Effect of Ar\(^+\) ion implantation on the properties of electrodeposited CdTe thin films

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Abstract. Semiconducting nanomaterials of II–VI groups are the key elements of continued technological approaches made in the field of optoelectronic, magnetic and photonic devices due to their size-dependent properties. Ion beams create changes in the material along their track; this not only exhibits excellent properties but also tailors new materials. This article reports the effect of Ar\(^+\) ion implantation on the properties of cadmium telluride thin films of about 80 nm thickness. The implantation parameters were adjusted based on computer-aided learning using SRIM (stopping and range of ions in matter) software. The CdTe thin films were deposited by electrodeposition method on ITO substrate. Thin films of CdTe are exposed to Ar\(^+\) ions with different fluencies of \(1 \times 10^{15}, 5 \times 10^{15} \) and \(1 \times 10^{16}\) ions \(\text{cm}^{-2}\) at Ion Beam Centre, Kurukshetra University, Kurukshetra, India. After implantation, the films were characterized using UV–visible spectroscopy, photoluminescence (PL) and a four-probe set-up with a programmable current–voltage (I–V) source metre. The scanning electron microscopy of pristine film showed smooth and uniform growth of sphere-shaped grains on substrate surface. From optical studies, the values of optical band gap for as-deposited and argon-ion-implanted thin films were calculated. It was found that values of optical band gap decreased with the increase in fluence of ion beam. From PL studies it was found that the intensity got increased with ion fluence. A considerable increase in current was noticed from I–V measurements with ion fluence after implantation. Different properties of pre- and post-implanted thin films are studied.

Keywords. Thin films; scanning electron microscopy; Ar\(^+\) ion beam; structural analysis; optical band gap; electrical properties.

1. Introduction

Nanostructured materials with small size and dimension exhibit unique and significantly improved physical, chemical and biological properties, phenomena and processes remarkable in comparison with their bulk counterparts, which demonstrate their great potential applications in many novel devices of the future. A major motivation to study II–VI semiconductor group materials is that they are direct-band-gap materials \([1,2]\) with high optical absorption and emission coefficients. Materials based on thin films are the basic elements of sustained technological advances; they possess various unique properties due to their quantum confinement effects. The preparation of materials into thin films allows easy realization into different types of devices. Smooth and high-quality compound-semiconductor-based thin films usually depend on the growth process, e.g., rate of deposition, substrate temperature, synthesis temperature and pH of the solution, etc., generally at the nanometre scale \([3]\). Over several years, the study of II–VI binary semiconductor compounds related to cadmium chalcogenide group (CdS, CdSe and CdTe) has been intensified as they are considered to be very significant materials for photovoltaic applications \([4]\). Among widely used semiconductors, cadmium telluride (CdTe) is a material under consideration, which is one of the most promising binary II–VI group compound semiconductor used as an absorber in solar photocells because of its high absorption coefficient (>\(10^5\) \(\text{cm}^{-1}\)) in the visible range of solar spectrum, and optimum direct energy band gap of 1.44 eV, which is near the optimum for photovoltaic solar energy conversion \([5]\). Based on only thin-film technology, it is possible to build complete photovoltaic devices, which serve as one of the best feature of this semiconductor and possess higher efficiencies of 16.5% than those fabricated from single-crystal materials \([6]\). Moreover, the material also has applications in gamma ray detectors and infrared detectors along with photo-electrochemical applications \([7,8]\). Other areas of nanocrystalline thin-film material applications are in laser materials, thermoelectric devices, sensors, light amplifiers, large-screen liquid crystal display, etc. \([9,10]\).

Thin CdTe films can be synthesized by various techniques such as close-space sublimation \([11]\), metal–organic chemical vapour deposition \([12]\), molecular beam epitaxy \([13]\), thermal-vacuum evaporation \([14]\), electro-chemical deposition \([15]\), etc. Among these methods, electrodeposition is a simple and attractive method with the benefits of low-cost
technology, environment-friendly nature, isothermal process, mainly controlled by electrical parameters such as precursors of electrolyte solution, deposition potential, which decides the film quality, composition and morphologies of the films.

