitative process, which can be used to introduce controlled amounts of impurities into a layer adjacent to a semiconductor surface. Cd$_{1-x}$Zn$_x$Te (CZT) is a technologically important IIB-VIA semiconductor, which has potential applications in a variety of opto-electronic devices. Ion implantation into Cd$_{1-x}$Zn$_x$Te thin films with energetic ions cause lattice damage, which affects the structural, optical and electrical properties. When ion beam technology is used, problems arise due to the formation of radiation defects and their effects on the defect-sensitive properties of the bombarded material. Knowing the mechanism of defect formation and accumulation in Cd$_{1-x}$Zn$_x$Te thin films under ion bombardment is necessary in order to forecast the properties of ion-implanted layers and to develop by means of controlling these properties. To our best knowledge, no reports are available on the ion implantation into Cd$_{1-x}$Zn$_x$Te both in thin film and bulk form. In this section, a review of literature about the ion implantation effects on the II-VI and III-V materials has been discussed.

The effect of irradiation-induced disorder on the optical absorption spectra of CdS thin films was studied by Narayanan et al. [66]. The implantation of A$^+$ ions caused a decrease in the optical band gap of the CdS films and on thermal annealing the defects produced were annealed out.
Narayanan et al. [67] studied the effect of A⁺ implantation by XRD, Raman scattering and optical absorption techniques. He observed a decrease in the intensity or the predominant peak in the XRD spectra. The intensity of the Raman peak decreases and the FWHM increases due to implantation dose. The optical band gap of the CdS was found to decrease with increase of implantation dose, which may be due to the disorder produced by ion implantation.

Narayanan et al. [68] studied the Raman scattering spectra of A⁺ implanted CdS films. They observed an increase of the relative intensity of the Raman peak with implantation dose, which may be due to the surface roughness introduced on ion implantation.

Oldekop et al. [69] implanted Boron (¹²B) into CdTe and studied the effect of implantation by β-NMR Larmour resonance method. Wagner et al. [70] implanted Sb into CdTe at various doses ranging from 10¹²-10¹⁴ ions/cm² at 100 k eV and studied the effect of implantation over the photoluminescence properties of the CdTe films. They concluded that the implantation at 77 K creates Cd vacancies, and probably other defects, which act as non-radiative centers.

Meikle and Thompson [71] implanted Ar⁺ and As⁺ of 60 k eV into n-type CdTe and studied the I-V and photoluminescence studies. Also they found the good variation in the electrical conduction and PL properties on ion implantation. As⁺ implant converts the n-type CdTe to p-type. They introduced rapid thermal annealing process to anneal out the defects formed due to implantation.

James et al. [72] studied the effect of Copper ion implantation into CdTe. They observed an increase of resistivity due to ion implantation. The deep level impurities had been identified with photoluminescence measurements. A deep level at 0.6 eV was seen in the photoinduced transient current spectra from the Cu implanted samples.

Kernocker et al. [73] have implanted Fe⁺ into CdTe and studied the effect of ion implantation by photoluminescence measurements. In the 5 K PL spectra of Fe⁺ implanted and subsequently annealed CdTe samples two emission bands, peaked at 1.03 eV and 1.13 eV, respectively, appear. The intensity of these lines increases linearly with the implanted Fe⁺ dose. By varying the wavelength of the exciting laser radiation, they found that these lines are emitted from the implanted surface region only. Time resolved photoluminescence experiments reveal the time constant of the emission process.
Bowman et al. [74] have studied the optical and structural characterization of heavily Boron ion implanted CdTe. B⁺ ions with different energy range were implanted in the range of $10^{16}$ ions/cm². The degradation of crystallinity following the Boron implants was clearly evident by XRD, Raman and PL measurements. On annealing the implanted samples, the crystallinity improves.

Kalish et al. [75] have studied the effect of thermal annealing on Indium implanted CdTe. Annealing treatment to the implanted samples improves the crystalline properties of the samples.

Molva et al. [76] reported the photoluminescence studies on N⁺, P⁺ and As⁺ implanted CdTe crystals. After appropriate low temperature annealing, the samples have been studied with high resolution PL technique, and with a tunable dye laser as the excitation source. A chemical doping effect by the acceptors N, P and As on tellurium site, has been evidenced. The bound exciton lines, the two-hole transitions, the donor acceptor pair bands and the free electron-neutral acceptor transitions have been identified. The ground states of the acceptors N, P and As are respectively at 56.0 meV, 68.2 meV and 92.0 meV from the valence band.

