Final Project Report

Project Title: High Density Nano-electrode Arrays of Radiation Detection

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Abstract

Bulk single crystals of Cd$_{1-x}$Zn$_x$Te ($x=0.04$ to $x=0.2$) compound semiconductor is used for room temperature radiation detection. The production of large volume of Cd$_{1-x}$Zn$_x$Te with low defect density is expensive. As a result there is a growing research interest in the production of nanostructured compound semiconductors such as Cd$_{1-x}$Zn$_x$Te in an electrochemical route. In this investigation, Cd$_{1-x}$Zn$_x$Te ternary compound semiconductor, referred as CZT, was electrodeposited in the form of nanowires onto a TiO$_2$ nanotubular template from propylene carbonate as the non-aqueous electrolyte, using a pulse-reverse electrodeposition process at 130 ºC. The template acted as a support in growing ordered nanowire of CZT which acts as a one dimensional conductor. Cyclic Voltammogram (CV) studies were conducted in determining the potentials for the growth of nanowires of uniform stoichiometry. The morphologies and composition of CZT were characterized by using SEM, TEM and XRD. The STEM mapping carried out on the nanowires showed the uniform distribution of Cd, Zn and Te elements. TEM image showed that the nanowires were polycrystalline in nature. The Mott-Schottky analysis carried on the nanowires showed that the nanowires were a p-type semiconductor. The carrier density, band gap and resistivity of the Cd$_{0.9}$Zn$_{0.1}$Te nanowires were $4.29 \times 10^{13}$ cm$^{-3}$, 1.56 eV and $2.76 \times 10^{11}$Ω-cm respectively. The high resistivity was attributed to the presence of deep defect states such as cadmium vacancies or Te antisites which were created by the anodic cycle of the pulse-reverse electrodeposition process. Stacks of series connected CZT nanowire arrays were tested with different bias potentials. The background current was in the order of tens of picoamperes. When exposed to radiation source Americium-241 (60 KeV, 4 μCi), the stacked CZT nanowires arrays showed sensing behavior. The sensitivity of the nanowire arrays increased as the number of stacks increased. The preliminary results indicate that the CZT nanowire arrays can be used as a potential X-ray and low energy gamma ray detector material at room temperature with a much low bias potential (0.7 – 4V) as against 300 – 500 V applied in the commercial bulk detector materials.
Chapter 1
Introduction

The ability to detect high energy radiation such as X-rays, gamma-rays, and other charged particles has improved dramatically in recent years. Radiation detectors have become increasingly important for the long term monitoring of nuclear waste storage sites, environmental safety, and homeland security against terrorist threats. There are three types of detectors: 1) Gas Filled Detectors; 2) Scintillation Detectors and 3) Semiconductor detectors. Solid state semiconductor detectors are predominantly used because of their excellent energy resolution and better efficiency. Also the mean energy required to create an electron hole pair is much smaller for semiconductor detectors. The most commonly used semiconductor detectors are silicon and germanium single crystals. The main disadvantage of these detectors is that they have to be operated at low temperatures requiring liquid nitrogen cooling in order to reduce their noise levels. A range of compound semiconductor materials such as cadmium zinc telluride (CZT), cadmium telluride, gallium arsenide, indium phosphide, mercuric iodide and thallium bromide are available as radiation detector materials at room temperature. These compound semiconductor materials have high atomic number and high density which allows the ionizing radiations to interact with the material. Table 1.1 lists the properties of various detection materials. Out of which CZT is considered to be more advantageous for radiation detection due to its wider band gap and higher resistivity and it is the most commercially available one. The higher resistivity enables the CZT detectors to decrease the noise levels, which in turn increases the sensitivity of the detector. Figure 1.1 compares the detection efficiency of a 500 micron thick CZT with that of Silicon, Germanium and AlSb materials of same thickness. The efficiency is calculated based on the attenuation coefficient of individual material for a thickness of 500 micron. From the figure it can be seen that the detection efficiency of CZT is better than that of other semiconductor materials, especially at low energy levels for materials of same thickness.

Table 1.1: Properties of various detector materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Atomic Number</th>
<th>Density g/cm³</th>
<th>Band Gap (eV)</th>
<th>E pair (eV)</th>
<th>Resistivity (Ω-cm)</th>
<th>τμ (e) cm²V⁻¹</th>
<th>τμ (h) cm²V⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>14</td>
<td>2.33</td>
<td>1.12</td>
<td>3.6</td>
<td>10⁴</td>
<td>4x10⁻¹</td>
<td>2x10⁻¹</td>
</tr>
<tr>
<td>Ge</td>
<td>32</td>
<td>5.33</td>
<td>0.67</td>
<td>4.6</td>
<td>50</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>GaAs</td>
<td>31,33</td>
<td>5.32</td>
<td>1.43</td>
<td>4.2</td>
<td>10¹¹</td>
<td>10⁻⁴</td>
<td>5x10⁻⁴</td>
</tr>
<tr>
<td>InP</td>
<td>15,49</td>
<td>4.78</td>
<td>1.43</td>
<td>4.2</td>
<td>10⁶</td>
<td>5x10⁻⁶</td>
<td>2x10⁻⁵</td>
</tr>
<tr>
<td>CdTe</td>
<td>48,52</td>
<td>6.2</td>
<td>1.44</td>
<td>4.4</td>
<td>10⁹</td>
<td>3x10⁻⁵</td>
<td>2.6x10⁻⁵</td>
</tr>
<tr>
<td>Cd₀.9Zn₀.₁Te</td>
<td>48,30,52</td>
<td>5.78</td>
<td>1.57</td>
<td>4.6</td>
<td>10¹¹</td>
<td>7x10⁻⁵</td>
<td>9x10⁻⁵</td>
</tr>
<tr>
<td>PbI₂</td>
<td>82,53</td>
<td>6.2</td>
<td>2.3-2.6</td>
<td>4.9</td>
<td>10¹²</td>
<td>8x10⁻⁶</td>
<td>9x10⁻⁷</td>
</tr>
<tr>
<td>HgI₂</td>
<td>80,53</td>
<td>6.4</td>
<td>2.13</td>
<td>4.2</td>
<td>10¹³</td>
<td>10⁻⁴</td>
<td>4x10⁻⁵</td>
</tr>
<tr>
<td>TlBr</td>
<td>81,35</td>
<td>7.56</td>
<td>2.68</td>
<td>6.5</td>
<td>10¹²</td>
<td>3x10⁻⁵</td>
<td>1.5x10⁻⁵</td>
</tr>
</tbody>
</table>
Defects such as dislocations, grain boundaries, voids, cracks etc., present in the detector material act as charge recombination centres or traps and decrease the charge collection efficiency\(^{7,8}\). Further, impurities and defects present in the materials decrease the resistivity of the compound semiconductors and increase the leakage current under application of the bias potential and increased noise level. A minimum resistivity of \(10^9 \Omega\)-cm is required for detection applications.

\(\text{Cd}_{1-x}\text{Zn}_x\text{Te}\) crystals are manufactured by high\(^9\) or low\(^{10}\) pressure Bridgman techniques. Smaller thickness detector material is cut from a large ingot for integration into a sensor device. During the cutting operation a large amount of defects is introduced into the material. In order to minimize the surface defects and to provide with electrical contacts, the sawn surface is mechanically and chemically polished and coated with a noble metal layer. These processes alter the electronic properties of the material and result in deterioration of the performance. Figure 1.2 shows the optical photograph of \(\text{Cd}_{1-x}\text{Zn}_x\text{Te}\).
In recent years, the properties of low-dimensional nanoscale structure materials, such as nanotubes, nanowires, nanobelts, and other nano-structures have attracted much attention because of their interesting physical and chemical properties and potential to allow exploration of technological applications. The current work focuses on templated growth of CZT nanowires onto TiO$_2$ nanotubular template. The nanowires are one dimensional conductor. This helps in faster collection of electrons and holes generated during interaction of ionizing radiations, which in turn increases the charge collection efficiency. The current work is unique on its own as there has been no such study reported so far in the literature. Since it’s very difficult to synthesize large volume detector material with fewer defects through conventional processes (Bridgman method) an attempt was made to synthesize p-type CZT nanowires onto an n-type TiO$_2$ nanotubular template and study their sensing abilities. Preliminary results of this research work showed that nanowire configuration of CZT could be a potential alternate for x-rays and low energy gamma detection. Limitation on length of nanowires can be compensated by stacked arrays of nanowires of CZT as detector material.

Chapter 2 of this document work will give background about gamma interaction with the material and a brief literature survey. Chapter 3 will list the objective and scope of the present work. Chapter 4 will list the experimental parameters in synthesizing the CZT nanowires as well as other characterization techniques which were used to characterize these nanowires. Results and discussion will be presented in chapter 5. Chapter 6 lists the conclusions of the present work.
Chapter 2
Background & Literature survey

2.1 Semiconductor Detector
2.1.1 Semiconductor Radiation Interaction
Electromagnetic radiation such as X-rays and gamma rays interact with the detector material by the following three mechanisms:

1) Photoelectric Effect: The interacting photon transfers all its energy to the atomic orbital electron and disappears. A photoelectron is created from the k shell with energy equal to the incident photon minus the energy of the electron.

\[ T = E_\gamma - B_e \rightarrow 1 \]

Where \( E_\gamma \) = energy of the incident photon
\( B_e \) = binding energy of the photoelectron

Photoelectron will then interact with the semiconductor lattice by coulomb interaction and lose their energy by creating electron and hole pairs. The number of electron hole pair created is equal to the energy of the incident photon.

2) Compton Scattering: The Compton scattering transfers only a part of the energy to the electron. The remaining energy escapes or gets scattered. In the case of Compton scattering, the electron hole pair created is angle dependent.

3) Pair Production: Occurs due to the interaction of the incident photon with the nucleus of the atom. Due to this an electron positron pair is produced. Pair production occurs only when the energy of the incident photon is in excess of 1.02 MeV.

The probability of interaction of x-rays and gamma rays with a material is atomic number \( Z \) dependent and increases with increasing \( Z \). In case of photoelectric effect the interaction is proportional to \( Z^n \) (4<\( n < 5 \)), \( Z \) in case of compton scattering and \( Z^2 \) in the case of pair production. The photoelectric effect is the predominant form of interaction with the material.

2.1.2 Working Principle of Gamma Ray Detector:
Since photoelectric effect is the most predominant form of interaction of gamma’s with the semiconductor material, when a gamma photon interacts with the detector material it results in electron and hole pairs. The number of such pairs, \( n \), is proportional to the energy of the photons, \( E_0 \), and expressed as \( n = E_0/E_\phi \), where \( E_\phi \) is the ionization energy required to create an electron-hole pair. In order to collect the electron-hole pairs, an electric field, \( E \), is applied across the detector material that drifts the charges with drift velocities \( v_e \) and \( v_h \) towards anode and cathode respectively. Collection of the charge carriers at the electrode ends creates an induced charge, \( Q \), on the electrodes. If there is no trapping of electron-hole pairs and no recombination, the induced charge \( Q \) will be equal to the initially created charge \( Q_0 \). However, electron-hole traps are always present in the semiconductor and not all the created electron-hole pairs are collected at the electrode ends. The charge collection efficiency \( (\eta_{cc}) \) can be expressed as a function of ratio between carrier diffusion length and the thickness of the detector material.
\[ \eta_{ee} = \frac{\lambda_e}{L} \left[ 1 - e^{-\frac{L - X_0}{\lambda_e}} \right] + \frac{\lambda_h}{L} \left[ 1 - e^{-\frac{X_0}{\lambda_h}} \right] \]

Where, \( \lambda_e \) and \( \lambda_h \) are drift lengths of electron and hole respectively given by the relation \( \lambda_c = \mu_\tau E \), the subscript \( c \) stands for charge carrier electron or hole, \( \mu_\tau \) is carrier mobility, \( \tau_c \) = charge carrier lifetime, \( L \) = thickness of the detector material, and \( X_0 \) = distance between the cathode and charge creation site.

