CHAPTER V

SYNTHESIS AND CHARACTERIZATION OF CdTe SENSITIZER’S NANOPARTICLES FOR SSSCS
5.1: INTRODUCTION

Low cost and high efficiency solar cells were first introduced as DSSCs with inorganic ruthenium based dyes in early 90s [1]. From then onwards, numerous researches have been focused on the development and characterization of different dyes for application in DSSCs. These include but not limited to natural dye materials [2, 3] and synthetic organic dyes [4]. Based on the DSSC’s structure, semiconductor sensitizers were introduced as a replacement of dye due to its excellent opto-electronic properties [5-7] and size-dependent physical and chemical properties. Notable characteristics of semiconductor sensitizers include tunability of band gap energy, narrow emission spectrum, good photostability, broad excitation spectra, high extinction coefficient and multiple exciton generation [8-11]. With these advantages, researchers are able to fabricate solar cell devices achieving efficiency up to 7 % in SSSCs [12, 13]. Other upcoming trend is green SSSCs where less hazardous precursors are used during the preparation of semiconductor sensitizers [14]. Over the last few years, cadmium chalcogenide (CdX, X = S, Se or Te) sensitizers nanoparticles (SNPs) have attracted more attention in SSSCs. The widespread of research activities in CdX SNPs are due to their distinct properties such as ease of fabrication, tunability of band gap energy through size control and possible multiple exciton generation. It is noted that CdX absorbs photon efficiently because it has a bulk material band gap above 1.3 eV (band gap for CdS, CdSe and CdTe are 2.25 eV, 1.73 eV and 1.49 eV respectively) [15]. By altering the size of SNPs, the band gap can be tuned further to match a desired band gap range. It is therefore critical to understand the physics and chemistry of these CdX nanoparticles for a better research focus.

5.1.1: Working Mechanism

As it was elaborated in the first chapter the working mechanism of the SSSC is very similar to that of the DSSC. When the CdTe SNPs are subjected to band gap excitation, upon illumination, electron-hole pairs are formed in the SNPs. The electrons will enter into the conduction band (CB) of the SNP and the hole remains in the valence band (VB). The excited SNP injects the electron from its CB into the CB of the wide band gap semiconductor (e. g. TiO$_2$) and in doing so it itself is oxidized with the hole remaining in the valence band. The injected electron from the SNP percolates through the porous TiO$_2$ network and ultimately reaches the conducting glass.
From there it travels through the external load and completes the circuit by entering back through the counter electrode. The generated voltage is perceived as an evidence of the solar energy conversion to electric energy. This voltage corresponds to the difference between the quasi-Fermi level of the electron in the photoanode and the redox potential of the polysulfide electrolyte [16], which usually consists of a \((S^{2-}/S_x^{2-})\) redox couple. The oxidized SNP is then restored (hole is filled with electron) when it is reduced by \(S^{2-}\) from the electrolyte and in turn it is oxidized into \(S_x^{2-}\) that diffuses to the counter electrode. Chemically, the following reactions take place where oxidation occurs at the photoanode-electrolyte interface [17],

\[
\begin{align*}
S^{2-} + 2h & \rightarrow S \\
S + S_x^{2-} & \rightarrow S_x^{2-} (x = 2 \rightarrow 5)
\end{align*}
\]

and at the counter electrode, reduction occurs where the \(S_x^{2-}\) is reverted back to \(S^{2-}\)

\[
S_x^{2-} + 2e^- \rightarrow S_x^{2-} + S^{2-}
\]

The whole key processes of the photocurrent generation can be illustrated as in figure 5.1.

![Figure 5.1 Schematic of an energy diagram of a SSSC stack under flat band conditions. Key processes leading to the generation of photocurrent are shown in (a)–(e).](image-url)
It should be concluded that SNPs have a photovoltaic response upon illumination which results in photocurrent and voltage generation. They have the tendency of charging up to a state that changes the relative energetics within the cell which ultimately influence the generation and recombination processes [18].

5.1.2: Charge Separation and Transport in TiO$_2$/CdTe SSSCs

In the DSSC, charge separation occurs at the interface between wide band gap semiconductor/dye and electrolyte. For SSSC, charge separation reactions are at the surface between wide band gap semiconductor/SNPs and redox electrolyte. Upon illumination, the excited CdTe SNPs will generate electron–hole pairs [19-21];

\[
\text{CdTe} + h\nu \rightarrow \text{CdTe} (e + h) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5.4)
\]