By enhancing the p-type doping level from about $2 \times 10^{14}$ to more than $10^{17}$ cm$^{-3}$ in CdTe solar cells, conversion efficiencies of more than 20% have been achieved [16]. This doping could be done with group-I or group-V elements on a cadmium or tellurium site, respectively. However, problems in attaining adequate doping of wide-band-gap II–VI semiconductor materials, both p- and/or n-type, are the main impediments in their applications. As reported in [17], the solution to doping problem should be accomplished using non-equilibrium processes such as ion implantation. Ion implantation is an attractive method for doping CdTe, but generation of defects and accompanying damage due to radiation have to be taken into account. For instance, CSS-grown polycrystalline CdTe layers were implanted with phosphorous (group-V element) in order to obtain increased p-type doping close to back contact of CdTe-based solar cells [18]. Some authors studied the effect of Ar$^+$ ion implantation on thin films and reported ion-beam-induced grain growth and surface modification [19], implantation-induced structural modifications [20] and its impact on optical properties, particularly in gas sensing application [21]. As per literature, effect of Ar$^+$ ion irradiation on structural and optical properties of e-beam-evaporated CdTe thin films has been investigated, and considerable variation in structural parameters such as internal strain, crystallite size, etc., with high Ar$^+$ ion flux was found [22]. Also, formation of Cd metallic clusters and improvement in optical band gap and absorption coefficient has been reported from Ar$^{+}$- and N$^{+}$-ion-implanted CdS films [23]. It can be used to improve surface morphology of thin films [24], which plays an important role when they are used for applications. As regards the implantation technique, a suitable choice of experimental parameters such as type of ion species, energy, current and fluence allows determining the depth and remarkably affects the composition and shape of the modified nanostructure. It has diverse applications such as improving the electrical properties of semiconductors and the chemical or mechanical properties of alloys, metals and dielectrics. To the best of our knowledge, no study has been done on Ar$^+$ ion implantation effects on CdTe thin films deposited by electrodeposition route.

The present study is focused on the effect of Ar$^+$ implantation on the structural, optical and electrical properties of CdTe thin films of thickness about 80 nm.

2. Experimental

2.1 Synthesis of CdTe thin films

To prepare CdTe thin films, highly pure 3CdSO$_4$·8H$_2$O (99.9%) and TeO$_2$ (99.9%) purchased from Sigma Aldrich were used as cadmium and tellurium precursors, respectively. The films were deposited on transparent indium–tin oxide (ITO)-coated glass slides using a low-cost electrodeposition technique in aqueous solution. A conventional three-electrode set-up was employed, which consisted of saturated silver–silver chloride (Ag–AgCl) electrode as the reference electrode, an ITO-coated glass substrate as the working electrode and platinum wire as the counter-electrode for electrodeposition of CdTe-based semiconducting thin films. The electrodeposition was performed using a Biologic SP-240 potentiostat instrument. Among voltamperometric techniques, chronoamperometry is one in which a potential pulse is applied to the electrode and the current generated at the working electrode is recorded as a function of time. The potential applied for deposition is $-0.70$ V for a time period of 20 min and its current–time ($I$–$t$) response is shown in figure 1. The deposition process was carried out at high solution temperature (65–70°C). The conditions such as temperature, potential applied and pH were optimized by trials based on reported literature [25–27]. The electrolyte contained Cd$^{2+}$ ions from 0.3 M 3CdSO$_4$·8H$_2$O and a lower concentration of HTeO$_2^-$ ions from 0.7 mM TeO$_2$; in view of the low solubility of Te$^{4+}$ species in acidic bath [27].
precursor, the solution was adjusted to pH 1–2 using H2SO4. Before synthesis, the ITO substrates were ultrasonically cleaned with deionized water and acetone successively to remove additional impurities.