Romeo et al. [77] have doped Sb into ZnTe thin films and studied the electrical properties. They obtained good films with desired electrical and optical properties of the ZnTe films with Sb doping.

Norris studied [78] the origin of the 1.59 eV luminescence in ZnTe and the nature of the postrange defects from ion implantation. The 1.59 eV deep center luminescence in ZnTe was attributed to a V_Zn donor complex based on the results of the heat treatment, donor doping and radiation experiments. They also found that the properties of the ZnTe were improved on thermal annealing.

Jaroszewicz et al. [79] studied the role of ion implantation for fabrication of p-n junctions with modified silicon surface for photovoltaic devices. For that they have used $^{31}$P⁺ ions and observed the surface modifications caused by implantation, which enhance the junction performance.

Biasse et al. [80] implanted 100 keV B⁺ ions to form p⁺-n junction in silicon. They found the variation of the sheet resistance with respect to the implantation dose. Also the variation of junction depth with implantation dose was observed.
Boron ion implants were performed by Kao and Sigmon for HgCdTe (MCT) [81]. They used RBS to study the composition analysis of the MCT wafers prior and after implantation and SIMS was used to confirm the depth profiling of the implanted species. They observed an increase in the Hall mobility with increase in implantation dose and on thermal annealing the Hall mobility has been increased further.

Destefanis have reported [82] the effect of ion implantation on the HgCdTe. The general properties of the boron ion implanted MCT were described in detail. On Boron ion implantation he observed a saturation of carrier concentration of defects creation and the junction migration in the MCT. The annealing process was used to improve the quality of the MCT properties.

Conway et al. [83] have implanted $^{11}$B$^+$ into epitaxial HgCdTe held at 77 K. They studied the effect of ion implantation with Rutherford backscattering and ion channeling. An n-p junction was observed at a depth of 5.5 μm by electron beam induced current (EBIC) method. A diode was fabricated on the layer exhibited a very sharp I-V curve with reverse breakdown occurring at 12 V and an $R_0A$ of $> 10^7 \ Ω\ cm^2$ at 77 K.

Bublac et al. [84] have explored the characteristics of ion implanted HgCdTe epitaxial layers. The implant induced junction depth has been found to be controllable and stable under a range of annealing conditions. Differential capacitance measurements showed that the carrier concentration in the junction region was 10-100 times lower than the as-grown acceptor concentration in the base material.

Wu et al. [85] investigated the effect of implantation and annealing temperatures on implantation induced damage in HgCdTe. Rutherford backscattering spectrometry was used to study the surface condition and distribution of implantation induced defects in the crystal. Secondary ion mass spectroscopy (SIMS) was used to determine the implanted Boron profiles. The migration and depth distribution of defects under various thermal annealing conditions in HgCdTe implanted at room temperature and at 77 K were described.

Baars et al [86] have studied the effect of Boron ion implantation into HgCdTe. Boron was implanted in p-type Hg$_{1-x}$Cd$_x$Te ($0.23 < x < 0.28$). The implantations were carried out using fluences between $10^{13}$ to $10^{16}$ B$^+$ ions/cm$^2$ and the ion energies of 120 and 350 keV with the samples either at room temperature or at 80 K. Electrical and
optical studies have been carried out after implantation and 150° C anneal. After the implantation and annealing process the samples showed n-type conduction.

Cotton and Wilson [87] studied the effect of ion implantation on deep electron traps in Hg$_{0.7}$Cd$_{0.3}$Te by deep level transient spectroscopy (DLTS). The ion implantation process was used to create n$^+$ on p junctions of photovoltaic detectors in HgCdTe. From the DLTS study they found a new trapping center at -0.19 eV, which may be attributed to implantation, induced damage.

Schaake [88] studied damages caused by B$^+$ and As$^+$ implantations. On higher doses ($10^{15}$ ions/cm$^2$) dislocation loops and a small density of vacancy-type defects were also observed. At higher energy implantations (200 keV) dislocation lines were also observed which may cause a reduction in the device performance.