The charge carriers generated in the detector flow through the external circuit as current pulses and the current is integrated into charge pulses. These charge pulses are collected by charge sensitive preamplifier. The output is a voltage pulse whose amplitude is proportional to the charge pulse and the deposited photon energy. A pulse height spectrum is created using a multichannel analyzer by creating a histogram of the pulse heights. The peaks in the spectrum correspond to the energies of the incident radiation. Figure 2.1 shows the schematic illustration of the working principle of a semiconductor radiation detector.

\[ \text{Figure 2.1: Schematic illustration of the working principle of a semiconductor radiation detector.} \]

2.1.3 Defects in Semiconductor

Semiconductor materials require a greatest level of impurity control. The properties of a semiconductor differ based on the presence of impurities. Impurities are introduced intentionally or unintentionally during the growth process. Impurities which are introduced intentionally during the growth process to modify the material to suit certain applications are called as dopants. Semiconductors in general may contain variety of structural defects and transient defects. Structural defects can be classified as (i) point defects (substitutional, interstitial and vacancies), (ii) line defects (dislocations), (iii) planar defects (grain boundaries, twins and stacking faults) and (iv) volume defects (voids and inclusions). Transient defects are due to elementary excitations such as phonons. Thus these defects can interact and form a variety of
possible combinations and they may also act as attractive centers for electrons and holes. Thus defects play a crucial role in understanding the semiconductor behaviour as well as the operation and reliability of the devices. The point defects have sufficiently low formation energies, and may be formed in thermal equilibrium and their number density increases with thermal ionization. Since most semiconductors are grown through high temperature synthesis, it’s difficult to obtain uniform stoichiometry in the material due to solidification problems encountered during the synthesis process. The presence of defects gives rise to localized energy level within the band gap. These defects are classified as shallow or deep level defects depending on their position in the band gap. The deep level defects can act as charge traps or recombination sites or sometimes as generation sites too. Hence the defect densities in the semiconductor have to be reduced to sufficiently low levels so that it does not affect the semiconductor properties as well as the device performance.

2.1.4 Requirements of the Detector Material

The nuclear detectors should have the following qualities:

- High detection efficiency (detection of shielded nuclear material)
- High spectral resolution (identification of radiation source)
- High sensitivity (identify faint signals and distinguish from background noise)
- High stand-off capability (ability to operate as a fixed system and hand held system as well)
- Operate at ambient conditions (No external cooling facility)
- No false alarms (should not deteriorate with exposure to severe environment)

In order to meet the above qualities, the detector material should have the following requirements:

- High atomic number and high density so that it helps in more interaction of the gammas with the material
- Wider band gap to minimize leakage current
- Electron-hole ionization energy smaller than 5 eV
- Resistivity higher than $10^9$ ohm-cm (never less than $10^8$ ohm-cm) to reduce the background noise level which in turn helps in increasing the detection efficiency.
- Higher carrier drift lengths (product of mobility ($\mu$), carrier lifetime($\tau$) and applied field($E$))
- Low defect density for good charge transportation and collection in the circuit
- Free from polarization effect (due to applied field) and stable under irradiation.
- Large area detector material with fewer defects so that it helps in increasing the sensitivity and efficiency of detection.

Based on the above requirements, there are only certain semiconductor materials (as listed in Table 1.1) available for gamma ray detection. Out of which Cadmium Zinc Telluride (Cd$_{1-x}$Zn$_x$Te or CZT) has been the most widely grown and commercially available material for gamma ray detection because of its excellent energy resolution and detection efficiency. As shown in figure 1.1 the detection efficiency of CZT is much higher when compared to most semiconductors as well as the mobility carrier lifetime of electrons and holes are much better than the high atomic number materials available for detection.
2.2 About Cadmium Zinc Telluride (Cd\(1-x\)Zn\(x\)Te or CZT)

Cadmium telluride (CdTe) and cadmium zinc telluride (CZT) compound semiconductors are used widely in infra-red (IR), X-ray and gamma ray radiation detection applications and in solar cell panels\(^{23,24}\). CZT is considered more advantageous than CdTe in radiation detection because of wider band gap and higher resistivity, which provides low noise level during detection. Further, Cd\(1-x\)Zn\(x\)Te with \(x = 0.04–0.07\) finds application in infra-red detectors and \(x < 0.4\) in solar cell applications\(^{24}\). In order to minimize the leakage current, room temperature radiation detector CZT materials are required to have very high resistivity, in the order of \(10^{10} \Omega\)-cm.

2.2.1 Crystal Structure of CZT

CdZnTe has a zinc-blende structure. The structure of CZT can be regarded as CdTe lattice with a fraction of Cd substituted by Zn as shown in figure 2.2. This structure is considered as two f.c.c sub-lattices interpenetrating with an offset of \(\frac{1}{4}\)th of a unit cell body diagonal\(^{25}\). One sub-lattice is occupied by Cd or Zn and the other is by Te. In the lattice, every atom is surrounded by four hetero atoms and held by covalent bonds. Mathematically, this structure is most conveniently described as an f.c.c Bravais lattice with a two-point basis. The basis can be taken as

\[
\sigma_1 = (0, 0, 0) \quad \rightarrow \quad 3
\]

\[
\sigma_2 = (\frac{1}{4}a, \frac{1}{4}a, \frac{1}{4}a) \quad \rightarrow \quad 4
\]

![Figure 2.2: Lattice Structure of CZT (a) Shows the two interpenetrating f.c.c (b) is the simplified version of the structure\(^{\pm}\).](image)

CZT is a direct band gap semiconductor and the band gap varies as a function of Zn content. Addition of Zn in the CdTe lattice decreases the lattice constant, \(a_0\) (from 0.6482 nm for CdTe to 0.61 nm for ZnTe) and increases the band gap in the range of 1.49 eV (CdTe) – 2.26 eV (ZnTe). The relation between band gap and \(x\) is given by the following expression\(^{\pm}\).
\[ E_g = 1.5045 + 0.631X + 0.128X^2 \]

Where \( E_g \) is the band gap of the alloy formed.
1.5045 is the band gap of CdTe.

### 2.2.2 Phase Diagram of CZT.

Figure 2.3 shows a pseudo binary phase diagram of CdTe-ZnTe. The phase diagram has a liquidus and solidus curve as pointed out by the arrows. The end points correspond to the melting point of pure CdTe and ZnTe respectively. The concentration of Zn in CZT, determines the melting point of the alloy. The Phase diagram indicates that the growth of CZT occurs at high temperatures. The area in between the two curves corresponds to a two phase region. From the phase diagram it can be seen that the CZT forms a solid solution along the entire alloy range. It can also be seen from the phase diagram that there are no separate phases formed in the CZT. Since the growth process takes place at high temperature there are solidification problems (such as segregation) encountered during the growth which results in non uniformity in the stoichiometry. These can act as a potential trap for electron and holes during device performance.

![Pseudo Binary Phase Diagram of CdTe-ZnTe](image)

**Figure 2.3:** Pseudo Binary Phase Diagram of CdTe-ZnTe.

### 2.2.3 Growth Methods:

The Cd\textsubscript{1-x}Zn\textsubscript{x}Te has been grown by various techniques such as traveling wave heat method, bridgman method, physical vapor transport, electrodeposition. Commercially, the CZT is manufactured through the Bridgman method. In the case of Bridgman method, the crucible containing the melt is passed through a furnace designed to provide a suitable
temperature profile. The furnace may be either vertical or horizontal. There are two types of Bridgman process. High pressure Bridgman and low pressure Bridgman process. In the case of high pressure Bridgman process an over pressure usually argon is maintained at 20 to 150 atm to reduce the loss of volatile components. Since cadmium has high vapour pressure the cadmium escapes leaving the melt to be enriched in tellurium. The horizontal Bridgman technique offers potential advantages over the high pressure Bridgman method. The growth is perpendicular to the gravitational field. The growth interface is not subject to the weight of the liquid, as in the case of high pressure vertical Bridgman method. The method has been used to produce Cd$_{1-x}$Zn$_x$Te with x in the region of 0.04-0.12. Figure 2.4 shows the schematic representation of vertical and horizontal Bridgman method.

![Schematic showing the temperature gradient during growth process of CZT](image)

**Figure 2.4:** Schematic showing the temperature gradient during growth process of CZT.

### 2.2.4 Current Status in the growth of CZT

Both single crystal and slices of polycrystalline material are used with a standard commercial volume of 500 mm$^3$ and the largest commercial volume of about 1700 mm$^3$. The mobility-lifetime product ($\mu\tau$) in CZT is $1.5 - 3\times10^3$ cm$^2$/V for electrons and $2\times10^5$ cm$^2$/V for holes. The single crystal growth of CZT through Bridgman method faces a lot of challenges. The vapor pressure of cadmium is very high, thus cadmium escapes which results in excess tellurium precipitates formed. Figure 2.5 shows an optical micrograph of tellurium precipitates.
Maintaining stoichiometry of CZT has become a major problem during growth using these high temperature processes. Figure 2.6 illustrates various kinds of manufacturing defects present within a single crystal. Two types of macro defects are present in the CZT. They are pipes and inclusions. Pipes are tubular structures running intermittently and parallel to the growth axis of the HPB CZT ingots. A high density of more irregular pipes are usually observed in the tip of the ingot and a more regular array of pipes with gradually decreasing density is observed in the middle and heel regions of the ingot. The origin and the mechanism for formation, of pipes are not yet resolved in HPB CZT. The predominantly hollow nature of these defects, however, indicates that they could be formed by the trapping of gas bubbles at the growth interface. The presence of inclusions is attributed to the loss of Cd which results in enriched Te precipitates formed at the heel during the growth process. Further slicing of these CZT crystals causes more structural defects such as cracks. The electrical resistivity is typically 2-3 orders of magnitude lower than the intrinsic resistivity of CdZnTe and falls in the $10^6 - 10^8 \, \Omega\text{-cm}$ range. The low resistivity indicates incomplete electrical compensation in the material. These kinds of structural defects, affects the energy resolution and results in poor spectral resolution of the energy spectrum. Also it can increase the noise level of the detectors which results in poor detection efficiency.
2.2.5 Defects in CZT Crystal

In this section the point defects in CZT will be discussed. There are various kinds of point defects in CZT. The defects include cation vacancy $V_m$ ($V_{Cd}$, $V_{Zn}$), anion vacancy $V_x$ ($V_{Te}$), interstitial sites ($M_i$, $X_i$) and antisites ($M_x$, $X_m$) corresponding to $M$ atom occupying $X$ atom site and vice versa. Apart from these defects there are defects due to donors and acceptors. In order to minimize the leakage current, the resistivity of the CZT should be very high which makes the material semi insulating type. In defect compensation models, the compensation was described by shallow donors, which compensated the shallow acceptors. But it was shown recently that compensation by shallow levels only would not allow one to grow high resistivity crystals\(^{41}\). The compensation in such a case can only be achieved for selected areas of a grown crystal, because the concentration of the shallow donors has to be exactly the same as the shallow acceptors. This means controlled doping concentration with an accuracy of a few parts per billion (weight) for the complete crystals. This is not possible, because the segregation of the shallow donor leads to a variation of the concentration over several orders of magnitude.