2.2 Argon implantation

Argon ion implantation of the CdTe thin films was carried out at Ion Beam Centre, Kurukshetra University, Kurukshetra, Haryana, India, for different fluencies of $1 \times 10^{15}, 5 \times 10^{15}$ and $1 \times 10^{16}$ ions cm$^{-2}$. The implantation of 80 keV Ar$^+$ ions in thin films was performed at the pressure of $10^{-6}$ Torr. The current was fixed at 0.94 $\mu$A cm$^{-2}$. Using SRIM (stopping and range of ions in matter)-2006 (version 2008.04) computer-based software the projectile range was found to be 51.9 nm, which is much smaller than the thickness of films (80 nm).

2.3 Characterization

The XRD patterns of pristine and Ar$^+$-ion-implanted CdTe thin films were analysed using a Rigaku Mini-Flex X-ray diffractometer and a Cu-K$\alpha$ radiation source operating at a wavelength ($\lambda$) of 1.54 Å at 30 kV, 15 mA and a scanning rate of 2° min$^{-1}$ for angles ($2\theta$) of 20–60°. The morphology of thin films was studied by JSM-6390 scanning electron microscopy (SEM). For SEM analysis, pristine samples were coated with gold palladium alloy to make films surface conducting in nature. Optical properties of samples were recorded using a UV–visible double-beam 550 spectrophotometer (Camspec) at room temperature. To investigate photoluminescence (PL) spectra of pristine and implanted samples, a SHIMADZU RF-530 Spectro fluorometer in the range of 700–900 nm was used. Electrical properties of all films were obtained using a Keithley 2400 series source metre and probe station. A surface profilometer was used to measure thickness of the samples.

3. Results and discussion

3.1 Morphology and thickness measurement

SEM is a convenient and versatile technique to investigate the microstructure of the films. A SEM image of CdTe thin film is shown in figure 2. The SEM pictures indicate that small particles are aggregated and form well-connected grains that are uniform in nature. The image also reveals that the films have homogeneous distribution of small grains and are free from crystal defects like cracks. The measured thickness of the thin-film samples is about 80 nm.

3.2 SRIM-TRIM calculation

To recognize the energy loss mechanism, ion range and distribution of the projectiles, SRIM-TRIM simulation was performed. Simulation parameters for the 80 keV Ar ion implantation like stopping powers ($S_e$ and $S_n$) and projected range were calculated. The range of argon ion was found to be 581 Å, which is much less than the 80 nm film thickness of thin film. Values of electronic ($S_e$) and nuclear ($S_n$) energy losses are, respectively, $2.865 \times 10^4$ and $5.615 \times 10^4$ eV Å$^{-1}$. Both the energy loss processes have values in the same range; hence contributions from both the processes are equivalent. As indicated by the TRIM simulation, a single Ar ion of this much energy can produce 741 displacements including 741 vacancies and no replacement collision before stopping as shown in figure 3a. Out of 80 keV energy of a single Ar ion, 32.6 keV energy produces ionization, 45.1 keV energy produces phonons and 2.24 keV energy creates damage in the target material as shown in figure 3b.

3.3 Structural properties

The X-ray diffraction (XRD) technique is employed to study structural details of the materials. This technique is used to analyse the formation of the nanocrystalline phases and determination of the average crystallite sizes. The phenomenon of XRD can be illustrated as a reflection of the incident beam from the lattice plane. The structural studies for both pristine and Ar$^+$-ion-implanted CdTe thin films were carried out using a Rigaku Mini-Flex X-ray diffractometer at a scanning rate of 2° min$^{-1}$ for angles ($2\theta$) of 20–60°. Crystalline structures for both pristine and Ar$^+$-ion-implanted CdTe thin films deposited on ITO substrate were characterized using XRD measurements as shown in figure 4. In all the patterns, reflections of CdTe were seen close to $2\theta = 23.90^\circ$, 27.85°, 31.93°, 34.68°, 40.19° and 47.70°. These peaks are in good agreement with the standard JCPDS XRD powder data file (Data file 893011), corresponding to the cubic phase of the CdTe. The appearance of well-defined and sharp structural peaks confirms the polycrystalline nature, and crystallinity of all samples is improved. No indication of the presence of any impurity phase could have been recorded after Ar$^+$
implantation, as no new peak was seen in the patterns. Also, there is no significant shifting in the peak position \((2\theta)\) of diffraction peaks in the pattern, which assures the stability of the cubic structure of the implanted CdTe thin films. Variation in the peak intensity is clearly visible. A change in the peak intensity after the implantation shows that implantation has affected the plane orientation, due to which intensity of some planes increases, and decrease for some other intensities takes place. Hence, here we can also say that some peaks intensity is increased at the expense of other reflections. Energy imparted by energetic ion to the host material leads to the plane orientation. The lattice vibration initiated by ionic particle helps the reorientation of these regions. The enhanced crystallinity and crystal quality of the films after exposure to the ions and increment in the peak intensity imply that implantation enlarges the crystallite size of the thin films. During implantation, the energy imparted to the target material by ion releases the strain between grains, which further increases the crystal quality. In this way, increase and decrease in the plane intensity take place on account of exposure to ions.