In the present investigation, mass analyzed Boron ions ($^{10}$B$^+$) were implanted into Cd$_{0.96}$Zn$_{0.04}$Te thin films and the effect of ion implantation was studied by XRD, surface roughness, Raman scattering and optical transmission measurements.

1.5. Surface Passivation

The characteristics of semiconductor devices, in particular, narrow-band-gap semiconductors, are largely governed by the properties of the semiconductor surface [89-91]. Mercury Cadmium Telluride (MCT) is widely used as a material for infrared detection. Nevertheless, the weakness of the Hg-Te bonds, which tends to be weakened even more due to the presence of Cd-Te bonds, is often a source of problem. Therefore, the surface of semiconductor devices based on this material is passivated [7,92] in order to stabilize the surface against chemical, randomly induced changes, as well as to control the surface recombination process and related noise [93,94]. In relation to that, the interface properties are very important in the fabrication of heterostructures, which are applied in metal-insulator-semiconductor (MIS) devices [8]. HgCdTe surface passivation is complex because of the compound nature of the semiconductor, the difference in the chemical properties of the constituents and also due to the tendency of electrically active defects to form in the interface region during the passivating process. In addition, due to the extreme temperature sensitivity of bare HgCdTe surface, passivation treatments and deposition processes are limited to near room temperature. The important requirements of
a good passivating layer are (i) it should have low fixed charge density and thus low surface recombination velocity, (ii) it should have stable and well controlled interfacial electrical properties, (iii) should protect the MCT surface both physically and chemically and (iv) should have good adhesion to the MCT surface and must exhibit excellent transmission in the relevant spectral region.

In the early stage of the opto-electronic devices, the passivating layers were anodic oxides obtained by anodic [95], chemical or photochemical oxidation [96,97]. In the course of the development of epitaxial methods, such as MBE or MOCVD, it turned out that II-VI materials show passivating properties much better than the oxides [98-100], due to their properties, such as, transparency in infrared, band gap width, good adhesion and above all good adjustment of the lattice constants.

Juang et al. [101] studied the current-voltage and dynamic resistance-voltage characteristics of Hg$_{1-x}$Cd$_x$Te (x = 0.22) p-n junction photodiodes passivated with ZnS/CdS layers. They studied the mechanisms of surface leakage currents in the device and also modeled the tunneling current mechanism of n$^+$-p Hg$_{1-y}$Cd$_y$Te photodiode.

The surface leakage current analysis of ion implanted ZnS passivated n-on-p HgCdTe diodes in weak inversion was studied by Kim et al. [102]. They developed the surface leakage current model to explain R$_0$/A value change with the fixed charge density when the surface is in weak inversion.

Nimirovsky et al. [103] studied the surface, optical and electrical properties of p-type HgCdTe passivated with native sulfides (ZnS and CdS). They got good interfacial properties with the native sulfide passivated HgCdTe. The properties of the interface between HgCdTe and its native sulfide suggested potential applications for improving the surface passivation of photovoltaic diodes implanted on p-HgCdTe.

Nimirovsky et al. [104] reported the CdTe epilayers grown by MOCVD on bulk HgCdTe crystals grown by the traveling heater method (THM). The CdTe layer shows nearly lattice matching with Hg$_{1-y}$Cd$_y$Te and have a good adhesion to the substrate surface. The electrical properties are studied by capacitance-voltage measurements. Also they suggested that the CdZnTe (Zn = 4%) could provide even superior passivation for Hg$_{1-y}$Cd$_y$Te (y = 0.22), because of the perfect lattice matching between the epilayer and the substrate and because of the larger band gap of CdZnTe.
Bubulac et al. [105] studied the physical and chemical structure of the CdTe films using SIMS and AFM and demonstrated the usefulness of these analytical techniques in determining the characteristics of CdTe passivation films deposited by different techniques on HgCdTe.

Ariel et al. [106] reported the electrical and structural properties of epitaxial CdTe/HgCdTe interface. Two types of layers were investigated. One was grown directly, in-situ immediately following the growth of HgCdTe. The second type of CdTe was grown indirectly, on top of the previously grown epitaxial HgCdTe samples. Electrical properties of the CdTe/HgCdTe heterostructures were determined by C-V characterization. They concluded that the directly grown CdTe on HgCdTe as the better passivating layer than that of the indirectly grown CdTe.