Intentional doping of donor and acceptor impurity elements such as Al, V etc. has been studied\(^{42}\). Alternatively, native deep level defects can also be introduced during manufacture of the detector material. Chu et al.\(^{43}\) produced high resistivity $p$-type $Cd_{0.9}Zn_{0.1}Te$ crystals using a modified Bridgman technique by doping In impurity at a level of $1-5 \times 10^{15}$ cm$^{-3}$. The negative effect of the doping with deep donors is the reduction of the mobility–lifetime products of the charge carriers. The deep donors are traps for the electrons or the holes, depending on the cross sections of the
deep donors. The mobility–lifetime products of vanadium doped material is a factor of 100 times lower than the mobility–lifetime products of tin doped crystals. In the case of intentionally undoped semi-insulating material, the highest mobility–lifetime products were obtained by the compensation with a deep intrinsic defect. Kršmanović et al. reported high resistance of CZT by intrinsic defect compensation. They observed that the resistivity of the CZT increased sharply when the concentration of deep donors exceeded the concentration of the uncompensated acceptors. Tellurium antisites (Te\textsubscript{Cd}) are considered as deep donors as the crystal growth in high pressure Bridgman technique was carried out with Te rich condition. Even though deep defect levels pin the Fermi energy at the mid band gap and increase the resistivity, excess concentration could act as traps and affect the charge carrier transportation. Figure 2.7 shows the position of the ionization energy levels of native defects, impurities, and defect complexes in semi-insulating Cd\textsubscript{1-x}Zn\textsubscript{x}Te.

![Figure 2.7: Position of the ionization energy levels of native defects, impurities, and defect complexes in semi-insulating Cd\textsubscript{1-x}Zn\textsubscript{x}Te.](image)

2.3 Electrodeposition of CZT
The electrochemical deposition technique can be considered as a promising alternative for fabricating large area detector material with fewer defects. The problems encountered with traditional high temperature applications can be avoided in the case of electrochemical deposition. The advantages of electrodeposition can be listed as follows:

- Electrodeposition helps in preparing thin films of uniform stoichiometry and thickness by varying the composition in the solution and also by adjusting the potentials for deposition.
• In electrodeposition process the material can be synthesized at a lower temperature.
• Electrodeposition is a simple and scalable process.
• The doping of impurities is much easier and precise using electrodeposition process

The art and science of electrodepositing metal and metallic alloys have been developed for more than a century. The application of the electrodeposition technique to semiconductors, however, has been limited until recently, mainly because of complexities in the electrodeposition of semiconductors. Research and development in the area of semiconductor electrodeposition have been continued after the pioneering work by Kröger and Panicker et al. They have deposited both n and p-type polycrystalline CdTe layers by cathodic electrodeposition using acidic sulphate electrolytes containing Cd$^{2+}$ and HTeO$_2^-$ ions. There has been a lot of compound semiconductor thin films synthesized using electrodeposition techniques such as CuInSe$_2$, CuInS$_2$, CuInTe$_2$, GaP, and GaAs.

2.3.1 Electrodeposition of CdTe and ZnTe and CZT Thin Films
The electrodeposition of CdTe from both alkaline and acidic baths has been reported, but the former usually yielded a poorly adhering deposit to the substrate, since Te is stable only at pH < 7. A systematic study of the electrodeposition of CdTe in an aqueous bath containing 1 M CdSO$_4$ and TeO$_2$ in saturation at pH 2.5-3.0 was reported by Panicker. The aqueous acidic bath has poor solubility for TeO$_2$. A number of subsequent studies employed baths similar to that of Panicker for the electrodeposition of CdTe. Electrochemical preparation of thin films of ZnTe was first reported by Basol and Kapur using a two stage process involving electrodeposition of Te and Zn stacked layers from aqueous electrolytes followed by annealing. Single-step electrodeposition of ZnTe films from an aqueous solution has been reported by Spallart et al. Thin films of CZT have been electrodeposited using aqueous solutions. The deposition was carried out through a two stage process involving deposition of a layer of CdTe followed by ZnTe and then subsequent annealing in argon atmosphere to form CZT thin film layers. It has been reported that the adhesion of Zn in aqueous deposition conditions gets rendered due to the hydrogen evolution that could arise due to the large negative potentials employed during deposition. Electrodeposition of CdTe using non aqueous solution has been reported to result in crack free thin films. A single step electrodeposition of ternary systems such CdHgTe using non aqueous solution has also been reported. Electrodeposition of nanowires of CdTe compound semiconductor has been reported using a templated process. On the nanoscale, the physical properties, and the chemical properties of materials are different from their bulk counterparts. In the recent decades, nanostructured materials, especially 1D nanostructure, in particular nanowires and nanotubes, have received a great deal of attention from the scientific and industrial communities due to their unique properties and potential applications.

2.4 Nanostructured Materials

2.4.1 1D Nanostructure
On the nanoscale, the physical properties, and the chemical properties of materials are different from their bulk counterparts. In recent decades, nanostructured materials, especially 1D nanostructure, have received a great deal of attention from the scientific and industrial communities due to their unique properties and potential applications. In the case of bulk materials the conducting electrons are delocalized and can move...
freely in all three directions. Thus bulk materials can be considered as materials which have zero confinement. When one or more dimensions of a material are reduced to very small scales, it approaches several times the spacing between the atoms in the lattice. When such a situation occurs, delocalization of electrons is impeded and the electrons experience confinement. If one dimension is confined and the other two dimensions are delocalized, then we obtain a structure known as quantum well. If two dimensions are confined and one dimension is delocalized then we obtain a structure known as quantum dot. The quantum wires are mostly used in the electronic industry due to the tunable aspect ratios. Aspect ratios of up to 1000 have been reported so far.

Numerous methods for preparing 1D nano-scale materials have been developed. The most successful approaches for the preparation of nanoscale materials include: chemical vapor deposition, physical vapor deposition, electrodeposition. The electrodeposition technique is considered to be the simplest, cheapest and easily scalable method when compared to the other synthesis method.

2.4.2 Template Synthesis of Ordered 1D Nanostructures
Assembling 1D structure on a large scale into highly ordered arrays, especially keeping them in good orientation and arrangement as well as building them onto various substrates will probably lead them to practical applications. The template-assisted synthesis of nanowires is conceptually a very simple technique to fabricate nanostructures. These templates contain very small cylindrical pores or voids within the host material, and the empty spaces are filled with the chosen material, which adopts the pore morphology, to form nanowires. In template-assisted synthesis of nanostructures, the chemical stability and mechanical properties of the template, as well as the diameter, uniformity and density of the pores are important characteristics to consider. Templates frequently used for nanowire synthesis include anodic alumina (Al2O3), nano-channel glass, ion track-etched polymers.

2.5 Radiation damage in semiconductors
In semiconductors radiation damage is due to two basic types of mechanisms. They are displacement damage and ionisation damage. In the case of displacement damage, the incident radiation displaces an atom from their lattice which results in disordered structures. These resulting defects can alter the electrical characteristics of the material. In the case of displacement damage it depends on the energy and momentum transferred to the lattice. The effects of displacement damage can lead to increase of capture and recombination which leads to non equilibrium charge carriers, which in turn leads to poor charge collection.

In the case of ionization damage, the energy absorbed due to ionization leads to charge carriers. This can lead to unintended concentrations of charge which leads to charged regions in the material. The ionization damage depends on the absorbed energy and independent of the type of radiation. The ionization damage is proportional to the energy absorbed per unit volume, usually expressed in rad or gray.
Chapter 3
Objectives
The main objective of this study was to develop an electrodeposition technique to grow uniform stoichiometry of Cd$_{1-x}$Zn$_x$Te nanowires using a template process which can be used as a gamma ray detector by stacking the nanowire array templates. Based on the above discussion, the primary and secondary objectives of this work are:

**Primary Objective:**
1. Synthesis of detector quality nanowires of Cd$_{1-x}$Zn$_x$Te (x=0.04, 0.1 and 0.2) by a single step non-aqueous pulsed-reverse potential electrodeposition method using TiO$_2$ nanotubular templates.
2. Introduction of deep energy level defects such as V$_{cd}$ and Te antisites into the nanowires by modulating the electrochemical potentials.
3. Characterization of the nanowires for their size, shape and also uniformity in stoichiometry using SEM, XRD and TEM.
4. Determine the band gap of the material using UV-Vis spectrometry.
5. To characterize the nanowires for their electrical properties.

**Secondary Objective:**
1. To test the sensing ability of the stacked nanowire arrays of the most commonly used detector grade CZT with x=0.1 with the available source Am-241 having energy level 60KeV and intensity 4μCurie.
2. To compare the sensing ability of the nanowire array with that of the thin film array.
Chapter 4
Experimental Section

4.1 Template Preparation:
Titanium (99.9%) foils of thickness 0.2 mm (0.009”), obtained from Electronic Space Products International metals (ESPI-metals, Oregon, USA), were mechanically cut into 16 mm diameter circular discs. These round samples were then washed in de-ionized (DI) water, and finally in ethanol to remove the impurities and greasy layer present on the surface. The anodization procedure developed in our laboratory was used to form ordered TiO$_2$ nanotubes. For the electrochemical experiments (anodization), the samples were placed in a Teflon flat specimen holder. The surface area exposed for anodization was around 0.7 cm$^2$. The electrochemical setup consisted of a conventional electrolysis cell with a platinum electrode used as cathode and the work piece used as anode. The anodization was carried in a solution of 0.5M phosphoric acid, 0.14M sodium fluoride and pH of 2.0. Anodization was carried out at 20V and 25°C for about 45 min. A platinum flag with 4 cm$^2$ surface area was used as the counter electrode. After anodization the TiO$_2$ nanotubes were annealed at 500°C for 6 hrs under continuous oxygen purging. Figure 4.1 (a) & (b) shows the schematic and the actual set up of the anodization process respectively.

![Figure 4.1](image)

(a) Schematic (b) Photograph of the actual set up for producing TiO$_2$ nanotubular template.