The average crystallite size \(D\) was calculated from the Debye–Scherer formula \([28]\). The average crystallite size was found to be 40 nm for the pristine film and 42, 44 and 52 nm for fluence of \(1 \times 10^{15}\), \(5 \times 10^{15}\) and \(1 \times 10^{16}\) ions cm\(^{-2}\), respectively, and the average lattice strain was found to be 0.004, 0.004, 0.004 and 0.003 at the respective doses. Clearly, the increase in size indicates that crystallinity of the material increases after implantation. This may be attributed to the coalescence of small grains by collapse of grain boundaries.

### 3.4 Optical properties

Optical absorption spectroscopy is the most conventionally used technique by which quantum effects in semiconducting nanostructures can be studied. Optical absorption analysis has been extensively proven to be an important and active tool in interpreting and exploring the increase or decrease of energy gap, and progress of discrete characteristics in the spectra can be revealed. Thus, study of the optical properties of the materials is important due to the capability of the technique to give information on the electronic band structures, localized states, trapping levels and electronic transition. From the absorption spectra, absorption peak around 690 nm for the pristine thin films was shifted towards higher wavelength (up to around 752 nm) due to the influence of argon ion implantation as shown in figure 5a. The observed red-shift of the absorption edge may be attributed to the larger grain size and thermal defects \([29]\). We have examined the optical band gap of pristine and argon-implanted CdTe thin films deposited on ITO with the help of Tauc plot using absorption spectra of the films as shown in figure 5b. The variation in band gap corresponding to the photon energy shows that the band gap value decreases as argon ion fluence increases. According to the theory of optical transitions (direct or indirect) in solids, close to absorption edge, the absorption coefficient \(\alpha\) is related to incident photon energy \(h\nu\) according to the well-known Tauc’s relation as given in equation (1) \([30]\):

\[
(\alpha h\nu)^m = A(h\nu - E_g)
\]
where ‘\( A \)’ is a constant, ‘\( E_g \)’ the optical band gap of a semiconductor, ‘\( h\nu \)’ the photon energy and ‘\( m \)’ an exponent, which can be assumed to have values of 1/2, 3/2, 2 and 3 depending on the nature of electronic transition responsible for the absorption: \( n = 1/2 \) for allowed direct transition, \( n = 3/2 \) for forbidden direct transition, \( n = 2 \) for allowed indirect transition and \( n = 3 \) for forbidden indirect transition. As CdTe has a direct band gap [31], it obeys the rule of direct transition, i.e., \( m = 1/2 \). Calculated optical band gap for as-deposited CdTe thin film was 1.8 eV. It can be observed from figure 5b that the value of band gap energy decreases gradually to a level of 1.65 eV with increasing implantation fluence of \( 1 \times 10^{15}, 5 \times 10^{15} \) and \( 1 \times 10^{16} \) ions cm\(^{-2}\). The decrease in the values of band gap during implantation can appear due to many factors such as the following: it may be due to increase in the concentration of carriers due to implantation and the creation of defect levels in the band gap. The creation of defects affects the corresponding energy width of the bands. As a consequence, there is a creation of localized energy states in the forbidden gap, near the valence and the conduction band edges, which incites radial changes in the carrier concentration. These new energy levels may be acceptor levels at the top of the valence band or donor levels at the bottom of conduction band. Consequently, it decreases the energy required to transit the charge carrier from valence band to conduction band [32]. The trend of progressive reduction in the band gap can be assigned to the increase of implantation-induced lattice disorder with implantation fluence [33]. As reported in literature, due to Ar\(^+\) implantation some metallic cadmium clusters were found in vacuum-evaporated CdS thin films but an increase in absorption was observed due to creation of defect levels in the band gap. Also, the value of optical band gap is reduced with increasing Ar\(^+\) implantation fluence in CrN films and after annealing of films at 700\(^\circ\)C the energy gap increases, leading to variation of the values in a very narrow range [34].

PL is the spontaneous emission of light from a material under optical excitation and it can be used for examining the energy level of CdTe. Room-temperature PL spectra of pristine and argon-implanted CdTe thin films in the wavelength range 710–740 nm with an excitation wavelength of 660 nm are as shown in figure 6 along with the holder and ITO peak in the inset. All the emissions take place at wavelength higher than the excitation wavelength. Pristine thin
Figure 5. (a) Plot of absorption coefficient vs. wavelength at various fluences. (b) Tauc plot showing band gap of Ar$^+$ ion-implanted CdTe thin films.

films show a prominent emission peak around 720 nm while after implantation, an increase in the PL efficiency of the films is observed with increase in fluence. The increment in PL intensity showed the increase in recombination rate. From figure 6, some other peaks around higher wavelength (around 730 nm) can also be observed. This may be due to the presence of impurity atoms. The PL emission generally resulted from the recombinations of excited electrons and holes. During the implantation process, the CdTe thin films were subjected to argon ions bombardment, which produced defects in the band gap of the material. The emission is in general accomplished by the electrons bound to various defects such as colour centres and mono- and divalent ion vacancies [35].

3.5 Electrical properties

Figure 7 displays the current–voltage characteristic (IVC) of pristine and implanted thin films. The curves are linear and are almost symmetric in positive and negative voltage regions. A four-probe arrangement, along with a Keithley 2400 source metre, was used to record the IVC of the thin films (pristine and implanted) in the voltage range −3 to 3 V. A four-probe arrangement consisting of four equally spaced (0.13 cm) tungsten metal tips with finite radius was used. Each metal tip is sustained by springs on the other end to minimize sample damage during probing and placed in a way such that four tips touch the surface of thin films deposited on ITO substrate. From the analysis, it is clearly evident that conductivity of thin films increases with the increase in dose rate. During the passage of energetic ions, generation of current carriers and formation of intermediate energy states within the energy band gap (shown in figure 8) are common processes, which result in the decrease of energy band gap [36]. Formation of intermediate energy states and increased carrier concentration lead to an increase in conductivity of CdTe thin films after implantation. Any modification in the surface condition of thin films during implantation process brings significant change in their transport behaviour. This type of changes may be due to the generation of electron–hole pairs and hence the conductivity of semiconducting thin films changes after implantation. Incident ions might transfer required energy to the valence band electrons to transit them to the conduction
Figure 7. $I$–$V$ characteristic of pristine and implanted CdTe thin films.

Figure 8. Defect levels between valence and conduction band.

4. Conclusion

In this study, the effect of argon ion implantation on structural, optical and electrical properties of electrodeposited CdTe thin films is reported. Following conclusions are drawn from the study:

- CdTe thin films of thickness 80–100 nm were successfully deposited on ITO substrate by electrodeposition technique and subsequently implanted with argon ions of different fluences of $1 \times 10^{15}$, $5 \times 10^{15}$ and $1 \times 10^{16}$ ions cm$^{-2}$.
- From the observed optical properties, it is extrapolated from the Tauc plot that the band gap of thin films reduces with increase in implantation fluence.
- From the PL spectrum, an increase in the total luminescence efficiency after argon implantation was observed.
- The band gap and intensities in the UV–visible spectra and PL are quite sensitive to Ar implantation. This may be due to the production of implantation-induced defects in the band gap of the films.
- The electrical conductivity of thin films increased upon exposure to argon ions due to the localized states produced in the forbidden gap and generation of charge carriers that takes place, which enhance the conductivity of thin film.

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References