Ariel et al. [107] investigated the epitaxial CdTe/Hgo.775Cd0.225Te heterojunctions by C-V profiling. The observed dependence of the C-V measurements on temperature was caused by either interface traps or carrier inversion at the CdTe/HgCdTe interface.

Lee et al. [108] developed a new surface treatment method for improving the interface characteristics of CdTe/HgCdTe heterostructure. The new surface treatment resulted in reproducible improvements in C-V characteristics, such as, low fixed charge and slow surface state densities. The improvements may be due to the surface smoothing function of the new treatment.

Agnihothri et al. [109] reported the photon-induced modifications in CdTe/HgCdTe heterostructure interfaces. The CdTe/HgCdTe heterostructures were subjected to pre and post-annealing. The C-V measurements showed that the pre and post-annealing indeed played an important role in reducing the defects and interface states. The electrical properties of the interface are drastically influenced by the CdTe growth temperature as well as the pre and post-treatments.

Lee et al. [110,111] used CdZnTe thin films as a passivating layer to HgCdTe. They deposited Cd0.96Zn0.04Te layers as a passivation layer to Hg1-yCdTe (y = 0.21 – 0.35). They found that the Cd0.96Zn0.04Te layers are lattice matched with Hg1-yCdTe. The Cd0.96Zn0.04Te layers had good adhesion to the substrate surface and are transparent to IR region. The In/ZnS/CdZnTe/HgCdTe MIS structure was fabricated and the C-V studies were carried out. From the C-V measurements they determined the flat band voltage, fast interface state density and the slow interface state density.
In the present investigation Cd$_{0.96}$Zn$_{0.04}$Te thin films were deposited onto thoroughly polished Hg$_{1-y}$Cd$_y$Te ($y = 0.22$) by thermal evaporation at room temperature and the C-V and I-V studies were carried out.

1.6. Scope of the thesis

The literature survey revealed that various deposition techniques, such as, two source vacuum evaporation, two-stage vacuum evaporation, hot wall epitaxy, molecular beam epitaxy, metalorganic chemical vapour deposition, pulsed laser deposition, vacuum evaporation have been employed for the preparation of polycrystalline Cd$_{1-x}$Zn$_x$Te thin films. Among these techniques, vacuum evaporation is a well-established technique and there are some reports available in the literature for the preparation of polycrystalline Cd$_{1-x}$Zn$_x$Te thin films and not much work has been done on the Cd$_{0.96}$Zn$_{0.04}$Te thin films. Hence in the present investigation, it is proposed to undertake systematic investigations on the vacuum evaporated polycrystalline Cd$_{0.96}$Zn$_{0.04}$Te thin films.

A thorough analysis of the effect of ion implantation in various semiconductors indicates that implantation is an ideal technique for the introduction of defects and impurities in a well-controlled manner in the materials. Even though much work has been done on the ion implantation effects on CdTe thin films, no reports are available for the ion implantation in Cd$_{1-x}$Zn$_x$Te both in bulk and thin film form. Hence in the present investigations, the effects of Boron ion ($^{10}$B$^+$) implantations on the structural and optical properties of Cd$_{0.96}$Zn$_{0.04}$Te thin films have been studied.

Surface passivation is a key technology to improve the performance of the HgCdTe IR detectors. Thorough literature survey was made and there are only a few reports available for surface passivation of HgCdTe by CdZnTe. Therefore, in the present investigation, vacuum evaporated Cd$_{0.96}$Zn$_{0.04}$Te thin films are used as the surface passivation layer to Hg$_{0.78}$Cd$_{0.22}$Te surface.

In the present work, polycrystalline Cd$_{0.96}$Zn$_{0.04}$Te thin films are prepared by vacuum evaporation and are annealed at different temperatures. The prepared films were implanted with mass analyzed Boron ions ($^{10}$B$^+$) and the effect of implantations is discussed in detail. The characterization of the prepared films by various techniques, such as, Rutherford backscattering spectrometry, energy dispersive analysis of X-rays, X-ray
diffraction, scanning electron microscopy, atomic force microscopy, optical transmittance, spectroscopic ellipsometry, Raman scattering and photoluminescence measurements are discussed in detail. The effect of ion implantation was analyzed by X-ray diffraction, roughness, Raman scattering and optical transmittance measurements. The Cd$_{0.96}$Zn$_{0.04}$Te thin films are deposited onto well-polished Hg$_{0.78}$Cd$_{0.22}$Te and the electrical properties are studied by C-V and I-V measurements.