4.2 Cyclic Voltammetry (CV):
Cyclic voltammogram (CV) studies were carried out to understand the growth mechanism’s of CZT. Aprotic non-aqueous solvent, propylene carbonate (P.C) was used as an electrolyte for growth of CZT. The major advantages of such a non-aqueous bath are a wider electrochemical window, better Faradaic efficiencies, and a better stoichiometric control of the compound deposition because of smaller differences in the redox potential values of the constituent ions as compared to the values reported for aqueous solutions.
Both platinum and nanoporous TiO$_2$ were used as electrodes during cyclic voltammetry. The following electrolytes were used for CV:

1. $25 \times 10^{-3}$ M NaClO$_4$ in PC
2. $5 \times 10^{-3}$ M CdCl$_2$ + $25 \times 10^{-3}$ M NaClO$_4$ in PC (Referred as Cd solution)
3. $0.5 \times 10^{-3}$ M TeCl$_4$ + $25 \times 10^{-3}$ M NaClO$_4$ in PC (Referred as Te solution)
4. $5 \times 10^{-3}$ M CdCl$_2$ + $0.5 \times 10^{-3}$ M TeCl$_4$ + $25 \times 10^{-3}$ M NaClO$_4$ in PC (CdTe solution)
5. $5 \times 10^{-3}$ M CdCl$_2$ + $10 \times 10^{-3}$ M ZnCl$_2$ + $0.5 \times 10^{-3}$ M TeCl$_4$ + $25 \times 10^{-3}$ M NaClO$_4$ in PC (CZT solution)
6. $1,10,25 \times 10^{-3}$ M ZnCl$_2$ + $0.5 \times 10^{-3}$ M TeCl$_4$ + $25 \times 10^{-3}$ M NaClO$_4$ in PC (Zn variance in ZnTe solution)
7. $5 \times 10^{-3}$ M ZnCl$_2$ + $1-8 \times 10^{-3}$ M CdCl$_2$ + $0.5 \times 10^{-3}$ M TeCl$_4$ + $25 \times 10^{-3}$ M NaClO$_4$ in PC (Cd variance in CdTe solution)
8. $5 \times 10^{-3}$ M ZnCl$_2$ + $5 \times 10^{-3}$ M CdCl$_2$ + $0.1$, $0.5$ and $1.0 \times 10^{-3}$ M TeCl$_4$ + $25 \times 10^{-3}$ M NaClO$_4$ in PC (CZT solution with Te variation)

The CV studies of CZT nanowires were carried out in a three-electrode cell at two different temperatures 95°C and 130°C (+/- 3 °C). CV tests were carried out using both Pt and nanoporous TiO$_2$ substrates at a potential sweep rate of 10 mV/s. 4 cm$^2$ platinum foil in the shape of a flag was used as the counter electrode; pure cadmium wire was used as the reference electrode and nanoporous titanium dioxide was used as the template for nanowire growth. 30 x $10^{-3}$ M NaClO$_4$ was used as the supporting electrolyte. All depositions were carried out in a controlled atmosphere inside a glove box. Ultra high purity argon was used as the inert atmosphere. Figure 4.2 shows the schematic set up of the cyclic voltammogram carried out to determine the deposition potentials.

![Figure 4.2: Schematic of the cyclic voltammogram setup to determine the deposition potentials for growth of CZT nanowires.](image-url)
4.3 Growth of CZT Nanowires:
The cyclic voltammogram carried out were useful in determining the deposition potentials as well as the concentration of the constituent elements for the growth of CZT nanowires. The concentration used was 10 mM ZnCl₂, 0.5 mM TeCl₄, 5mM CdCl₂ and 25 mM NaClO₄ (for increasing the ionic conductivity) in propylene carbonate. The depositions were carried out in a standard three-electrode cell at 130°C (+/- 2°C). Platinum foil (4 cm²) was used as the counter electrode. A pure Cd wire immersed in propylene carbonate saturated with CdCl₂ in a fritted glass tube was used as the reference electrode. The entire experiments were carried out in a controlled atmosphere using a glove box (Omni Lab System, Vacuum Atmospheres Company, USA). High purity argon was used as the inert atmosphere. The oxygen and moisture content of the glove box were controlled at low levels (<5ppm). Figure 4.3 shows the photograph of the experimental setup used for growth of CZT nanowires.

![Figure 4.3: Photograph showing the experimental setup for growth of CZT nanowires.](image)

Nanowires of CZT were deposited on the nanoporous TiO₂ template by pulsed potential method. A typical pulsed-potentials cycle consisted of two cathodic, two anodic and one open circuit potential, as depicted in figure 4.4. All potentials were applied with respect to the cadmium reference electrode. Cathodic pulsed potential used varied between -0.4V to -1.2 V and pulsed for 1second. The two anodic potentials were kept constant in all the runs. The two anodic potentials used were 0.3V for 3secs and 0.7V for 5secs. The deposition time was typically around 45 minutes. Once the depositions were done the samples were rinsed with anhydrous semiconductor grade methanol and dried in vacuum. The samples were then annealed at 350 ºC in a CVD furnace in high purity argon atmosphere (200 cc/min) for 1hr. The annealed samples were cleaned with methanol and the samples were then characterized.
4.4 Sample Characterization

4.4.1 Material Characterization:
The samples were observed under a field emission scanning electron microscopy (FESEM, S-4700, Hitachi) to record the surface morphology of the nanowires. The chemical compositions of the nanowires were characterized by X-Ray energy dispersive analysis (EDAX). Glancing angle X-Ray Diffraction (GXRD, Philips-12045 B/3 diffractometer, Cu target ($\lambda = 0.154$ nm)) and high resolution transmission electron microscopic studies (HRTEM, JEOL 2100F, Japan) were carried out at 200 kV.

4.4.2 Electrical Characterization:
4.4.2.1 Band Gap Measurement:
The electronic band-gap values of the CZT samples were measured from the optical absorption spectra using a UV–VIS spectrometer (Model: UV-2401 PC, Shimadzu Corporation, Kyoto, Japan) extended to the near infra region using a photomultiplier tube.

4.4.2.2 Mott–Schottky Analysis
Mott schottky analysis was done on the sample to study the electronic properties of the CZT nanowires in the annealed condition. The frequency used was 3000Hz and scan rate of 50mV/s. The interfacial capacitance $C$ was calculated by the system software using the relation $C = (-Z'' 2\Pi f)^{-1}$, where $Z''$ is the imaginary part of the impedance and $f$ is the frequency. Capacitance $C$ is related, in turn, to the charge carrier density, $N_d$, by the following equation:

$$\frac{1}{C^2} = \frac{2 \epsilon \epsilon_0 N_d}{e} \left[ E - E_{ss} - \frac{KT}{e} \right]$$

…………………………(5)
Where $e =$ elementary electron charge (positive for n-type and negative for p-type), $\varepsilon_0 =$ permittivity in vacuum, $\varepsilon =$ dielectric constant (11 for CZT and 86 for TiO2), $N_D =$ charge carrier density, $E =$ applied potential, $E_{FB} =$ flat band potential, $K =$ Boltzmann constant, $T =$ temperature.

According to Equation 1, the slope of $1/C^2$ vs. potential plot gives the charge carrier density, $N_D$, from the relation:

$$N_D = \frac{2}{\varepsilon \varepsilon_0 m}$$

(6)

Where $m$ is the slope of the Mott-Schottky plot in the region of interest. A positive slope indicates n-type semiconductor and a negative slope p-type.

### 4.4.2.3 I-V Characteristics

The CZT nanowire arrays grown onto the TiO$_2$ nanotubular template contained a thin Ti metal foil as a back ohmic type contact. The CZT nanowire grown area of 0.7 cm$^2$, was coated with a uniform thin layer of gold by electroless deposition using 5 mM chloroauric acid (HAuCl$_4$) solution, which acted as the top contact. Thin conducting leads were connected to the sample by means of a silver conducting epoxy. The entire configuration of the specimen is referred to as “CZT nanowire composite”. Figure 4.5 shows the schematic of the I-V measurement setup. From the measured resistance, the resistivity of CZT nanowires was calculated using the following formula:

$$\text{Resistivity (}\rho\text{ )} = \frac{(R \times A)}{L}$$

Where $A =$ Area $= 0.7$ cm$^2$:

$L =$ Thickness of the nanowire $= 2 \mu$m $= 2 \times 10^{-4}$ cm

**Silver Epoxy**

![Diagram](image)

**Figure 4.5:** Schematic of I-V characteristics of CZT nanowires.
4.5 Sensing Measurements:
Multiples of the CZT nanowires composite were connected in series and different bias potentials were applied to determine the sensing characteristics with and without exposing to radiation sources. The source used was Am-241 with an energy level of 60 KeV and the intensity of the source was 4μCurie. Figure 4.6 (a) shows the photograph of the stacked CZT nanowire composites in series. Figure 4.6 (b) shows the photograph of the CZT nanowire composite exposed to the source. The source was kept at a distance of 1cm away from the stacked CZT nanowire composite.

Figure 4.6: (a) shows the photograph of the stacked CZT nanowire composites in series. (b) shows the photograph of the CZT nanowire composite exposed to the source.
Chapter 5
Results and Discussion

5.1 Nanoporous TiO$_2$ Template

Figure 5.1 shows the current transient curve which was recorded during a typical anodization process. Large anodic current was measured at the instant of application of anodization potential indicating oxidation of Ti to Ti$^4+$ ions. The anodic current decayed rapidly due to the formation of an oxide layer (Stage 1, Figure 4). Stage 2 corresponds to the surface perturbation and nucleation. Stage 3 corresponds to the pore formation and nucleation. A detailed explanation of the pore formation mechanism, potential and anodizing time has been discussed elsewhere\textsuperscript{80,81}. Figure 5.2 a & b shows the nanoporous morphology of the titanium template. The pore diameter is 70-100 nm and the pore length is approximately 1μm.

After anodization the samples were annealed in oxygen atmosphere at 500°C for 6 hours with a flow rate of 200 SCCM. Annealing was carried out because in the as anodized condition the TiO$_2$ was amorphous in condition and the resistance of the template was not uniform. Figure 5.3 shows the XRD peaks in the as anodized and annealed condition for TiO$_2$. The samples were annealed at slow heating and cooling rate (1°C/min and 2.5°C respectively) so that cracks formed on the TiO$_2$ surface due to thermal stresses can be avoided. Figure 5.4 shows the SEM photograph of the difference in morphology which results due to faster heating and cooling to that of slower heating and cooling.

![Figure 5.1: Current density (A/cm$^2$) during titanium oxide nanotubes formation as a function of time(s). I: Titanium dioxide film formation II: Pore nucleation III: nanotubular oxide growth.](image)
**Figure 5.2:** SEM Micrographs (a) Showing the nanoporous TiO$_2$ with diameter around 70-100nm (b) Cross sectional view showing the length of the tubes (500-800nm).

**Figure 5.3:** XRD peaks in the as anodized and annealed condition for TiO$_2$. A and R represents anatase and rutile phases of the TiO$_2$ nanotubes. The un-marked peaks are from Ti substrate.
Figure 5.4: SEM Micrographs (a) Cracks observed on TiO$_2$ surface due to faster heating and cooling rate (b) TiO$_2$ surface due to slower heating and cooling rate.

5.2 Cyclic Voltammogram (CV)
The reference electrode used for cyclic voltammetry and growth of CZT nanowires was pure Cd and Zn wires. In order to have a comparison of results with the standard values available, the reference electrode potentials were measured with reference to a standard Ag/AgCl electrode. The Cd and Zn wires were immersed in 5mM and 10mM concentrations of their respective chloride salts dissolved in both aqueous and non aqueous solutions. Table 5.1 shows the comparison of reference electrode potentials measured in aqueous and non aqueous solutions at 95°C with reference to Ag/AgCl. It can be observed that in PC solution the reduction potential of Cd$^{2+}$/Cd and Zn$^{2+}$/Zn was about +0.2V and +0.4 V respectively when compared to that of the aqueous solution. Similar results were reported for lithium ions in PC.$^{82}$ Recently Bansal et al.$^{35}$ reported that addition of acetonitrile solution to aqueous salt solution of CZT resulted in the reduction potentials to come closer for Cd, Zn and Te species. In this study the reduction potentials of Cd and Zn were only 100mV apart instead of the reported 360mV. This helps in achieving the stoichiometry much better because at a single pulsing potential both Cd and Zn ions are available for deposition.