Where \( e \) and \( h \) denote electron and hole generated, respectively. At the interface between TiO$_2$ and the excited CdTe SNPs, charge transfer takes place,

\[
\text{CdTe(e + h)} + \text{TiO}_2 \rightarrow \text{CdTe(h)} + \text{TiO}_2(e) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5.5)
\]

\[
\text{CdTe(h)} + \text{R}_{ed} \rightarrow \text{CdTe} + \text{O}_x \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5.6)
\]

where \( R_{ed} \) and \( O_x \) are the reduced and oxidized conditions of the electrolyte. Thus, for CdTe/ TiO$_2$ system with polysulfide redox couple, the following reaction can be expressed as,

\[
\text{CdTe(h)} + \text{S}^{2-} \rightarrow \text{CdTe} + \text{S} \rightarrow \text{CdTe} + \text{S}_2^{2-} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5.7)
\]

It has been observed that the electron transfer is size dependent especially in SNPs-TiO$_2$ system and that the charge injection dynamics are determined by the SNPs [21].

5.1.3: Advantages of Semiconductor Nanoparticles as Sensitizers

Some of the advantages of semiconductor nanoparticles are tunable energy gaps, ability of multiple exciton generation, photostability, low cost and high absorption coefficient, which are known to reduce the dark current and increase the overall efficiency of solar cells [22]. Of all these, tunable energy gaps and multiple exciton generation features are the most desirable characteristics of semiconductor nanoparticles [8-11].

5.1.3 (a): Tunable Energy Gaps

Various research groups have studied the ability of semiconductor nanoparticles as sensitizers in SSSCs [10, 11, 23, 24]. The main motivation of using semiconductor nanoparticles as sensitizers in solar cell is due to their tunable energy band gaps, which can control their absorption range [7].
There are several reports in the literature showing that for example CdS and CdSe with tunable band gaps property are capable of converting visible light to electric energy [21, 25]. Vogel et al. [7] demonstrated that efficient charge separation can be optimized by tuning the size of the semiconductor nanoparticles utilizing the quantization effect. Masumoto et al. [26] separately reported that by varying the size of CdTe nanoparticles improvement in photoelectrochemical response and photoconversion efficiency can be obtained (Figure 5.2). With the decrease of CdTe particle size, photocurrent increases due to the shift of the CB to more negative potentials which in turn increases the driving force for charge injection. As a result, higher incident photon to converted electron (IPCE) is obtained at the excitonic band.

![Figure 5.2: Schematic diagram illustrating the energy levels of different-sized CdTe nanoparticles and TiO$_2$. The injection of electrons from CdTe nanoparticles into TiO$_2$ is influenced by the energy difference between the two conduction bands [21]](image)

On the other hand, if the particle size is increased, the particles will have better absorption in the visible region. The disadvantage of this is lower effectiveness of electron injection into TiO$_2$ as compared with smaller sized CdTe nanoparticles. This size dependent effect is made possible due to the quantum confinement effect exhibited by the semiconductor nanoparticles itself [24, 27]. Quantum confinement effect can be manifested when semiconductor nanoparticles in colloidal solution show different color corresponding to the change of particle size, which influences a different absorption band of light. When the semiconductor nanoparticles are sufficiently small, the effective band gap energy of the semiconductor nanoparticle is wider. Subsequently, the optical absorptions and emissions in relation with excitations across the band gap shift towards higher energies [9]. Quantum size effects have been demonstrated by Mastai et al. [28] with the observed blue shift of the optical spectra of CdTe films as the crystal size...
decreases. This phenomenon is also highlighted in CdS and CdSe nanoparticles, as reported by Thambidurai et al. [29] and Gorer et al. [30] respectively. Therefore, we can conclude that a combination of different semiconductor nanoparticles sizes in a cell will have better efficiency due to wider absorption of light by SNPs having a range of band gap.

5.1.3 (b): Multiple Exciton Generation

Multiple exciton generation (MEG) in semiconductor nanoparticles from a single photon have been widely studied [31-33]. In general, it is the generation of more than one electron–hole pair upon the absorption of a photon. This phenomenon was first demonstrated in PbS and PbSe semiconductor nanoparticles in year 2004–2005 [34-36]. In addition some latest investigations in CdSe and CdTe nanoparticles have shown interesting results [37-39]. Essentially, multiple excitons are generated when hot carriers produce more than one electron hole pair through impact ionization. More details of MEG can be found in the review by Nozik [23]. Upon absorption of solar radiation, photon with energies greater than the band gap creates electrons and holes. At this point, the excess kinetic energy is equal to the difference between the photon energy and the band gap, which creates an effective temperature condition for the carriers. The temperature of the carriers is higher than the lattice temperature. Thus, the term hot carriers (or hot electrons and hot holes) is used. The inverse of impact ionization is the Auger process, which is the recombination of two or more electron hole pairs to produce a single energetic electron hole pair. Given the possibility of Auger process, it is imminent that the impact ionization process to be faster than the carrier’s cooling or relaxation rate.