1.7. Organization of the thesis

Chapter I is an introductory chapter to the material, Cd$_{0.96}$Zn$_{0.04}$Te, and it narrates the ion implantation technique used in the present work and about the surface passivation layer to HgCdTe. A detailed literature survey on Cd$_{1-x}$Zn$_x$Te thin films, ion implantation effects in semiconductors and on surface passivation are given.

Chapter II explains the experimental techniques used in the present investigation. It describes about the vacuum coating unit and low energy accelerator used in the present investigation. The experimental techniques includes Rutherford backscattering spectrometry, X-ray diffraction, energy dispersive analysis of X-rays, scanning electron microscopy, atomic force microscopy, optical transmittance, spectroscopic ellipsometry, Raman scattering and photoluminescence measurements. Also the procedure used for cleaning the substrates is given in this chapter.

Chapter III deals with the preparation and characterization of polycrystalline Cd$_{0.96}$Zn$_{0.04}$Te thin films. The results obtained from RBS, EDAX, XRD, SEM, AFM, optical transmittance, spectroscopic ellipsometry, Raman scattering and photoluminescence studies are discussed.

Chapter IV deals with the effect of ion implantation on the properties of Cd$_{0.96}$Zn$_{0.04}$Te thin films. The implantation-induced effects are studied by using XRD, AFM, roughness, Raman scattering and optical transmittance measurements and Chapter V narrates the importance of the surface passivation layer to HgCdTe. The surface preparation methods are given in detail. The electrical studies, such as, C-V and I-V measurements of In/ZnS/CZT/MCT MIS structure are discussed.

The summary of the systematic investigations carried out on pure and Boron ion implanted Cd$_{0.96}$Zn$_{0.04}$Te thin films and the studies on surface passivated Hg$_{0.78}$Cd$_{0.22}$Te are presented in Chapter VI. The scope for the future plan of research in this area is also discussed.
1.8. List of publications

A part of the results presented in this thesis has been published in the form of following papers

International Journal Papers

1. Optical Constants of Vacuum Evaporated Cd$_{0.96}$Zn$_{0.04}$Te Thin Films measured by Spectroscopic Ellipsometry.
   M. Sridharan, Sa.K. Narayandass, D. Mangalaraj and Hee Chul Lee

2. Characterization of Vacuum Evaporated Polycrystalline Cd$_{0.96}$Zn$_{0.04}$Te Thin Films by XRD, Raman Scattering and Spectroscopic Ellipsometry.
   M. Sridharan, Sa.K. Narayandass, D. Mangalaraj and Hee Chul Lee
   Crystal Research and Technology 37(9) (2002) 964-975

3. Raman Scattering studies on B$^+$ Implanted Cd$_{0.96}$Zn$_{0.04}$Te Thin Films.
   M. Sridharan, Sa.K. Narayandass, D. Mangalaraj and Hee Chul Lee
   Vacuum (In Press)

4. Raman Scattering, Photoluminescence and Spectroscopic Ellipsometry Studies on Polycrystalline Cd$_{0.96}$Zn$_{0.04}$Te Thin Films.
   M. Sridharan, Sa.K. Narayandass, D. Mangalaraj and Hee Chul Lee
   Journal of Alloys and Compounds (In Press)

5. Studies on Polycrystalline Cd$_{0.96}$Zn$_{0.04}$Te Thin Films prepared by Vacuum Evaporation.
   M. Sridharan, Sa.K. Narayandass, D. Mangalaraj and Hee Chul Lee
   Vacuum (In Revision)

6. Effect of Boron Ion Implantation on the Structural and Optical Properties of Polycrystalline Cd$_{0.96}$Zn$_{0.04}$Te Thin Films.
   M. Sridharan, Sa.K. Narayandass, D. Mangalaraj and Hee Chul Lee
   Nuclear Instruments and Methods B (In Revision)