Table 5.1: Comparison of reference electrode potentials in aqueous and Propylene Carbonate media with reference to Ag/AgCl at 95°C

<table>
<thead>
<tr>
<th>Solution Media</th>
<th>Potential measured with Cd wire immersed in 5x 10^{-3} M CdCl$_2$ with reference to Ag/AgCl</th>
<th>Potential measured with Zn wire immersed in 10x 10^{-3} M ZnCl$_2$ with reference to Ag/AgCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturated KCl</td>
<td>-620</td>
<td>-942</td>
</tr>
<tr>
<td>Propylene Carbonate</td>
<td>-425</td>
<td>-510</td>
</tr>
</tbody>
</table>

5.2.1 CV on Platinum Substrate at 95°C:
Figure 5.5 shows the results of CV carried out in different non-aqueous solutions on the Pt surface at 95°C. The potentials were measured against a Cd wire immersed in 5 x 10^{-3} CdCl$_2$ in
PC. In the blank run without addition of any salt, the anodic and cathodic current peaks were not observed. This shows that the electrolyte was stable at the potential regions between -1.0V to 1.5 V (Cd). It is reported that PC has an electrochemical window of -2.2 V to +2.3 V (Ag/AgCl). Oxidation of ClO$_4^-$ occurs at potentials above 1.5V (Ag/AgCl). In Cd solution the cathodic current observed below a potential of -0.08V. On the reverse scan anodic peak was observed at 0.22V. This peak is attributed to the stripping of Cd. In Te solution, cathodic current started to occur at potential more negative to +0.9V vs. Cd. In aqueous solutions the reduction potential of the reaction Te$^{4+} + 4e^- \rightarrow$ Te was considered as 0.328V vs. SCE (0.573V vs. NHE) which is about 0.97V more positive than the reduction potential of Cd$^{2+} + 2e^- \rightarrow$ Cd. When considering a six electron reduction process:

\[
\text{Te}^{4+} + 6e^- \rightarrow \text{Te}^2- \quad E_0 = 0.046V_{\text{SCE}} = 0.291V_{\text{NHE}}
\]

This is about 0.7V more positive to that Cd$^{2+}$/Cd reaction. Therefore, the cathodic currents can be attributed to the reduction of Te from the non-aqueous solution. Similarly anodic peaks occurred more positive to 0.7V which corresponded to the reverse reactions:

\[
\text{Te}^2- \rightarrow \text{Te} +2e^- \quad \text{Te} \rightarrow \text{Te}^{4+} + 4e^-.
\]

![Cyclic Voltammogram on platinum electrode](image)

**Figure 5.5:** Cyclic Voltammogram on platinum electrode with only (a)Blank propylene carbonate, (b) 5 x10$^{-3}$ M CdCl$_2$ in propylene carbonate (c) 0.5 x10$^{-3}$ M TeCl$_4$ in propylene carbonate at 95°C.
In CdTe solutions a cathodic current was observed at potentials more negative to +0.9V and at +0.4 V a change in the slope of cathodic current occurred as shown in figure 5.6.

Figure 5.6: Cyclic Voltammogram on platinum electrode with (a) $5 \times 10^{-3}$ M CdCl$_2$+ $0.5 \times 10^{-3}$ M TeCl$_4$ in propylene carbonate at 95°C (b) $5 \times 10^{-4}$ M CdCl$_2$+ $0.5 \times 10^{-4}$ M TeCl$_4$+ $10 \times 10^{-3}$ M ZnCl$_2$ in propylene carbonate at 95°C.

From the current magnitude in comparison with that of Te solution, it can be suggested that only pure Te deposited at potentials between +0.9V and +0.5 V. At potentials between 0.5 V and 0V vs. Cd, it is suggested that there is under potential deposition of Cd in addition to the deposition of Te. Formation of CdTe compound cannot be ruled out because of favourable free energy conditions. A plateau current could be observed at potentials between 0 and -0.2V. The plateau region indicates slower kinetics of deposition at these potentials, which could be attributed to the competition for adsorption sites between CdTe and Cd. The mechanism of CdTe deposition can be suggested as occurrence of the following two reactions:

\[ \text{Te} + 2e^- \rightarrow \text{Te}^2^- \]
\[ \text{Cd}^+ + \text{Te}^2^- \rightarrow \text{CdTe} \]
At potentials more negative to 0 V, the Cd$^{2+}$ ions also compete for electrons for electro reduction reaction of Cd$^{2+}$+2e$^-$ → Cd. Therefore there was a current plateau with increase in potential. At more negative potentials, the cathodic increased with steeper slope which could be attributed to additional deposition of Cd along with CdTe.

Reversing the CV sweep in anodic direction resulted in two faint peaks at +0.26V and +0.5V. The first peak was similar to the anodic stripping of Cd observed in pure Cd solution and the second peak could be labelled as the dissolution of Cd from the CdTe compound lattice. Third anodic peak at more positive potential than 0.66V is attributed to the stripping of Te.

Cyclic voltammetry in CdZnTe solutions was more or less similar to the results of CdTe as shown in figure 5.6. The initial cathodic current waves were similar to that of CdTe indicating that at more positive potentials only Te got reduced and at less positive potentials deposition of CdTe occurred in spite of Zn addition in the solution. When the potential was more negative than 0V vs. Cd, almost similar plateau region was observed as observed in the case of CdTe solution. However, the cathodic current increased at less cathodic potentials in CZT solutions as compared to that in CdTe solution, indicating possible compound formation at much positive potential with reference to the reduction potential of Zn. From the values of free energy of CdTe (-92KJ/mol) and ZnTe (-141.6KJ/mol) it can be argued that free energy of formation of CZT lies between these values. Therefore, the increased cathodic current at lower cathodic potentials (as compared to that of CdTe solution) could be because of additional reduction of Zn to form a CdZnTe compound which required 8 electrons in total. During anodic sweep, 3 anodic peaks were observed as in the case of CdTe. The peak current potentials were shifted positively as compared to that of CdTe stripping.

Significant similarities were observed between CV of CdTe and ZnTe as shown in Figure 5.7 (a) & (b). The CV in ZnTe solution was carried out with reference to a Zn wire reference electrode. When calibrated against Ag/AgCl reference electrode the potential of Zn wire reference electrode was -0.515 V about 90 mV negative to that of Cd wire reference electrode. The cathodic reduction wave of ZnTe was observed at -0.274 V Zn (-0.364 V against Cd). The reduction wave of CdTe also was observed in the vicinity of this potential as shown in Fig 5.7 (a) indicating that both CdTe and ZnTe could deposit simultaneously. Similar to that of CdTe deposit, ZnTe also revealed two anodic stripping peaks at 0.15 V and 0.57 V vs. Zn. In case of CdTe the anodic peaks were at 0.26 and 0.5 V vs. Cd. Converting these potentials to Zn scale, it can be observed that the first anodic peak of ZnTe was about 0.2 V negative to that CdTe stripping; whereas, the second anodic peak of ZnTe almost coincided with the second anodic peak of CdTe. Figure 5.7 (c) shows the CV of CZT with varying amounts of Te. It can be seen from the CV that as the Te content increases we can see that there is only one anodic stripping taking place, which corresponds to tellurium deposition. The CV of 0.5mM Te CZT almost follows the CdTe CV having 5mMCd and 0.5mMTe.
Figure 5.7(a): Cyclic Voltammogram on platinum electrode in propylene carbonate with 0.5 \( \times 10^{-3} \) M TeCl\(_4\) + varying amounts of CdCl\(_2\) from 1 \( \times 10^{-3} \) M to 8 \( \times 10^{-3} \) M at 95°C.

Figure 5.7(b): Cyclic Voltammogram on platinum electrode in propylene carbonate with 0.5 \( \times 10^{-3} \) M TeCl\(_4\) + varying amounts of ZnCl\(_2\) from 1 \( \times 10^{-3} \) M to 25 \( \times 10^{-3} \) M at 95°C.
5.2.2 CV on TiO₂ substrate at 95°C

When the CV was carried out on anodized TiO₂ surface, not much difference was observed with the behaviour of cathodic current waves. However, the anodic behaviour was quite different with TiO₂ nanoporous surface. In TiO₂ surface only one anodic peak was observed, which occurred at 0.34V (Cd²⁺/Cd). This peak can be similar to the first anodic peak observed on Pt surface at 0.39V.

In order to understand the origin of the anodic strip, CV was carried out in CdZnTe solutions on TiO₂ surface by switching the scan directions at various potentials. When the forward (Cathodic potential) was switched (reversed) after reaching +0.3V and -0.4V, no specific anodic peak current was observed as shown in figure 5.8 (a) and (b). However there was dissolution as anodic currents were observed at potentials more than 0.5V. The dissolved species could be CZT compound and Te. When the anodic polarization extended till 1.5V (Cd²⁺/Cd), a rise in anodic current was observed at potential more positive to 1.2V in case of +0.3V switching potential. For -0.7V switching potential (Fig 5.8 (b)) the anodic peak occurred at 0.215V and no other anodic peaks were observed.

In porous surface, initially the deposition takes place deep inside the nanopores. During anodic sweep, the material deposited on the surface dissolves (strips first) followed by the dissolution of the material inside the pores. Therefore, for the sample with -0.7V switching potential (Fig 5.8(a)), material deposited at more negative potentials dissolved first showing a peak. The dissolved species could be predominantly Cd and Zn. As tellurium deposited first within the
nanopores, its dissolution was not observed till the potential was more positive than 0.9V with some over potential. Therefore it dissolved only above 1.2V, as observed in figure 5.8(a).

**Figure 5.8(a):** Cyclic Voltammogram on anodized TiO$_2$ electrode in propylene carbonate with 5 x 10$^{-3}$ M CdCl$_2$ + 10 x 10$^{-3}$ M ZnCl$_2$ + 0.5 x 10$^{-3}$ M TeCl$_4$ and reversing the potentials at -0.7V and +0.3V at 95°C.
Figure 5.8(b): Cyclic Voltammogram on anodized TiO$_2$ electrode in propylene carbonate with $5 \times 10^{-3}$ M CdCl$_2$ + $10 \times 10^{-3}$ M ZnCl$_2$ + $0.5 \times 10^{-3}$ M TeCl$_4$ and reversing the potentials at -1V and -0.4V at 95°C.