![Figure 5.3: Schematic diagram of (a) impact ionization and (b) Auger recombination processes. Electrons (filled circles), holes (empty circles), conduction band (CB) and valence band (VB)](image)

To remedy this, the hole is usually removed from the SNP core by a fast hole trap at the surface which eventually block the Auger process [23]. A simple schematic diagram depicting the impact
ionization and Auger recombination is shown in figure 5.3. Efficient multiple exciton generation is predicted to enhance the conversion efficiencies of SSSCs up to 44% [40].

5.2: LITERATURE REVIEW ON CdTe NANO PARTICLES

Among the most common II-VI semiconductor nanoparticles (NP), CdTe NPs are of great interest for applications in solar cells [41], light-emitting diodes [42, 43], and in biology [44, 45]. CdTe NPs found to be more advantageous over the more extensively studied CdSe ones because due to their higher valence band energy level, they present a lower barrier for hole injection while at the same time have a higher sensitivity toward oxidation [46].

From toxicity point of view the compound CdTe has different qualities than the two elements, Cd and Te, taken separately. Toxicity studies show that CdTe is less toxic than elemental cadmium. [47] CdTe has low acute inhalation, oral, and aquatic toxicity. Based on notification of these results to the European Chemicals Agency (ECHA), CdTe is no longer classified as harmful if ingested nor harmful in contact with skin, and the toxicity classification to aquatic life has been reduced [48]. Once properly and securely captured and encapsulated, CdTe used in manufacturing processes may be rendered harmless. Current CdTe modules pass the U. S. EPA’s Toxicity Characteristic Leaching Procedure (TCLP) test, designed to assess the potential for long-term leaching of products disposed in landfills [49]. At the present time, the price of the raw materials Cd and Te are a negligible proportion of the cost of CdTe solar cells and other CdTe devices. However, tellurium is a relatively rare element (1-5 PPB in the Earth’s crust). Through improved material efficiency and increased PV recycling systems, the CdTe PV industry has the potential to fully rely on Te from recycled end-of-life modules by 2038 [50].

There are several methods used to fabricate semiconductor NPs for SSSCs, such as chemical bath deposition (CBD) [51, 52] and successive ionic layer adsorption and reaction (SILAR) [53, 54]. These two techniques provide a high coverage of NPs with good anchorage to the wide band gap semiconductor (e. g. TiO₂). But there is a limitation of these methods, where it is difficult to control the size of the NPs and a broad size distribution of the deposited NPs is obtained. This problem can be overcome by fabricating the semiconductor NPs via electrodeposition technique. The first report on the electrodeposition of the CdTe, from an aqueous acidic solution of CdSO₄,
TeO$_2$ and H$_2$SO$_4$, dates back to 1928 [55]. A systematic study of the electrodeposition of CdTe in an aqueous bath containing 1M CdSO$_4$ and TeO$_2$ in saturation at pH 2.5-30 was reported by Panicker in 1978. Since then different deposition techniques have been employed, including close space sublimation [56], electrodeposition [57], close spaced vapor transport [58], spray pyrolysis [59], metal organic chemical vapor deposition [60] to obtain the photovoltaic quality cadmium telluride thin films. However, most of these methods are of low-throughput and not economically viable. The use of hard templates like AAO, for instance, is sometimes not desirable since template removal requires harsh chemical treatments. For PV development, the technology used should be cost effective, scalable and manufacturable in order to produce efficient low-cost solar panels for terrestrial energy conversion. The electrodeposition satisfies all these criteria mentioned above, and hence it is worth exploring and developing this technique for the production of solar energy materials and solar cells. Furthermore, electrodeposition makes it possible to easily control the size, density, surface morphology, and composition of the NPs by adjusting deposition conditions such as the applied charge density and potential. Moreover, it can enhance the electrical and physical properties of semiconducting nanostructures.

Electrodeposition of semiconducting materials represents a new challenge, not only from the academic point of view, but also from the economic point of view, since this method presents interesting characteristics for large area, low cost and generally low temperature and soft processing of materials [61]. Numerous research have been done on both alkaline and acidic baths, but the former usually yields a poorly adhering and powdery deposit, since Te is stable only at pH < 7 [55].