7. X-ray Diffraction and Raman Scattering studies on $^{10}$B$^+$ Implanted Cd$_{0.96}$Zn$_{0.04}$Te Thin Films prepared by Vacuum Evaporation.
   M. Sridharan, Sa.K. Narayandass, D. Mangalaraj and Hee Chul Lee
   Communicated to Journal of Materials Science: Materials in Electronics

8. Optical and opto-electronic properties of Polycrystalline Cd$_{0.96}$Zn$_{0.04}$Te Thin Films.
   M. Sridharan, Sa.K. Narayandass, D. Mangalaraj and Hee Chul Lee
   Communicated to Materials Chemistry and Physics
9. Structural, Optical and Raman Scattering studies on Vacuum Evaporated Cd$_{0.96}$Zn$_{0.04}$Te Thin Films.
   M. Sridharan, Sa.K. Narayandass, D. Mangalaraj and Hee Chul Lee
   Communicated to Optical Materials

10. Photoluminescence studies on Cd$_{0.96}$Zn$_{0.04}$Te thin films.
    M. Sridharan, Sa.K. Narayandass, D. Mangalaraj and Hee Chul Lee
    Communicated to Materials Letter.

International/National Conference/Symposium Papers:

1. Raman Scattering Studies on Boron ion Implanted Cd$_{0.96}$Zn$_{0.04}$Te thin films.
   IIT-2002, New Mexico, USA (Sep 2002)
   M. Sridharan, Sa.K. Narayandass, D. Mangalaraj and Hee Chul Lee

2. Studies on $^{10}$B$^+$ Implanted Cd$_{0.96}$Zn$_{0.04}$Te Thin Films prepared by vacuum evaporation.
   IBMM-2002, Kobe, Japan (Sep 2002)
   M. Sridharan, Sa.K. Narayandass, D. Mangalaraj and Hee Chul Lee

3. Spectroscopic Ellipsometry Studies on Boron Ion implanted Cd$_{0.96}$Zn$_{0.04}$Te Thin Films.
   M. Sridharan, Sa.K. Narayandass, D. Mangalaraj and Hee Chul Lee

4. Effect of implantation-induced disorder on the structural and optical properties of vacuum evaporated Cd$_{0.96}$Zn$_{0.04}$Te Thin Films.
   M. Sridharan, Sa.K. Narayandass, D. Mangalaraj and Hee Chul Lee

5. Opto-electronic properties of polycrystalline Cd$_{0.96}$Zn$_{0.04}$Te thin films.
   ACSSI-2002, Langkawi, Malaysia (Dec 2002 - accepted)
   M. Sridharan, Sa.K. Narayandass, D. Mangalaraj and Hee Chul Lee

6. Effect of implantation on the Structural and Optical properties of Cd$_{1-x}$Zn$_x$Te thin films.
   IWPSD-2001, New Delhi, India (Nov 2001)
   M. Sridharan, Sa.K. Narayandass, D. Mangalaraj and Hee Chul Lee

7. Optical properties of Cd$_{0.96}$Zn$_{0.04}$Te Thin Films.
   NACTTA-2002, Coimbatore, India (Feb 2002)
   M. Sridharan, Sa.K. Narayandass and D. Mangalaraj

8. Structural properties of Cd$_{0.96}$Zn$_{0.04}$Te Thin Films.
   NACTTA-2002, Coimbatore, India (Feb 2002)
   M. Sridharan, Sa.K. Narayandass and D. Mangalaraj

9. I-V and C-V characterization of In/p- Cd$_{1-x}$Zn$_x$Te/Si structures.
   IVSNS-1999, Indore, India (Nov 1999)
10. Temperature Dependence of optical properties of vacuum evaporated Cd$_{1-x}$Zn$_x$Te thin films.
NSRTMS-1999, Tirupathi, India (Nov 1999)
M. Sridharan, K. Prabakar, Sa.K. Narayandass, D. Mangalaraj and Vishnu Gopal

11. Some studies on thermally evaporated Cd$_{1-x}$Zn$_x$Te thin films.
IWPSD - 1999, New Delhi, India (Nov 1999)

12. Spectroscopic Ellipsometry studies on vacuum evaporated Cd$_{1-x}$Zn$_x$Te thin films.
ICMAT-2001, Singapore (July 2001)
References