The observations are further supported by considering the anodic scans after different holding times at different constant cathodic potentials in CdZnTe solution. Figure 5.9(a) illustrates the anodic stripping characteristic of film deposited on TiO$_2$ at -0.7V at different times. With increase in holding time the anodic peak current decreased and the corresponding peak potentials shifted to less positive potentials. This increased peak current at shorter holding time could be attributed to the adhesion characteristics of the deposited film. It is possible that at when the potential was maintained for longer time the adsorbed species rearrange to form a better adhered film. In general, Ti substrate is considered to be superior for electrodeposition of group II-VI chalcogenide thin films because of better adhesion properties. Otherwise, observations of thermal evaporation of CZT thin film indicated very low sticking coefficient of Zn. Similarly Ernst et al. reported low adsorption characteristics of Zn in aqueous solutions. Observations of this present study suggest that lower cathodic potential (-0.7 V) required longer holding time for better adhesion characteristics. Further, occurrence of anodic current at negative potentials with increased holding time indicates stripping of Zn or ZnTe. Typical composition of the film deposited at -0.7 V was 43% Cd, 3% Zn and balance Te. Whereas the film deposited at -1.0 V showed increased Zn content (~20%) and less Cd (~30%). Figure 5.9(b) shows the anodic stripping characteristic of the film deposited at -1.0 V with different holding times. At more negative potentials, increased holding time increased the anodic peak current and shifted the peak potential to more positive values. Occurrence of a single large anodic peak and anodic peak
potential shift to noble values could be attributed to the formation of a uniform CZT film at more negative potentials. Chemical analysis of thin films (using energy dispersive X-ray) deposited from non-aqueous solutions during CV tests and potential pulse depositions showed uniform presence of Zn content.
Figure 5.9(b): Cyclic Voltammogram on anodized TiO$_2$ electrode with propylene carbonate + $5 \times 10^{-3}$ M CdCl$_2$ + $10 \times 10^{-3}$ M ZnCl$_2$ and $0.5 \times 10^{-3}$ M TeCl$_4$ by applying -1V for different holding times and reversing the potential to +1V at 95°C.

5.2.3 CV on TiO$_2$ substrate at 130°C
CV was conducted using a nanoporous TiO$_2$ surface in the PC solution at 130°C. The reaction kinetics at the operating temperature of 130°C has been studied. Table 5.2 shows the open circuit potentials of pure Cd and Zn wires immersed in 5 and 10mM concentrations of their chloride salt solutions measured with reference to Ag/AgCl electrode at a temperature of 130°C. The equilibrium potential of Cd$^{2+}$/Cd and Zn$^{2+}$/Zn in PC was about +0.285 V and +0.55 V more positive respectively than the values reported in the aqueous solution. In addition to this, the equilibrium potential of zinc was only 55 mV less than that of cadmium when compared to 100mV difference observed at 95°C (Table 5.1).

Table 5.2: Reference electrode potentials in Propylene Carbonate media with reference to Ag/AgCl at 130 ºC.

<table>
<thead>
<tr>
<th>Solution Media</th>
<th>Potential measured with Cd wire immersed in $5 \times 10^{-3}$ M CdCl$_2$ with reference to Ag/AgCl</th>
<th>Potential measured with Zn wire immersed in $10x \times 10^{-3}$ M ZnCl$_2$ with reference to Ag/AgCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propylene Carbonate</td>
<td>-335mV</td>
<td>-390mV</td>
</tr>
</tbody>
</table>
The more positive equilibrium potentials at higher temperature indicated that for a given cathodic applied potential the over potential available for reduction to take place was more. This ensured higher cathodic current density and increased deposition rate. Further, the narrowed gap between the equilibrium potentials of different species at high temperature indicated a better control over the stoichiometry during a single potential electrodeposition step. The potential pulses were applied with reference to Cd/Cd$^{2+}$ reference electrode. As the equilibrium potential of Zn/Zn$^{2+}$ in the PC solution was -0.055 V vs. Cd/Cd$^{2+}$, reduction of Zn would occur below this potential.

Figure 5.10 shows the CV reversed at various cathodic switching potentials. CV was carried out by switching the potential sweep direction at different negative potentials. Initially the potential sweep was carried out in the cathodic direction from positive to negative potential and then switched back to the anodic direction. From figure 6 it can be seen that the cathodic current increased with increase in the negative potential. For -0.4 V switching potential, the first anodic peak was not that predominant as observed in the case of -0.7 and -1 V switching potentials. In the case of -0.4 V and -0.7 V switching potentials, two more anodic peaks occurred at around +0.8V and +1.2 V. The peak at +0.8 V can be attributed to the dissolution of tellurides. The peak at +1.2 V can be attributed to the dissolution of elemental Te. In the case of -1 V switching potential, a single large anodic current wave occurred between +0.7 V to 1.5 V. This could be attributed to the dissolution of telluride compounds in addition to the elemental Te.

Table 5.3 shows the compositions obtained at various switching potentials. The concentration of Cd increased and Te content decreased in the deposit when the switching potentials became more negative. Interestingly, there was no significant change in the Zn content. Presence of Zn containing deposits even at high positive potentials could be attributed to the induced co-deposition phenomenon because of possible complex formation with the propylene carbonate.
Figure 5.10: Cyclic Voltammogram on anodized TiO$_2$ electrode in propylene carbonate with 5 x 10$^{-3}$ M CdCl$_2$ + 10 x 10$^{-3}$ M ZnCl$_2$ + 0.5 x 10$^{-3}$ M TeCl$_4$ and reversing the potentials at -1.0V, -0.7V and -0.4V at 130 ºC.

Table 5.3: Composition of Cadmium, Zinc and Tellurium when the CV was reversed at different switching potentials at 130°C

<table>
<thead>
<tr>
<th>Potential Switching</th>
<th>Cadmium Composition in Atomic %</th>
<th>Zinc Composition in Atomic %</th>
<th>Tellurium Composition in Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CV reversed at -1 V</td>
<td>40</td>
<td>5</td>
<td>55</td>
</tr>
<tr>
<td>CV reversed at -0.7 V</td>
<td>32</td>
<td>4</td>
<td>64</td>
</tr>
<tr>
<td>CV reversed at -0.4 V</td>
<td>15.5</td>
<td>3.5</td>
<td>81</td>
</tr>
<tr>
<td>CV reversed at 0 V</td>
<td>16</td>
<td>3</td>
<td>81</td>
</tr>
<tr>
<td>CV reversed at +0.3 V</td>
<td>18</td>
<td>2</td>
<td>80</td>
</tr>
<tr>
<td>CV reversed at +0.7 V</td>
<td>6</td>
<td>2</td>
<td>92</td>
</tr>
</tbody>
</table>

In order to understand the dissolution behaviour during anodic sweep, a constant cathodic potential of -0.7V was applied for 60 and 300sec and then the anodic stripping was carried out by reversing the potential from -0.7 V to +1.5V. Figure 5.11 shows the anodic stripping behaviour after holding the potential at -0.7V for different times. It is observed that the increased holding time increased both the anodic dissolution current as well as shifted the peak potential to more
positive values. The increase in the second anodic peak can be attributed to CdTe dissolution or Te. This was further verified by conducting the anodic stripping till the first and second anodic peak potentials after applying a potential of -0.7V for different holding times. Table 5.4 shows the composition obtained by reversing the CV till the occurrence of the first and second anodic peaks after applying -0.7V for different holding times. Increasing the holding time at -0.7V increased the Cd content at the expense of Te. The composition of the deposit obtained by interrupting the CV at the first anodic peak showed decreased Cd content and increased Te content. The decrease in the Cd content could be attributed to anodic dissolution of Cd compound or preferential leaching of Cd from the deposit. In spite of the predominant anodic current, increase in Te was observed in the remnant deposit. The same increasing trend of Te concentration was observed after the second anodic peak also. These results could be attributed to the deposition of elemental tellurium at the positive potentials. It should be noted that the redox potential of Te/Te$^{4+}$ is about 0.97 V vs. Cd/Cd$^{2+}$. Therefore, reduction of Te could occur during dissolution of Cd and Zn compounds. When the CV was interrupted at the second anodic peak potential, it resulted in decrease in composition of Cd and increase in Zn (Table 5.4).

![Cyclic Voltammogram on anodized TiO$_2$ electrode in propylene carbonate with 5 x 10$^{-3}$ M CdCl$_2$ + 10 x 10$^{-3}$ M ZnCl$_2$ + 0.5 x 10$^{-3}$ M TeCl$_4$ by applying a potential, -0.7V for different holding times and reversing the potential to +1.5V at 130 °C.](image)

**Figure 5.11:** Cyclic Voltammogram on anodized TiO$_2$ electrode in propylene carbonate with 5 x 10$^{-3}$ M CdCl$_2$ + 10 x 10$^{-3}$ M ZnCl$_2$ + 0.5 x 10$^{-3}$ M TeCl$_4$ by applying a potential, -0.7V for different holding times and reversing the potential to +1.5V at 130 °C.
Table 5.4: Composition of Cadmium, Zinc and Tellurium at -0.7V for different holding times and as well as when reversed till different anodic peaks

<table>
<thead>
<tr>
<th></th>
<th>Cadmium composition in atomic %</th>
<th>Zinc composition in atomic %</th>
<th>Tellurium composition in atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.7 V for 60sec</td>
<td>68</td>
<td>3</td>
<td>29</td>
</tr>
<tr>
<td>-0.7 V for 300sec</td>
<td>78</td>
<td>2</td>
<td>20</td>
</tr>
<tr>
<td>-0.7 V for 300sec and reversed till 1\textsuperscript{st} anodic peak</td>
<td>67</td>
<td>3</td>
<td>29</td>
</tr>
<tr>
<td>-0.7V for 300sec and reversed till 2\textsuperscript{nd} anodic peak</td>
<td>54</td>
<td>3</td>
<td>43</td>
</tr>
</tbody>
</table>

5.3 Growth of CZT Nanowires:
The cyclic voltammogram carried out, helped in determining the deposition potentials for the growth of the CZT nanowires. The potentials for deposition and time of each pulse were determined by a series of trial experiments. Only the optimized results are reported here. Each pulsing cycle consisted of two cathodic, two anodic and an open circuit potential (as shown in figure 4.4). At the open circuit potential, the ionic concentration gradient would be relaxed at the electrode interface. In order to understand the nucleation of the Cadmium Zinc Telluride crystals during pulsed reverse electrodeposition, pulsing cycles were initially carried out onto a glassy carbon substrate. Nucleation of CZT occurred uniformly over the entire surface during the first few pulse cycles and the nucleation number density remained almost a constant during subsequent cycles. Figure 5.12 (a)-(c) show the atomic force microscopic images of the CZT nucleation and growth after applying 3, 5 and 10 pulse cycles onto a glassy carbon substrate. No preferential crystallographic planes could be observed during the initial growth process. However, the growth in the radial direction was limited and certain nuclei preferred grow in the axial direction as observed in figure 5.12 (c).
(a) 3 cycles of CZT deposition  (b) 6 cycles of CZT deposition  (c) 10 cycles of CZT deposition

**Figure 5.12:** Atomic force microscopic views of the CZT nuclei on the glassy carbon after (a) 3 pulse-cycles, (b) 6 pulse cycles and (c) 10 pulse cycles. One deposition cycle contained two cathodic pulses at -0.6V for 1 sec, -0.7V for 1 sec two anodic pulses at +0.3 for 3 sec, +0.7 V for 5 sec and open circuit potential for 3 sec.

Table 5.5 shows the variation of the composition of the CZT nuclei with number of pulse cycles. The values are average of five samples analyzed at different locations by energy dispersive X-ray analysis. The Te content of the nuclei did not vary much throughout the electrodeposition process. During the initial pulse cycles, the Zn and Cd contents varied considerably. However after 10 cycles, the composition was almost stabilized.

**TABLE 5.5:** Chemistry of the CdZnTe nuclei after different number of pulse cycles

<table>
<thead>
<tr>
<th>Number of Pulse cycles</th>
<th>Composition of the CZT nuclei</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cd</td>
</tr>
<tr>
<td>3 cycles</td>
<td>43.8</td>
</tr>
<tr>
<td>6 cycles</td>
<td>35.2</td>
</tr>
<tr>
<td>10 cycles</td>
<td>41.1</td>
</tr>
<tr>
<td>100 cycles</td>
<td>44.6</td>
</tr>
<tr>
<td>300 cycles</td>
<td>46.1</td>
</tr>
</tbody>
</table>

The following experiment showed that the pulsing cycle resulted in almost exact stoichiometry right from the beginning of the pulse cycle.

5.3.1 Growth Mechanism of the CZT nanowires:
Figure 5.13 shows the TEM image of the CZT nanowire grown from inside the nanoporous TiO$_2$ template. When a cathodic potential was pulsed, the nucleation of CZT crystal was predicted to occur at the bottom of the nanotubes rather at the top. This hypothesis was based on the potential drop occurring across the oxide layer. TiO$_2$ nanotubes showed a higher electrical resistivity after annealing in the oxygen atmosphere. Therefore, a potential gradient existed under electrical polarization as schematically illustrated in figure 5.14. At the bottom of the pore, the potential
loss would be minimal because of a thinner barrier layer. At the top surface only a less over potential would be available, diminishing the chances of cathodic reduction reaction to take place. When a cathodic potential was pulsed for a short time, Cd$^{2+}$, Zn$^{2+}$, Te$^{4+}$ ions were electrostatically attracted to the bottom surface of the nanotubes because of more negative potential available at these sites. Therefore, preferential nucleation of CZT was expected at the bottom of the nanotubes.

![TEM image showing the growth of the CZT nanowires from inside the nanotubular TiO$_2$ nanotubes](image)

**Figure 5.13:** TEM image showing the growth of the CZT nanowires from inside the nanotubular TiO$_2$ nanotubes

**Figure 5.14:** Schematic illustration of potential drop across the TiO$_2$ nanotubes because of the high electrical resistance of the oxide film which results in CZT nucleation preferentially from the bottom of the pores.

### 5.3.2 Morphology of CZT Nanowires

Figure 5.15 shows the CZT nanowires after 45 minutes of pulse deposition. The diameter of the wires was 70 to 100 nm and the length was approximately around 2μm (Figure 5.15). It was also observed that the wire growth was initially straight from the nanoporous template and as the deposition time increased they started to get tangled. The tangling of nanowires can be attributed to over growth and to the insufficient length of the nanotubes.
5.3.3 EDAX Analysis:
Table 5.6 shows the compositions of CZT nanowires obtained at different deposition conditions. In these experiments, only the cathodic potentials were varied and other parameters such as anodic potentials and pulse time for each potential step were kept as constants. From the table it is seen that when the cathodic potential becomes more negative it results in the deposition of more zinc, whereas when the deposition potential is less negative it results in the deposition of more zinc and less tellurium.

Table 5.6: Comparison of Chemical Composition of CZT obtained at different cathodic potentials (The anodic potential pulses were kept constant).

<table>
<thead>
<tr>
<th>Cathodic Potentials</th>
<th>Cadmium composition in atomic %</th>
<th>Zinc composition in atomic %</th>
<th>Tellurium composition in atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.4V for 1sec -0.6 V for 1sec</td>
<td>48-49</td>
<td>1-2 (for solar cell applications)</td>
<td>50</td>
</tr>
<tr>
<td>-0.6 V for 1sec -0.7 V for 1sec</td>
<td>45-46</td>
<td>4-5 (Detector Grade Material)</td>
<td>50</td>
</tr>
<tr>
<td>-1.0 V for 1sec -1.2 V for 1sec</td>
<td>40-42</td>
<td>10-12</td>
<td>48</td>
</tr>
</tbody>
</table>
5.3.4 Compound analysis through XRD

The nanowires deposited were analyzed by XRD after annealing in argon at 350°C for 1 h. In the annealed conditions, the CZT peaks show up more prominently when compared to the as-deposited condition. Figure 5.16 (a) shows the XRD peaks of the CZT nanowires corresponding to Cd$_{0.96}$Zn$_{0.04}$Te. Figure 5.16(b) shows the XRD peaks of the CZT nanowires corresponding to Cd$_{0.90}$Zn$_{0.10}$Te.

Figure 5.16 (a): XRD peaks of the CZT nanowires corresponding to Cd$_{0.96}$Zn$_{0.04}$Te.
Figure 5.16 (b): XRD peaks of the CZT nanowires corresponding to Cd$_{0.9}$Zn$_{0.1}$Te.

5.3.5 TEM Analysis:
Figure 5.17 (a) shows the TEM image of an individual nanowire. The length of the nanowire was about 550 nm which was shorter than that observed in SEM. This could be attributed to the breakage of nanowires during ultrasonication. However, the diameter of the nanowire was 70 nm, similar to that observed in SEM. Figure 5.17 (b) shows the HRTEM for a Cd$_{0.9}$Zn$_{0.1}$Te nanowire. The HRTEM image shows that the lattice fringe is approximately 0.22 nm which matches with the theoretical value of 0.229 nm for the (2 2 0) plane.\textsuperscript{15} The dark regions in the HRTEM could be attributed to the carbon species from the propylene carbonate solution. The TEM image shows that the CZT nanowires are polycrystalline.
Figure 5.17: (a) TEM micrograph showing the CZT nanowire along with the diffraction pattern showing the crystallinity of the wire. Wire length = 550 nm and width = 70 nm (b) HRTEM of CZT nanowire along with the diffraction pattern

Figure 5.18 shows the STEM image of the as deposited CZT nanowire cluster and X-ray elemental mapping of Cd, Zn and Te of the cluster. Almost a uniform distribution of the elements could be observed in the nanowires. This showed that pulsed electrodeposition resulted in uniform stoichiometry along the entire length of the nanowire.
Figure 5.18: STEM image of the as deposited CZT nanowire and X-ray elemental mapping of Cd, Zn and Te on the nanowire

5.4 Electrical Characterization:

5.4.1 Band Gap Analysis:

Figure 5.19 shows the band gap measured for different stoichiometry of the CZT nanowires. Table 5.7 compares the measured value of the band gap with the value calculated using the expression proposed by Tobin et al.:

\[ E_g = 1.5045 + 0.631X + 0.128X^2 \]

From the table it can be seen that the experimental and the calculated value of the band gap of the Cd\(_{1-x}\)Zn\(_x\)Te for different values of x were almost the same. The absorption at 400nm is attributed to the TiO\(_2\) nanotubular template.
Figure 5.19: Absorption spectrum of the Cd$_{1-x}$Zn$_x$Te nanowires with $x=0.04$, $x=0.1$ and $x=0.2$ TiO$_2$ nanotubular template derived from the diffusive reflectance UV-VIS spectroscopy measurements. The 400 nm absorbance was due to the TiO$_2$ anatase.

Table 5.7: Comparison of Band Gap of Cd$_{1-x}$Zn$_x$Te for different values of $x$ experimentally and using the expression proposed by Tobin et al.\cite{26}.

<table>
<thead>
<tr>
<th>Composition of CZT nanowires</th>
<th>Experimental Band Gap</th>
<th>Band Gap Calculated using the expression $E_g=1.5045 + 0.631X + 0.128X^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd$<em>{0.96}$Zn$</em>{0.04}$Te</td>
<td>absorption at 815 nm 1.521 eV</td>
<td>1.529 eV</td>
</tr>
<tr>
<td>Cd$<em>{0.9}$Zn$</em>{0.1}$Te</td>
<td>absorption at 788 nm 1.575 eV</td>
<td>1.5686 eV</td>
</tr>
<tr>
<td>Cd$<em>{0.8}$Zn$</em>{0.2}$Te</td>
<td>absorption at 771 nm 1.608 eV</td>
<td>1.63 eV</td>
</tr>
</tbody>
</table>

5.4.2 Mott-Schottky Analysis
Figure 5.20 shows the Mott-Schottky analysis carried out on TiO$_2$ template at 3000HZ in 0.5M H$_2$SO$_4$ solution (pH=0.5). Positive slope of the potential vs. $1/C^2$ (Mott-Schottky) plot indicates that the TiO$_2$ nanotubular template is an n-type semiconductor which is the typical behavior of TiO$_2$ nanotubes. Figure 5.21 (a), (b) and (c) shows the Mott-Schottky plots of the Cd$_{1-x}$Zn$_x$Te nanowire with $x=0.04$, $x=0.1$ and $x=0.2$ respectively. Irrespective of the Zn content p-type
semiconductivity was observed from the Mott-Schottky plots (negative slope). p-type semiconductivity has been reported for Cd$_{1-x}$Zn$_x$Te semiconductors when $x > 0.07$ by other investigators. In this present investigation, Cd$_{0.96}$Zn$_{0.04}$Te also indicated p-type semiconductivity. Transition in type of semiconductivity was attributed to the increase in Cd vacancies and presence of ionized Te atoms located in Cd vacancies as Te$_{Cd}^+$ or Te$_{Cd}^{2+}$. In this investigation, both cathodic and anodic potentials were applied for controlled growth of nanowires. Application of anodic potentials such as 0.7 and 0.3V resulted in dissolution of species; particularly Cd. Observations of CV indicated that at 0.3V, Te could still be reduced. Therefore, it is possible that at anodic potentials Cd dissolved creating Cd vacancies and these vacancies could have been occupied by Te, inducing conditions for p-type conductivity. Table 5.8 summarizes the carrier density for different composition of Cd$_{1-x}$Zn$_x$Te nanowires.

Figure 5.20: Mott-Schottky plot of TiO$_2$ nanotubular template. The semiconducting behaviour was n-type with a charge carrier density of $5.47 \times 10^{18}$ cm$^{-3}$. 
Figure 5.21 (a): Mott-Schottky plot of Cd$_{0.96}$Zn$_{0.04}$Te nanowires grown onto TiO$_2$ nanotubular template. The semiconducting behaviour was p-type with a charge carrier density of 1.96 x 10$^{15}$ cm$^{-3}$.

Figure 5.21 (b): Mott-Schottky plot of Cd$_{0.9}$Zn$_{0.1}$Te nanowires grown onto TiO$_2$ nanotubular template. The semiconducting behaviour was p-type with a charge carrier density of 4.29 x 10$^{13}$ cm$^{-3}$.
Figure 5.21 (c): Mott-Schottky plot of Cd$_{0.8}$Zn$_{0.2}$Te nanowires grown onto TiO$_2$ nanotubular template. The semiconducting behaviour was p-type with a charge carrier density of $9.28 \times 10^{12}$ cm$^{-3}$.

Table 5.8: Charge carrier density of Cd$_{1-x}$Zn$_x$Te for different values of x determined from the Mott-Schottky Plot.

<table>
<thead>
<tr>
<th>Composition of CZT nanowires</th>
<th>Carrier Density /cm$^3$ of holes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd$<em>{0.96}$Zn$</em>{0.04}$Te</td>
<td>$1.96 \times 10^{15}$</td>
</tr>
<tr>
<td>Cd$<em>{0.9}$Zn$</em>{0.1}$Te</td>
<td>$4.29 \times 10^{13}$</td>
</tr>
<tr>
<td>Cd$<em>{0.8}$Zn$</em>{0.2}$Te</td>
<td>$9.28 \times 10^{12}$</td>
</tr>
</tbody>
</table>

5.4.3 I-V Characteristics

Figure 5.22 (a), (b) and (c) shows the I-V characteristics of the Cd$_{1-x}$Zn$_x$Te nanowire with x=0.04, x=0.1 and x=0.2 respectively. Rectifying behavior was observed during the negative bias for all the composition of x of the CZT nanowires. The rectifying behavior is attributed to the p-n junction formed between the CZT nanowire and the TiO$_2$ nanotubular template. Therefore an increased negative bias is needed to cross the barrier which is formed by the p-n junction. Resistance is calculated by taking the inverse slope of the I-V characteristics curve. Table 5.9 shows the resistivity obtained for different composition of Cd$_{1-x}$Zn$_x$Te nanowires. It is well documented that for high resistivity CZT material, the shallow level donors and acceptors should be well compensated and the Fermi level should be pinned at the center of the band gap. It’s observed from the table that the resistivity increased as the concentration of x increased in the CZT nanowire. With increase in Zn concentration the density of V$_{Cd}$ increases and that of Te$_{cd}$ decreases because of the reduction in the lattice parameter. Thus when Zn concentration
increases in the CZT, it could lead to uncompensated acceptors which can act as traps. The increase in resistivity with increase in Zn can be attributed to the pulsed potentials which have been employed during the growth of CZT nanowires. The pulse potentials which was employed during the growth of nanowires could be compensating the charges at $x=0.1$, but as the concentration of Zn increases towards $x=0.2$ Zn there might be uncompensated deep level acceptors which are created due to $V_{Ca}$. This is supported by Mott-Schottky analysis which showed that as the concentration of Zn increased from 0.1 to 0.2, the carrier density of holes decreased which could be attributed to the deep level traps. Table 5.10 shows the mobility of holes calculated using the following relation:

$$\mu_h = \frac{1}{Rqn}$$

Where $\mu_h =$ mobility of the holes (cm$^2$/V-s)
$R =$ resistance of the nanowire
$n =$ charge carrier density
$q =$ elementary charge ($1.6\times10^{-19}$ Amp/S or Coulomb)
$d =$ thickness of the nanowire (2 microns)

Also its been reported that depending on the energy level of the deep level defects the resistivity of the material changes for the same composition as shown in figure 5.23. Thus its necessary to know the type of defect level as well as the concentration of the defect so that the pulsed potentials can be varied accordingly to achieve a high resistive material by pinning the Fermi level at the center of the band gap as well increasing the charge transport for faster charge collection.

**Figure 5.22 (a):** I-V Characteristics of Cd$_{0.96}$Zn$_{0.04}$Te nanowires grown onto TiO$_2$ nanotubular template.
Figure 5.22 (b): I-V Characteristics of Cd$_{0.9}$Zn$_{0.1}$Te nanowires grown onto TiO$_2$ nanotubular template.

Figure 5.22 (c): I-V Characteristics of Cd$_{0.9}$Zn$_{0.1}$Te nanowires grown onto TiO$_2$ nanotubular template.
Table 5.9: Resistance and Resistivity values of Cd$_{1-x}$Zn$_x$Te for different values of x calculated from the I-V characteristics

<table>
<thead>
<tr>
<th>Composition of CZT nanowires</th>
<th>Resistance (Ω)</th>
<th>Resistivity Ω-cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd$<em>{0.96}$Zn$</em>{0.04}$Te</td>
<td>$0.36 \times 10^6$</td>
<td>$1.26 \times 10^9$</td>
</tr>
<tr>
<td>Cd$<em>{0.9}$Zn$</em>{0.1}$Te</td>
<td>$79 \times 10^9$</td>
<td>$2.76 \times 10^{11}$</td>
</tr>
<tr>
<td>Cd$<em>{0.8}$Zn$</em>{0.2}$Te</td>
<td>$3.45 \times 10^9$</td>
<td>$1.206 \times 10^{13}$</td>
</tr>
</tbody>
</table>

Table 5.10: Mobility of holes of Cd$_{1-x}$Zn$_x$Te for different values of x

<table>
<thead>
<tr>
<th>Composition of CZT nanowires</th>
<th>Mobility of holes cm$^2$/V-s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd$<em>{0.96}$Zn$</em>{0.04}$Te</td>
<td>4400</td>
</tr>
<tr>
<td>Cd$<em>{0.9}$Zn$</em>{0.1}$Te</td>
<td>922</td>
</tr>
<tr>
<td>Cd$<em>{0.8}$Zn$</em>{0.2}$Te</td>
<td>98</td>
</tr>
</tbody>
</table>

Figure 5.23: Calculated resistivity for x = 0.12 as a function of $E_A$, showing that the maximum resistivity is predicted at $0.47 \cdot E_g^{ss}$.

5.5 Sensing Measurements:
The sensing behaviour of the nanowire was studied only for the widely used detector grade composition which is Cd$_{0.9}$Zn$_{0.1}$Te. Figure 5.24 (a), (b) and (c) shows the sensing behavior of the CZT nanowire composite arrays for 3, 5 and 8 stacks when exposed to Americium-241 source having energy level of 60KeV and intensity of 4μCurie. The applied bias voltage varied from 0.4V to 4 V depending on the stacks. The sensitivity of the nanowire composite arrays increased with respect to the number of stacks. Table 5.11 shows the average of the sensitivity values with respect to the number of stacks of the nanowire composite. Sensitivity was calculated by taking
ratio of the difference in current after and before exposing to radiation source to that of the current before exposing to radiation source. The spikes in the response to the CZT nanowire arrays could be attributed to the trapping of charges due to the presence of deep level defects which are created during the anodic pulses. The deep level defects which compensate the charges of the shallow level defects can act as trapping sites and can degrade the detector performance. Figure 5.25 shows the electron and hole trap decay time of the CdZnTe with respect to the trap thermal ionization energy at room temperature. It can be seen from the plot that the shallow level traps can be detrapped at much shorter time when compared to that of the deep level traps. Although deep level defects are needed for pinning the Fermi level at the center of the band gap their by increasing the resistivity of the CZT, they can also act as trapping sites which could hamper the detection measurement. Hence the best detector material can be obtained only by having the concentration of deep level traps to a minimum value. Thus knowing the energy level of the deep defects and concentration becomes an important aspect to achieve a suitable detector material.

Figure 5.24 (a): Sensing response of 3 stacked arrays of CZT nanowire composite.
Figure 5.24 (b): Sensing response of 5 stacked arrays of CZT nanowire composite.
Figure 5.24 (c): Sensing response of 8 stacked arrays of CZT nanowire composite.

Table 5.11 Sensitivity of \( \text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te} \) nanowire composites with different stacks

<table>
<thead>
<tr>
<th>Number of Stacks</th>
<th>Sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.77</td>
</tr>
<tr>
<td>5</td>
<td>0.92</td>
</tr>
<tr>
<td>8</td>
<td>1.35</td>
</tr>
</tbody>
</table>

Figure 5.25: Electron and Hole decay time vs. trap thermal ionization energy at room temperature for CZT.

In order to show that the pulsed electrodeposition growth of nanowires results in high resistivity as well as uniform stoichiometry, thin films of CZT having the same detector quality composition of \( x=0.1 \) was prepared by constant potential deposition. The concentration and the temperature used for deposition was similar to the one which was used for nanowire growth except that the films were grown at constant potential of -0.7 V for 30 mins. The substrate used was \( \text{TiO}_2 \) thin films. Figure 5.26 shows the SEM photograph of the CZT thin films. Figure 5.27 shows the XRD plot of the thin film CZT. From the XRD plot it can be seen that the composition of the thin film is not uniform. It has peaks corresponding to CdTe also.
Figure 5.26: SEM micrograph of thin film of CZT after 30 minutes of constant potential electrodeposition.

Figure 5.27: XRD peaks of the CZT thin films grown on TiO$_2$ thin film

The resistivity measured in the case of thin films was 1.51x10$^8$Ω-Cm. This is 3 orders of magnitude less than that of the one obtained for CZT nanowire having same composition. The
decrease in resistivity of the thin films can be attributed to the non uniform stoichiometry. 3 stack arrays of thin films of CZT were prepared in the similar manner as to that of the nanowire arrays and were tested for sensing response using the same source Am-241 at 1V. Figure 5.28 (a) shows the sensing response of the thin film array with respect to 1 V. The response at 1V was smaller when compared to that of the nanowire arrays and the sensitivity was only 0.06.

![Graph](image)

**Figure 5.28 (a):** Sensing response of 3 stacked arrays of CZT Thin films at 1V.

Thus the initial experiments of the growth of CZT nanowires using pulsed electrodeposition showed promising results for detection of low energy gamma ray detection. But it needs further understanding of the energy level of the deep defects as well as the concentration of these defects which will help in fine tuning the potentials for pulsed deposition there by becoming a potential X-ray or low energy gamma ray detector material.
Chapter 6
Conclusions

The main objective of this work was to synthesize the Cd$_{1-x}$Zn$_x$Te nanowires onto TiO$_2$ nanotubular template using pulsed-reverse electrodeposition and to characterize the nanowires for size, shape, uniformity in stoichiometry as well as for their electrical properties.

The cyclic voltammetry experiments carried out helped to understand as to how the stoichiometry varied at different anodic and cathodic potentials. The potentials for the growth of CZT nanowires were determined from the cyclic voltammetry studies. Pulsed-cathodic and -anodic potentials resulted in growth of nanowires of CZT with uniform stoichiometry. By varying the cathodic pulses three different stoichiometry of Cd$_{1-x}$Zn$_x$Te nanowires with x=0.04, 0.1 and 0.2 was synthesized. The SEM and TEM characterization carried out showed that the nanowires have the same diameter as that of the nanotubular TiO$_2$ template. The diameter of the nanowires was 70 nm and the length was 2 μm after 45 mins of deposition. TEM characterization carried out showed that the nanowires were polycrystalline in nature. The XRD characterization showed the compound formation for various concentrations of x in Cd$_{1-x}$Zn$_x$Te. The band gap of the Cd$_{1-x}$Zn$_x$Te for different compositions of x=0.04, 0.1 and 0.2 were 1.52 eV, 1.57 eV and 1.608 eV respectively. The resistivity of the Cd$_{1-x}$Zn$_x$Te for x=0.1 was $2.76 \times 10^{11} \Omega$-cm, and as the concentration of x increased towards 0.2 the resistivity obtained was $1.206 \times 10^{13} \Omega$-cm. The increase in resistivity as the concentration of Zn increased is attributed to the fact that there could be uncompensated acceptors which could act as traps. This was further supported by the mobility measurements which showed that with increase in concentration of Zn the mobility of holes decreased.

The sensing results of the stacked array of nanowires showed detection capability for low energy gamma source Am-241 (69 KeV, 4 μCurie). The sensing capability of the nanowires increased from 0.77 to 1.35 as the number of stacks increased from 3 to 8. The spikes in the sensing measurement is attributed to the deep level defects created in the nanowires by pulsed potentials, which can act as traps for the charges created. Thus the stacked nanowire arrays can be a potential material for X-rays and low energy gamma ray detection.