5.3: MOTIVATION FOR THE PRESENT WORK

In recent years, the controlled growth of CdTe nanostructures by low-temperature techniques has become the focus of world attention. Therefore, much effort has been made to provide an insight into the effects of process parameters on the growth behavior of CdTe semiconductor materials. At present, it has been proved that the growth of CdTe nanoparticles can be manipulated by adjusting the deposition voltage during electrodeposition [62]. This is a fast, simple, and reproducible method which does not require any template, catalyst, or surfactant but can control...
the morphology of CdTe. So far, there are very few reports on low-temperature electrochemically synthesis of CdTe NPs from acidic solution for SSSCs. Yet most of the research is based on basic solution which provides the formation of n-type CdTe semiconductor material. With this motivation in present study, we demonstrate a systematic electrodeposition of p-type CdTe nanostructures with controlled size, composition, shape, and morphology on FTO glass substrate. Properties such as film thickness, bonding configuration, optical absorption and optical band gap and structure are reported as a function of deposition potential and deposition time. The photovoltaic properties of CdTe nanostructures on FTO glass substrate demonstrate excellent photoresponse to visible light, suggesting their potential application in nanostructured solar energy conversion devices especially in SSSCs.

5.4: EXPERIMENTAL DETAILS

In this study the electrodeposition of CdTe was performed in a three-electrode electrochemical cell with FTO glass substrate as the working electrode, a graphite plate as the counter electrode and a saturated Ag/AgCl electrode as the reference electrode (See figure 5.4).

![Figure 5.4: The schematic diagram of electrochemical assembly used in the present study](image)

Instead of commonly used TeO₂, water-soluble Na₂TeO₃ was used as a source of tellurium ions. The prepared electrochemical bath contains 0.7 M Tartaric acid, 10 mM CdSO₄ and 6 mM Na₂TeO₃ with the solution pH of 2. The tartaric acid was employed to keep the pH of the electrolyte bath constant during the electrodeposition procedure and prevent the two precursors from generating a milky precipitate in the electrolyte solution. The electrochemical synthesis was...
carried out at ambient condition for three different potential -0.40V, -0.45V and -0.50V for 20 minutes. After synthesis, samples were rinsed extensively with double distilled water in order to remove the excess reactants from the substrate. As it is found by cyclic voltammetry analysis and confirm by XRD analysis, pure CdTe thin film nanostructure can be obtain at applied potential -0.45 V. Therefore, in the next experimental step the applied potential was considered constant at -0.45 V and the new samples were deposited for deposition time 10, 20, 30 and 40 minutes.

5.5: RESULTS AND DISCUSSION

5.5.1: Electrochemical Behavior and Growth Mechanism

In order to determine the electrodeposition mechanism and the appropriate deposition potential for each precursor, cyclic voltammetry measurements were carried out on FTO glass substrates. All potentials were referred to an Ag/AgCl electrode immersed vertically in the appropriate solution. A typical cyclic voltammogram for Cd in a solution of 10 mM CdSO$_4$ and 0.7 M Tartaric acid is shown in Figure 5.5(a). The potential was changed between +1 V and -1 V with the scan rate of 10 mVs$^{-1}$. The Cd$^{2+}$ has been reduced to elemental Cd at -0.78 V. In the reverse scanning the anodic peak of the elemental Cd is observed at -0.42 V. The chemical reaction process is described as follow [63]:

$$\text{Cd}^{2+} + 2\text{e}^{-} \rightarrow \text{Cd} \quad \text{……。(5.8)}$$

A bright silver gray film formed on the surface of the working electrode at room temperature confirms the occurrence of above chemical reaction. The voltammetric behavior of the Cd is identical to the finding of Li et. al [64]. The cyclic voltammogram of the Te on a FTO glass electrode was carried out in 6 mM Na$_2$TeO$_3$ and 0.7 M Tartaric acid solution and shown in figure 5.5(b). In the range of electrode potential between -1.0 V and 1.0 V, the voltammogram is characterized by one cathodic and two anodic peaks. The cathodic peak at -0.53 V correspond to the reduction of Te$^4$- to elemental Te. The reaction is represented as follow [65]:

$$\text{TeO}_2^2_- + 3\text{H}_2\text{O} + 4\text{e}^- \rightarrow \text{Te}^0 + 6\text{OH}^{-} \quad \text{……。(5.9)}$$

$$\text{Te}^0 + 2\text{e}^- \rightarrow \text{Te}^2^- \quad \text{……。(5.10)}$$

Figure 5.6(a) illustrates the cyclic voltammogram of the electrodeposition from the electrolyte containing both Cd$^{2+}$ and Te$^4$- species. For the formation of nanostructure CdTe, Te$^4$- should
reduce to \( \text{Te}^{2-} \) to react with \( \text{Cd}^{2+} \) and then \( \text{CdTe} \) can be formed as a result of the electrostatic attraction on the FTO substrate [66].

\[
\text{TeO}_2^2^- + \text{Cd}^{2+} + 3\text{H}_2\text{O} + 6\text{e}^- \rightarrow \text{CdTe} + 6\text{OH}^- \quad \ldots (5.11)
\]

Figure 5.6(b) shows the change of cathodic current density with time at the potential of -0.45 V versus Ag/AgCl reference electrode for the first 240 s. It was observed that the cathodic current density increases quickly at initial time and then decreases slightly. During electrodeposition, first, all the current densities increase abruptly due to nucleation on the substrate surface.

**Figure 5.6:** a) Cyclic voltammograms of FTO substrate in electrolyte solutions containing 10 mM \( \text{CdSO}_4 \) + 6 mM \( \text{Na}_2\text{TeO}_3 \) + 0.7 M Tartaric acid and, b) Change in current during potentiostatic electrodeposition at potential -0.45 V from solutions containing 10 mM \( \text{CdSO}_4 \) + 6 mM \( \text{Na}_2\text{TeO}_3 \) + 0.7 M Tartaric acid within the first 240 seconds
After the attainment of uniform nucleation on the entire surface, the current density becomes constant and the film growths begin. In a word, the sudden increase in current density, then gradual decreasing to a constant value corresponded to the formation of CdTe nucleus and growth of CdTe layer on the FTO glass substrate, respectively [67].

5.5.2: Low angle XRD Analysis

Figure 5.7 shows the XRD pattern of nanostructured CdTe deposited at three different potentials (b) = -0.40 V, (c) = -0.45 V, (d) = -0.50 V using electrodeposition technique. Diffraction peaks of tin oxide glass substrate are shown in curve (a) which is marked by dotted lines.

Regardless the peaks corresponding to FTO glass substrate, all the diffraction peaks of figure (c) located at 2θ~ 24°, 27.8°, 39.7°, 49.2° and 57.4° were indexed as (111), (200), (220), (222) and (400) planes assigned to cubic zinc-blende crystal structure of CdTe, respectively (JCPDS data card # 75-2086). For this XRD pattern no peak arising from possible impurity phases such as Cd and Te were observed. Figure (b) shows two peaks related to existence of elemental Te which has been deposited at potential -0.40 V. This result corresponds to Te-rich CdTe compounds. At more negative potential -0.5 V, figure (d), most of Cd\(^{2+}\) ions are absorbed on Te atoms; however,
excess Cd\(^{2+}\) ions react with electrons to produce Cd-rich CdTe compounds [68]. Polycrystalline CdTe has been observed to grow predominately in the (111) orientation, based on studies related to solar cell research [69, 70]. Therefore growth of nanoparticles was happened mostly in this direction as supported by SEM and TEM images.

The average particle size \(d\) for crystallites can be determined using the Debye–Scherrer formula:

\[
d_{\text{x-ray}} = \frac{0.9 \lambda}{\beta \cos \theta_B}
\]

Where \(\lambda\) is the wavelength of x-ray radiation, \(\beta\) is the full-width at half-maximum (FWHM) in radians and \(\theta_B\) is the angular position of the peak. The estimated average particle size of the pure nanocrystalline CdTe was found to be 29 nm. Figure 5.8 represents the XRD diffraction pattern of electrodeposited thin films of CdTe at constant applied potential -0.45 V for four different deposition times at the same scan rate of 10 mVs\(^{-1}\).

The most intense diffraction peak was observed at \(2\theta = 24^\circ\) corresponding to (111) plane of cubic zinc-blende crystal structure of CdTe. As the deposition time increases from 10 to 40 minutes, the intensity of (111) diffraction peak increases. This indicates that the crystallites in the film have a preferred growth in this direction [71].

**Figure 5.8:** Low angle XRD pattern of the FTO substrate, CdTe electrodeposited at potential \(v = -0.45\) V for deposition time of 20, 30, 40 and 50 minutes.
5.5.3: Scanning Electron Microscopy (SEM) Analysis andThickness Measurement

To know about the surface morphology of electrodeposited thin films SEM analysis has been done. Figure 5.9 shows SEM images of samples at two magnifications deposited at applied potential -0.45 V for three different deposition times. By increasing the deposition time, the morphology of the thin films can be changed from smooth spherical grains to rod-like grains, which grown upward. The films are found to preserve a dense and homogeneous microcrystalline structure composed of almost spherically shaped grains of 200-300 nm size.

Figure 5.10 shows the thickness variation of the CdTe thin films deposited on the FTO glass substrate with the deposition time. It can be observed that initially as the deposition time increases, thickness of the CdTe nanospheres increase, attains maximum value of 0.60 µm and then reduces with further increase in the deposition time. The maximum thickness is attained in the first 30 minute and with further increase in growth time, the thickness decreased to 0.50µm for the deposition time of 40 minute. This is attributed to the increase in the rate of dissolution than the rate of deposition after attaining the maximum length [67].

![SEM images of CdTe thin films at three deposition times](image1)

**Figure 5.9:** Scanning Electron Microscopy (SEM) images of CdTe thin films at three deposition time of (a) 20, (b) 30 and (c) 40 minutes at two different magnifications. Here DT stands for deposition time, HM for high magnification image and LM for low magnification

The histograms of particle size distribution of the CdTe nanospheres are shown in figure 5.11. The measurement was carried out by counting 100 nanoparticles on the SEM images using imageJ software. It can be observed that for two samples which are deposited for 10 and 20
minutes most of the spheres have the diameter of 300 nm. In contrast for the resultant film deposited for 30 minutes the diameter was reduced and the majority of the spheres have the diameter of 200 nm.

![Graph](image1.png)

**Figure 5.10:** Variation of CdTe film thickness as a function of deposition time.

Comparing this result with the corresponding thickness it can be understood that by increasing the growth time, diameter of spheres are decreased whereas the thickness of CdTe nanostructure materials are increased.

![Histograms](image2.png)

**Figure 5.11:** Histograms of diameter distributions of CdTe nanospheres for deposition time of (a) 10, (b) 20, and (c) 30 minutes.
Precise observation of SEM images illustrate that for the thin film deposited for 30 minutes the length of spheres are enhance and the formation of rod-like structure are vivid. The same trend was found by Sisman [72] et al. and Li et al [67]. Furtherer more this statement is confirmed with TEM results.

5.5.4: Raman Spectroscopy Analysis

To look more closely at the structure and surface roughness of the electrodeposited CdTe thin films, Raman spectroscopy was employed. Figure 5.12 gives the Raman spectrum of the CdTe electrodeposited thin film for (a) 10, (b) 20 and (c) 30 minutes deposition time. The spectra reveal three sharp bands at 120, 140, and 165 cm\(^{-1}\) and a broad band centered at 330 cm\(^{-1}\). The presence of bands at 120, 140 and 165 cm\(^{-1}\) for all three samples proved the formation of CdTe [73, 74]. We did not observed the weak bands around 450 cm\(^{-1}\) in any samples, which have been related to the Te–O–Te linkages [74-77]. The Raman peaks at 140 and 165 cm\(^{-1}\) are due to the fundamental transverse optic (1TO) [78-80] and longitudinal optic (1LO) phonon modes of CdTe. The peak at 122 cm\(^{-1}\) corresponds to Te–O bond confirming the presence of oxide in the resultant film [73, 79, 80]. It is reported that, the Raman spectroscopy can be used as a non-contact technique to detect the mean surface roughness of thin films.

Figure 5.12: Raman spectra of CdTe thin films electrodeposited at potential v=−0.45 V for deposition time of (a) 10, min, (b) 20 min and (c) 30 minutes.
Frausto et al. [78] found that Raman spectroscopy with 632.8 or 514.5 nm wavelengths cannot be used to detect changes in the surface roughness, but it can be used as an on-line surface roughness monitor on the CdTe growth with an excitation wavelength of 830.0 nm. At this excitation wavelength it is remarkable that the amplitude of peaks is a function of roughness. Therefore the increase in the intensity of the curve (c) can be attributed to enhancement in roughness. Moreover, the appearance of the optical phonon modes/peaks at 331 cm\(^{-1}\) is due to the roughness of this sample.

5.5.5: UV-Visible spectroscopy Analysis

To know about the optical properties of CdTe electrodeposited thin film, UV Visible spectroscopy has been carried out. Figure 5.13 shows the absorption spectra of CdTe thin films on FTO glass substrates at different deposition time intervals in the wavelength range of 300–800 nm. The absorption edges become more pronounced and shift to lower energy with increasing deposition time. This shift in the absorption edge as a function of thicknesses (deposition time) is caused by quantum confinement effects in the CdTe layers [72].

![Figure 5.13: Optical absorption spectra of CdTe films deposited at potential -0.45 V for 20, 30 and 40 minutes](image)

The optical band gap of films was determined by applying the Tauc relationship [81] given by;

\[
\alpha = \frac{A(h\nu - E_g)^\gamma}{h\nu}
\]

Where \( h\nu \) is the photon energy, A and \( \gamma \) are constants. The exponent \( \gamma \) depends upon the type of transition and has value of 2 and 1/2 for indirect and direct transition, respectively. The optical band gaps of the films was determined from the extrapolation of the linear plot of \((\alpha h\nu)^{1/2}\) versus
$h\nu$ at $\alpha = 0$ (See figure 5.14). The band gaps of electrodeposited CdTe thin films for 20, 30 and 40 minutes were found to be 1.53, 1.50 and 1.45 eV, respectively. Similar blue shifts of the electrodeposited CdTe thin films have been observed by Singh et al. [82] and Mastai et al. [83]. It can be seen that the band gap energy reduces while the deposition time increase. It is expected to have thicker CdTe thin films at longer times because the thickness of the CdTe thin film is directly proportional to the electrodeposition time for the first 40 minutes.

![Figure 5.14: plot of $(ah\nu)^2$ versus $h\nu$ of CdTe thin films deposited at potential -0.45 V for 20, 30 and 40 minutes](image)

5.5.6: Energy Dispersive X-ray (EDX) Analysis

The compositional analysis of the CdTe thin films electrodeposited at potential -0.45 V for 40 minutes was carried out using Energy Dispersive X-ray Analysis (EDX) technique. A typical EDX spectrum recorded in the binding energy region of 0-10 KeV for CdTe thin film deposited at potential -0.45 V is shown in figure 5.15. The EDX data is given in Table 5.1.

![Figure 5.15: Typical EDX spectrum of CdTe thin film electrodeposited on FTO glass substrate at potential -0.45 V for 30 minutes](image)
It shows the presence of only Cd, Te and Sn (from the substrate) indicating the purity of deposited material. EDX data reveals the Cd:Te atomic ratio of almost 1:1 which confirms the good stoichiometric characteristics of the films. This result suggest that the electrochemical reaction of Cd\(^{2+}\) and TeO\(_3^{2-}\) takes place in one step, without the formation of elemental Te \[67\].

Table 5.1: EDX data of CdTe film on FTO glass substrate at deposition potential -0.45 V.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic %</th>
<th>Mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>47.96</td>
<td>48.14</td>
</tr>
<tr>
<td>Te</td>
<td>51.77</td>
<td>51.28</td>
</tr>
<tr>
<td>Sn</td>
<td>0.27</td>
<td>0.85</td>
</tr>
</tbody>
</table>

5.5.7: Hall Effect Measurement

The electrical properties of CdTe thin films electrodeposited at constant potential -0.45 V for three different time intervals of 20, 30 and 40 minutes were obtained by using Hall Effect measurement set-up (ECOPIA HMS-3000) at current of \(I = 1\ mA\) and applied magnetic field of \(H = 0.54\) Tesla. The data of Hall Effect parameters including bulk and sheet charge carrier concentrations \((n)\), mobility \((\mu)\), conductivity \((\sigma)\), resistivity \((\rho)\) and Hall coefficient \((R_H)\) is given in Table 5.2. The bulk and sheet charge carrier concentrations were found of the order of \(10^{15}\) and \(10^{11}\) respectively. The mobility of majority charge carrier electrons is found to be in the range of \(5.37 \times 10^1\) to \(15.07 \times 10^1 \text{cm}^2/\text{Vs}\) for the CdTe thin films deposited at different deposition time. The highest value of conductivity obtained from this experiment is found to be \(1.82 \times 10^{-1} \text{1/Ωcm}\) for the CdTe thin film with thickness of 0.6 \(\mu\)m. Moreover, observed values of conductivity indicate the semiconducting nature of CdTe thin films electrodeposited at potential -0.45 V.

Table 5.2: Hall Effect parameters for CdTe thin films electrodeposited at constant potential -0.45 V with different deposition time

<table>
<thead>
<tr>
<th>Deposition Time (min)</th>
<th>Bulk concentration (\text{cm}^3)</th>
<th>Sheet concentration (\text{cm}^3)</th>
<th>Mobility (\text{cm}^2/\text{Vs})</th>
<th>Resistivity (\text{Ω cm})</th>
<th>Conductivity (1/\text{Ω cm})</th>
<th>Average Hall Coefficient (\text{cm}^3/C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>(1.75 \times 10^{15})</td>
<td>(1.84 \times 10^{11})</td>
<td>(5.37 \times 10^1)</td>
<td>(7.18 \times 10^1)</td>
<td>(1.39 \times 10^{-2})</td>
<td>(3.65 \times 10^3)</td>
</tr>
<tr>
<td>20</td>
<td>(5.39 \times 10^{15})</td>
<td>(8.04 \times 10^{11})</td>
<td>(6.49 \times 10^1)</td>
<td>(2.28 \times 10^1)</td>
<td>(4.38 \times 10^{-2})</td>
<td>(1.47 \times 10^3)</td>
</tr>
<tr>
<td>30</td>
<td>(7.92 \times 10^{15})</td>
<td>(13.52 \times 10^{11})</td>
<td>(15.07 \times 10^1)</td>
<td>(5.48 \times 10^0)</td>
<td>(1.82 \times 10^{-1})</td>
<td>(7.15 \times 10^2)</td>
</tr>
</tbody>
</table>

The negative value of current observed in Hot Probe experiment [84, 85] and positive sign of average Hall coefficient indicate the p-type nature of CdTe thin films deposited at different time.
intervals. The obtained results are comparable with the results obtained by Sharma et al. [86] and Miyake et al. [87].

5.5.8: Transmission Electron Microscope (TEM) Analysis

The crystal structure of electrodeposited CdTe thin films were further investigated by transmission electron microscopy (TEM). Figure 5.16 shows typical TEM, HR-TEM and Selected Area Electron Diffraction (SAED) pattern of electrodeposited CdTe thin films at potential -0.45 V for different deposition time.

Figure 5.16: Typical TEM, HR-TEM and SAED pattern of electrodeposited CdTe thin films for: 10 min (a1, a2, a3), 20 min (b1, b2, b3) and 30 min (c1, c2, c3)

As can be seen from the TEM images [Figure 5.16 (a1, b1, c1)], the deposition time has a significant effect in nanoparticles morphologies. For the growth time of 10 minutes the
nanoparticles have a solid sphere shape which is converted to hollow spheres for the growth time of 20 minutes. Further increase in deposition time provides the possibility of growth of nanorod structures as it was seen in SEM images.

Clear and well-resolved lattice fringes appear in high resolution TEM images indicate that the CdTe nanostructures are highly crystalline. As indicated in figure 5.16 (a2), (b2) and (c2), the crystalline lattice spacing of HR-TEM images were measured and found to be 0.37 nm in all the tree samples. The d spacing of 0.37 nm corresponds to the (111) reflection of the cubic CdTe structure. These results are consistent with XRD analysis (see figure 5.8). Similar observations have been reported by Miao et al. [88, 89], Shen et al. [90] and Pan et al. [91] for CdTe nanocrystals. The rings of electron diffraction pattern of CdTe thin films electrodeposited for 10 minutes are sharper indicating a larger size of particles and polycrystalline nature of the material [Figure 5.16 (a3)]. In contrast presence of dots in the sample electrodeposited for 20 minutes specifies improved crystallinity of the material [Figure 5.16 (c2)]. Electron diffraction pattern of electrodeposited film for 30 minutes was taken for a single nanorod which illustrates the single crystal nature of that specific region, figure 5.16 (c3).

5.5.9: Atomic Force Microscopy (AFM) analysis

To illustrate the surface morphology and roughness of the electrodeposited CdTe thin films AFM analysis has been carried out. Figure 5.17 shows AFM images of the electrodeposited CdTe thin films at potential -0.45 V for three different growth times. From images it is clear that the surface morphologies consist of spherical grains without any void. The spherical grains were also reported for CdTe thin films obtained by RF-Sputtering technique and quasi-closed volume technique [92, 93]. The larger grain size may provide more surface area for liquid electrolyte/electrode junction photoelectrochemical and photovoltaic devices [94]. It was observed that as the deposition time increase, the grain size reduced. Therefore, the growth time has a great influence on the grain size of the thin films. The root mean square (RMS) roughness is defined as the standard deviation of the surface height profile from the average height, is the most commonly reported measurement of surface roughness [95]. \( R_{\text{rms}} \) and \( R_a \) (the average roughness) of the thin films were investigated using three dimensional AFM images (not shown) and tabulated in Table 5.3.
This result suggests that the most roughness can be achieved at 30 minutes time interval where as the least roughness is happened at initial growth time of 10 minutes.

Table 5.3: Roughness values of electrodeposited CdTe films at potential -0.45V for three different time intervals

<table>
<thead>
<tr>
<th>Deposition time (min)</th>
<th>$R_a$ (nm)</th>
<th>$R_{rms}$ (nm)</th>
<th>$R_{MAX}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>18.77</td>
<td>19.64</td>
<td>34.72</td>
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<tr>
<td>20</td>
<td>27.60</td>
<td>28.72</td>
<td>52.20</td>
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<tr>
<td>30</td>
<td>31.25</td>
<td>32.59</td>
<td>54.69</td>
</tr>
</tbody>
</table>

5.6: CONCLUSIONS

In present work we have successfully synthesized p-type CdTe nanostructure thin films on FTO glass substrate from acidic bath using three-electrode electrodeposition technique. Influence of applied potential and electrodeposition time on the structural, morphological and opto-electrical properties of the deposited films has been systematically investigated. Raman spectroscopy, low angle XRD, and HR-TEM analysis suggest that electrodeposited thin films have zinc blende cubic crystal structure. At optimized deposition conditions, we have found that CdTe thin films have direct band gap in the range 1.42-1.53 eV with a blue shift in absorption edge which may caused by quantum confinement effects in the CdTe thin films. These optimized parameters which include applied voltage and electrodeposition intervals were used further for sensitization of TiO$_2$ nanoarrays.
REFERENCES:


