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The effect of growth voltage on the structure, electrical and optical properties of CdTe thin films prepared by electrodeposition method

A.U Yimamu[1,2]*, M.A Afrassa[2], B.F Dejene [3], K.G Tshabalala[1] S.Z Werta[4], J.J Terblans[1], H.C Swart [1] and S.J Motloung [1]

1 Department of Physics, University of the Free State, Bloemfontein/QwaQwa Campus, South Africa
2 Department of Physics, Adama Science and Technology University, Adama, Ethiopia
3 Department of Physics, Walter Sisulu University (Mthatha), Mthatha, South Africa
4 Department of Physics, Dire Dawa University, Dire Dawa, Ethiopia
**Corresponding Author: Email tlousj@gmail.com, ahemed.dilla2010@gmail.com*

Abstract

Cadmium Telluride (CdTe) thin films were grown using a low-cost two-electrode electrodeposition method in an aqueous acidic solution. The solution contained 1 M of cadmium acetate dihydrate (Cd (CH$_3$OO)$_2$. 2H$_2$O) as cadmium precursor and 2 ml of tellurium dioxide (TeO$_2$) as tellurium precursor. The thin films were deposited on coated glass florin doped tin oxide (FTO) substrate with a sheet resistance of 8 ohm/square. The deposition voltage was varied from 1200 to 1450 mV with a 50 mV increment to investigate the range of deposition voltage. The X-ray diffraction (XRD) results show that CdTe thin films were polycrystalline cubic zinc blend structures, and the best crystallinity was observed at deposition voltage of 1250 mV with crystallite size of 26 nm. Ultraviolet-visible (UV-VIS) measurements revealed that the maximum absorbance was recorded at 1250 mV, and the energy band gap of CdTe thin films varies from (1.46 to 2.02) eV. At the voltage of 1250 mV, the band gap was 1.46, which is near the bulk energy band gap of CdTe (1.45 eV). Photoelectrochemical cell (PEC) measurement confirmed that the conductivity of CdTe varies with deposition voltage. It has exhibited a p-type conductivity due to Te-rich CdTe at low voltage and becomes n- type Cd-rich CdTe film at high voltage.

Keywords: Electrodeposition, Thin film, CdTe, Two electrodes, deposition voltage, electrolytic solution.

1. Introduction

Compound semiconductor thin film materials with group (II-IV) chalcogenide families such as CdTe, CdS, CdSe, ZnTe, ZnS, and ZnSe are the most common ones for p-n junction solar energy devices. The main focused research area for solar energy conversion was the thin film of this group to reduce the challenges of the high cost of crystalline Si solar cells due to the manufacturing process. Especially cadmium telluride (CdTe) thin films were used as absorber material due to their direct energy band gap. The band gap was near the ideal energy band gap of absorber materials at 1.5 eV. The simplicity of fabrication, environmental stability, and high conversion efficiency of CdTe has gained popularity on a global scale [1]. Having these unique properties, the film is used for various applications such as sensors [2], medical imaging resonance [3], X-ray and gamma-ray detectors [4], light-emitting devices [5], and solar cells [6].

**Corresponding Author: Email: tlousj@gmail.com , ahemed.dilla2010@gmail.com*

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Physical and chemical properties of CdTe thin films depend on the growth conditions and the source of chemicals used for the electrolyte solution. There are several methods employed to grow CdTe thin films, such as closed space sublimation (CSS) [7], chemical vapor deposition [8], pulsed laser deposition (PLD) [9], vacuum evaporation [10], chemical bath deposition (CBD) [11], and electrodeposition (ED) [12]. Although all deposition techniques have advantages and disadvantages, chemical-based techniques such as CBD and ED methods are preferable to others.

When we compare CBD with ED, in the case of CBD, the solution is used once and then become wasted, leading to the wastage of toxic chemicals like Cd and less abundance of Te. However, the ED technique is one of the waste reduction ways, and it has other advantages, such as manufacturability, scalability, simplicity, long bath lifetime, and self-purification [13].

Optimizing deposition parameters significantly controls the structure, electronic and optical properties of CdTe thin films. These parameters are deposition voltage, pH of the electrolytic solution, deposition period, stirring rate, deposition temperature, ion concentration in the solution, and electrode configuration used.

In the electrodeposition of CdTe thin film growth, different Cd sources such as cadmium chloride ($CdCl_2$) [14], cadmium sulfured $CdSO_4$ [15], and cadmium nitrate $Cd(NO_3)_2.4H_2O$ [16] in both two and three electrode configurations were reported. A limited number of reports explain the electrodeposition of CdTe thin film from a cadmium acetate as a Cd precursor. However, to the best of our knowledge, no experimental work has been reported using two electrode electrodeposition configuration.

2. Material and Method

CdTe thin films were grown from electrolyte solution containing 1.0 M of cadmium acetate dihydrate [$Cd(CH_3OO)_2.\ 2H_2O$] with 98% purity as cadmium precursor and 2 ml of tellurium dioxide TeO_2 with 99% purity as tellurium precursor by electrochemical deposition method. Both chemicals were laboratory reagent grade with $Cd(CH_3OO)_2.\ 2H_2O$, and TeO_2 purchased from Sigma Aldrich.

These thin films were deposited using the two-electrode electrodeposition method on the coated glass/fluorin doped tin oxide (FTO) substrate with a sheet resistance of 8 ohm/square. The glass substrate was cut into 2.5 x 2.5 cm and washed ultrasonically followed by ethanol, acetone, and methanol, respectively and dried in air. The pH of the electrolyte solution was maintained at

2.00 at room temperature. The deposition temperature of the electrolyte solution bath was maintained at 85°C, and during deposition, the electrolyte solution was stirred at a moderate stirring rate using a magnetic stirrer. The source for electrical power used for the two-electrode system was a computerized Gill AC potentiostat (ACM instrument, United Kingdom). An insulating polytetrafluoroethylene (PTFE) thread seal tape was used to attach the glass substrate to carbon plate which was used as the working electrode (cathode), and the graphite rod as a counter electrode (anode).

Cd-containing solution having 1 M Cd $(CH_3OO)_2$. $2H_2O$ was prepared in 400 ml deionized (DI) water in 600 ml beaker and stirred for 1 hour. The Te-containing solution was prepared by dissolving 2g of TeO_2 in 30 ml of dilute HCl in 50 ml beaker and then stirred for 2 hours since Te is a semi-metallic element that is soluble in an acidic medium. From the solution, only 2 ml of Te-containing solution was added to the Cd-contained solution and then stirred for 5 hours to keep the uniformity of the solution and the deposition was done without further purification. Cyclic voltammetry (CV) measurements were taken to optimize the range of deposition voltage. From CV measurement analysis, CdTe was deposited in the voltage range from (1200-1450) mV. The deposition occurred in the voltage range of 50 mV intervals (1200, 1250, 1300, 1350, 1400, and 1450) mV. All the other parameters were kept constant, and the film was grown for 2 hours. The structure, electronic, and optical properties of the electrodeposited CdTe thin films were investigated for all the samples. Figure 1 shows the experimental setup for two electrode electrodeposition configuration.

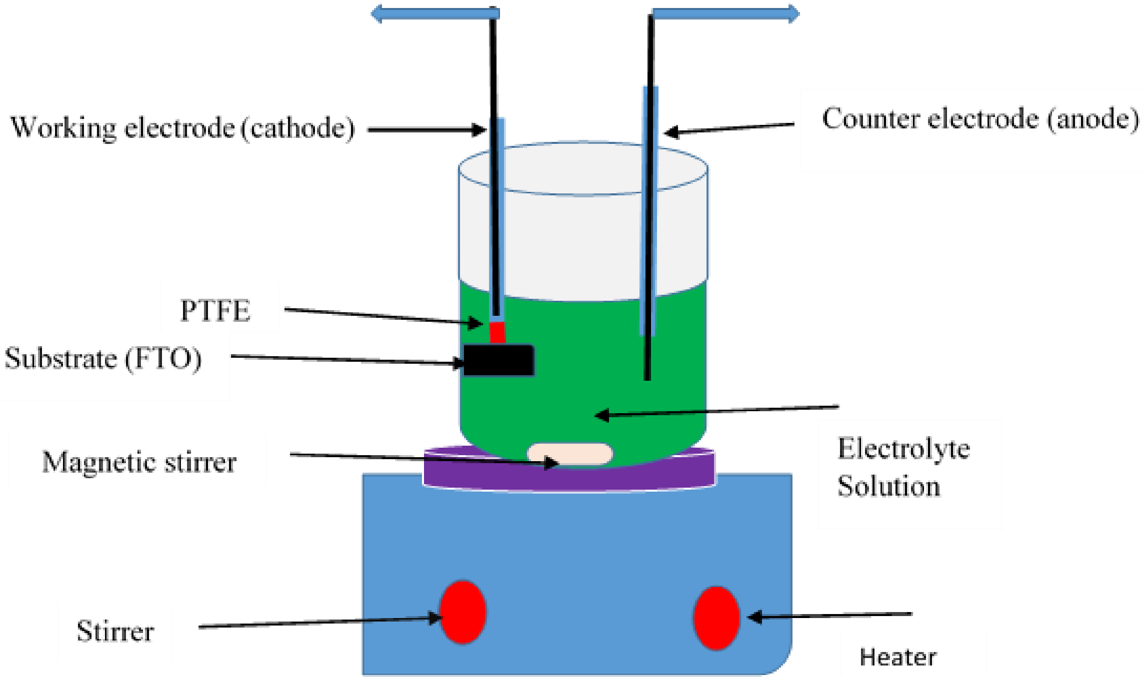

Figure 1. Two- electrode electrodeposition set-up

3. Result and Discussion

3.1. Cyclic Voltammetry study (CV)

During CV measurements, the deposition temperature was maintained at 85° C, and the electrolytic solution pH at 2.00. The cathodic deposition voltage was gradually raised from (0 – 2000) mV with the cyclic sweep of 10mV/s, as shown in figure 2. For the electrodeposition of CdTe thin films, the optimization of deposition parameters is significant for the growth of stoichiometric composition of both elements in the thin film. Growth voltage optimization is the first task in the electrodeposition technique. For this, CV measurements were used to investigate the range of growth of CdTe thin films. Tellurium deposits first during the electrodeposition process because its standard reduction potential is +593 mV with respect to the typical H_2 electrode, which is more favorable than that of cadmium with a standard reduction potential value of −403 mV [14].

Figure 2 shows that in the forward direction, Te started to deposit at a cathode voltage of 290 mV near region (A). As the voltage is increased to 945 mV near region (B), Cd started to deposit. In these regions, co-deposition of Cd and Te appeared on the substrate, and the thin film was Te-rich. The current density was on the range of CdTe thin film deposition when the voltage increased from (1200 -1450) mV near region (C). Further increase in cathode voltage (1450-1500) mV near region (D), Cd rich CdTe thin films were formed. Beyond 1500 mV, there is a high increase in current density, which is hydrogen evolution at the cathode or Cd dendrites formation; and these were also observed and reported by Diso et al [17].

In the reverse direction of CV measurement, as shown in figure 2, the negative current density was observed, indicating the removal of elemental Cd, CdTe, and Te from the cathode surface. Therefore, CV measurement is a vital tool for optimizing the deposition voltage range.

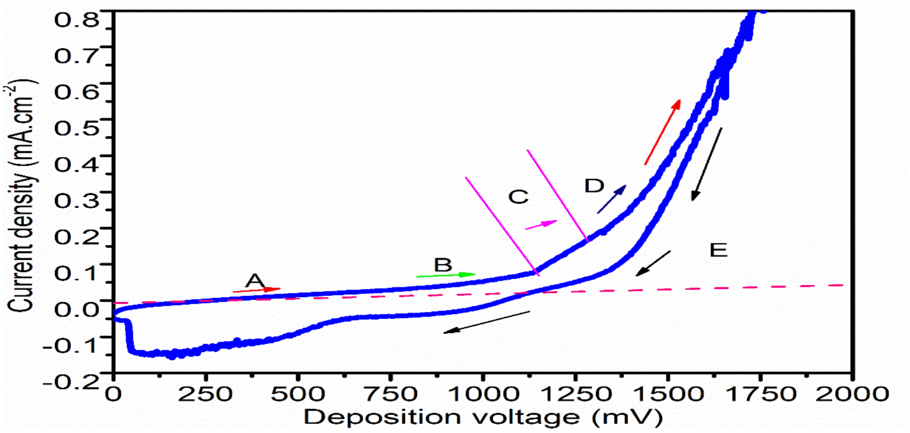

Figure 2. A typical CV measurement for two electrode-electrolyte solutions contains 1.0 M Cd $(CH_3OO)_2.2H_2O$ and 2 ml of TeO_2.

3.2. Structural properties

D8 Advance diffractometer X-ray Diffraction measurements were used to identify the degree of crystallinity and crystal structure of CdTe layers grown on glass/FTO substrates. The X-ray generator tension and current were kept to 40 kV and 40 mA, respectively. The XRD measurements were performed in a two-theta range from 20 to 70°.

The crystallite size, D, of the ED CdTe thin film was calculated using the Scherer's formula in equation 1 [18]

$$D = \frac{0.9\,\lambda}{\beta\cos\theta} \qquad 1$$

where β is the full width at half maximum (FWHM) in radian, λ is the wavelength of the X-rays (0.15406 nm for Cu Kα), and θ is the Bragg's diffraction angle in degree.

The dislocation density, which describes the length of dislocation lines per unit volume of the crystal in the CdTe thin-film via electrodeposition technique, is estimated using equations provided in the literature. (2) [19]

$$\delta = \frac{1}{D^2} \qquad 2$$

Where δ dislocation density, and D is crystallite size

The micro strain (ε) can be calculated by using the relation in equation (3) [20]

$$\varepsilon = \frac{\beta_{hkl}}{4\tan\theta} \qquad 3$$

Figure 3 shows that CdTe thin films were polycrystalline cubic zinc blend structures, and the preferential (111) peak intensity varies with deposition voltage. At the voltage of 1200 mV, a peak at 22.9° is attributed to Cd_xTeO_y [21], which shows that Te-rich CdTe thin film was deposited, and the crystallite size was 20 nm with FWHM of 0.40. When the voltage was 1250 mV, the CdTe peak was reduced, the intensity of the preferential orientation (111) was increased, and a better crystallinity was observed.

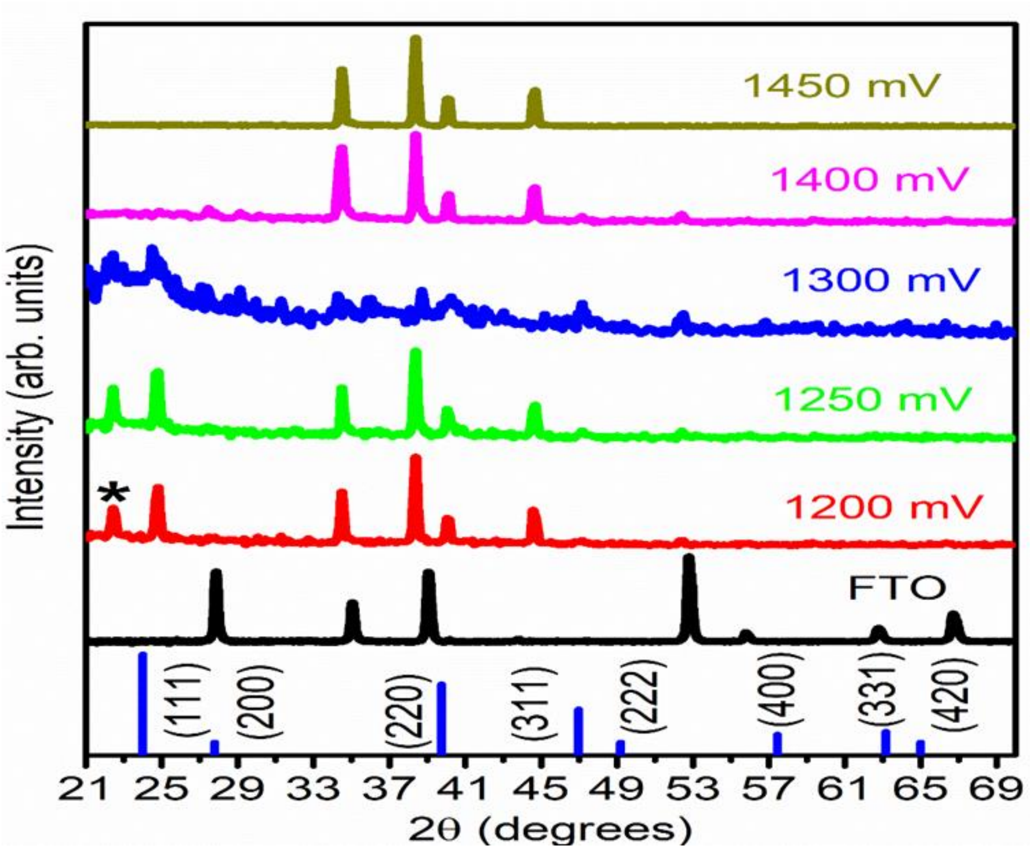

Figure 3. XRD spectra of CdTe thin films with different deposition voltage

The estimated crystallite size was 26 nm while the FWHM was reduced to 0.31. Further increase in the voltage to 1300 mV, the thin film crystallite size and the FWHM remain unchanged, but the peak intensity was reduced. For 1400 mV voltage, the FWHM was increased to 0.92 and the crystallite size was reduced to 9 nm. When the voltage was further increased to 1450 mV, the CdTe thin film showed amorphous nature. From these results, it is observed that when the deposition voltage changes, the crystallite size of the electrodeposited CdTe thin films were varied. The results are in good agreement with the JCPDS card of 752083 and other published reports [22].

Figure 4 shows that the dislocation density at 1200 mV deposition voltage is 2.4 x10^{15} line /meter^2. When the deposition voltage is 1250 and 1300 mV the dislocation density is 1.4 x10^{15} line /meter^2. Further increase in the voltage to 1400 mV the dislocation density was increased to 12.8 x10^{15} line /meter^2.

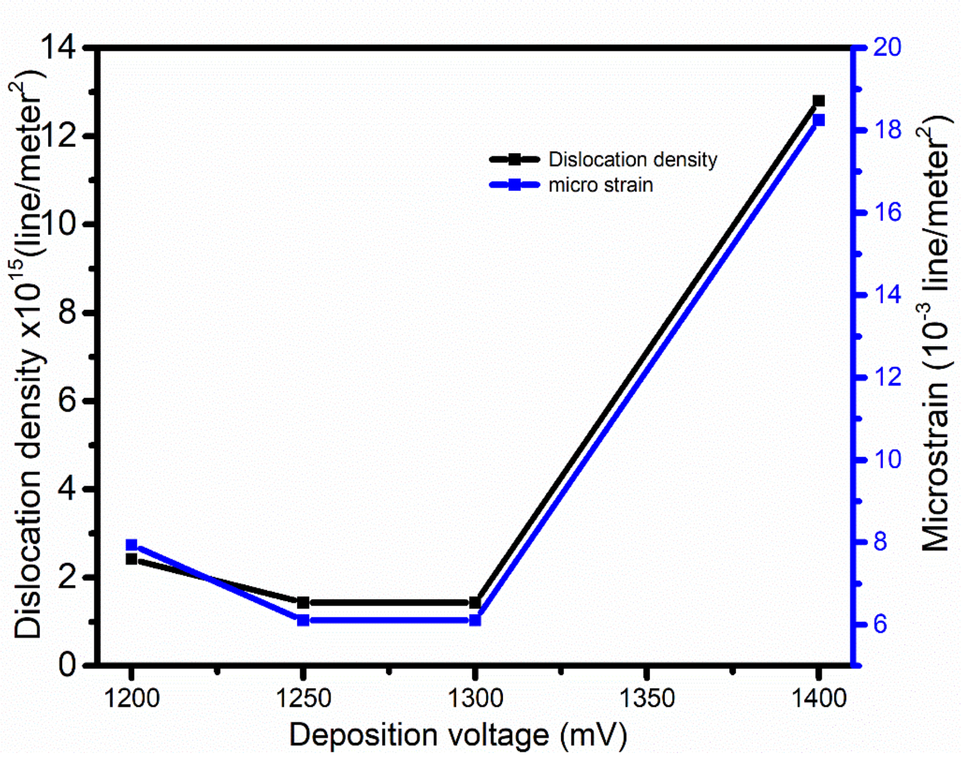

Figure 4. Dislocation density and microstrain vs deposition voltage

Figure 4 also confirmed that the microstrain at deposition voltage of 1200 mV is 7.9 x10^{-3} line/meter^2. The decrement in microstrain was visible when the deposition voltage was increased to 1250 mV and it was recorded as 6.10 x10^{-3} line/meter^2. Further increase in deposition voltage to 1400 mV, the microstrain was increased to 18.25 x10^{-3} line/meter^2. From these two analyses low dislocation density and microstrain were observed. Further optimization in the range between 1250 to 1300 mV was done, but this is not reported in this paper.

3.3. Photoelectrochemical cell analysis (PEC)

Photoelectrochemical cell (PEC) measurements were carried out to estimate the electrical conductivity types of ED-CdTe layers. This experimental technique was carried out on the potential barrier formation at the solid/liquid interface between CdTe and a suitable electrolyte solution by immersing glass/FTO/CdTe as cathode and graphite rod as the anode, which was connected to a digital voltmeter to measure the potential when the circuit is under dark and illumination conditions [23]. The PEC results were the difference between the voltages under illumination and the dark. The electrolyte solution containing 0.1 M Na_2SO_4 in 20 ml of deionized water in a 50 ml beaker was stirred for 2 hours to make it uniform.

Figure 5 shows that the conductivity of CdTe thin film at deposition voltage of 1200 to 1350 mV is p-type, while at 1350 to 1450 mV, becomes n- type. This is due to excess of Te and Cd in the film respectively. In addition to this, the conductivity of the material was changing due to the presence of Cl in the film. The results are in good agreement with the other Cd source for CdTe thin film grown by electrodeposition method [24].

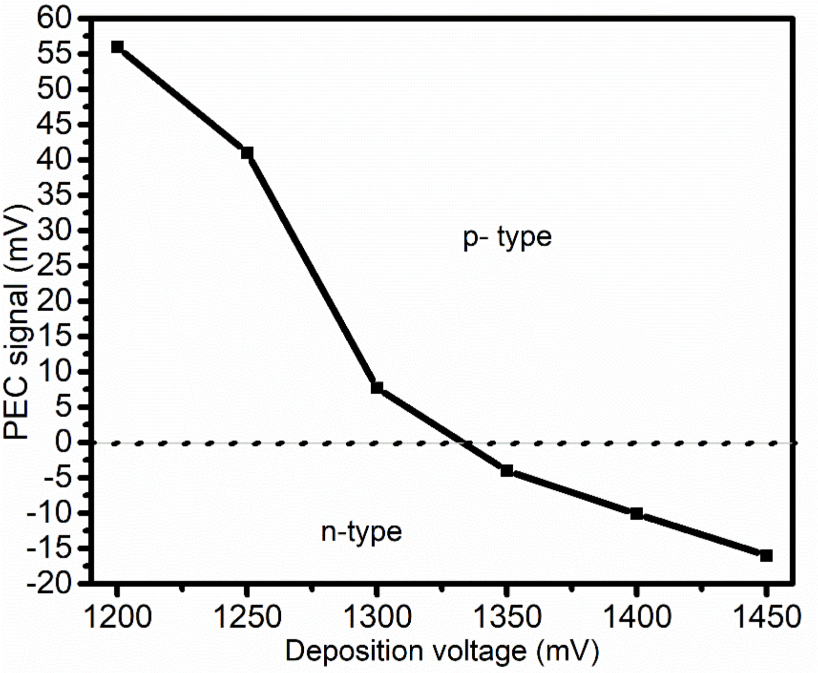

Figure 5. PEC measurements for different deposition voltage

3.4. Optical properties

Optical absorbance properties were investigated by using UV- VIS spectrophotometry wins lab-scan lambda 950. The absorbance as a function of wavelength was plotted as shown in figure 6 (a). The minimum absorbance was recorded at 1450 mV due to Cd-rich, thin films, and the maximum absorbance was at 1250 mV, showing better Cd and Te composition. High absorbance is required for CdTe thin film for the absorber layer in solar cells application. Therefore, 1250 mV was the best deposition voltage, which is in good agreement with XRD results.

As shown in figure 6 (b), the optical energy band gap was calculated by plotting absorbance square as a function of photon energy and by extrapolation of a tangent line to the graph towards ($(abs)^2 = 0$). The energy band gap of electrodeposited CdTe varies as deposition voltage varies. Accordingly, at deposition voltage of 1200, 1250,1300,1350,1400 and 1450 mV, the energy band gap was recorded 1.55, 1.46, 1.71, 1.95, 1.95 and 2.02 eV respectively. From the experimental analysis , the energy band gap of the electrodeposited CdTe thin film deposited at 1250 mV is 1.46 eV, approximately near the bulk energy band gap of CdTe of 1.45 eV [25].

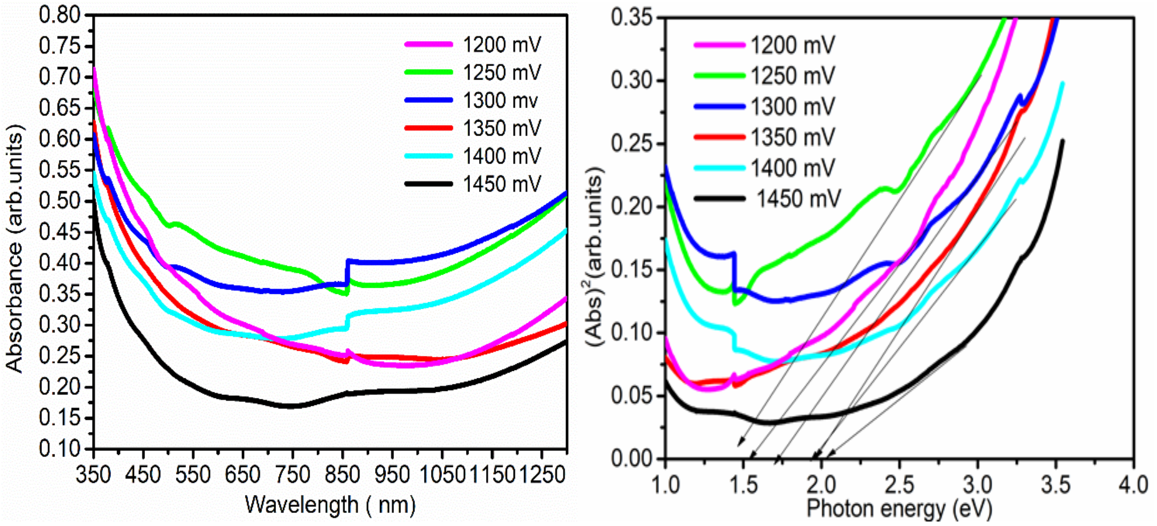

Figure 6. (a) the absorbance vs wavelength (nm) (b) (absorbance) ^{2} vs photon energy (eV)

4. Conclusion

Electrodeposition of CdTe thin films was successfully grown on a conductive glass substrate (FTO) from an electrolytic bath solution containing cadmium acetate as Cd source and tellurium oxide as Te source. The XRD measurement confirmed that CdTe thin film varies with deposition voltage. It was a polycrystalline cubic zinc bend structure at (111) preferential orientation, and the best crystallinity was recorded at 1250 mV and crystallite size was 26 nm and dislocation density and microstrain was calculated. UV-VIS analysis shows that the absorbance was varied with deposition potential, and the maximum was recorded at 1250 mV. The band gap calculation shows that CdTe thin films have 1.46 eV at 1250 mV deposition voltage near a band gap of 1.45 eV. PEC measurement shows that the thin film CdTe conductivity varied with voltage and p-type at low and n-type at high deposition voltage which indicates Te and Cd rich thin film respectively. This result agreed with previously reported results from different Cd sources.

5. Acknowledgments

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6. Conflict of interests

The authors state that they have no conflicting interests.

7. References

[1] S. S. Oluyamo, A. A. Faremi, O. I. O. Olusola, and Y. A. Odusote, "Tunability of conductivity type and energy band gap of CdTe thin film in the electrodeposition technique," Mater. Today Proc., vol. 38, pp. 558–563, 2021, doi: 10.1016/j.matpr.2020.02.962.

[2] H. Shams, H. A. Gabal, M. Soliman, S. Ebrahim, and S. Agamy, "Electrochemical Deposition of CdTe Thin Film for CdS / CdTe X-Ray Sensor," vol. 5, pp. 85–103, 2020.

[3] J. Kang, E. I. Parsai, D. Albin, V. G. Karpov, and D. Shvydka, "From photovoltaics to medical imaging: Applications of thin-film CdTe in x-ray detection," Appl. Phys. Lett., vol. 93, no. 22, 2008, doi: 10.1063/1.3042212.

[4] O. Maslyanchuk et al., "Charge transport features of CdTe-based X- and γ-ray detectors with Ti and TiOx Schottky contacts," Nucl. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers, Detect. Assoc. Equip., vol. 988, no. October 2020, p. 164920, 2021, doi: 10.1016/j.nima.2020.164920.

[5] N. P. Gaponik, D. V. Talapin, A. L. Rogach, and A. Eychmuller, "Electrochemical synthesis of CdTe nanocrystal/polypyrrole composites for optoelectronic applications," J. Mater. Chem., vol. 10, no. 9, pp. 2163–2166, 2000, doi: 10.1039/b001958p.

[6] A. J. Clayton et al., "MOCVD of II-VI HRT/Emitters for V," pp. 1–11, 2022.

[7] K. S. Rahman et al., "Influence of deposition time in CdTe thin film properties grown by Close-Spaced Sublimation (CSS) for photovoltaic application," Results Phys., vol. 14, no. March, p. 102371, 2019, doi: 10.1016/j.rinp.2019.102371.

[8] D. A. R. Barkhouse, O. Gunawan, T. Gokmen, T. K. Todorov, and D. B. Mitzi, "Yield predictions for photovoltaic power plants: empirical validation, recent advances and remaining uncertainties," Prog. Photovoltaics Res. Appl., vol. 20, no. 1, pp. 6–11, 2015, doi: 10.1002/pip.

[9] P. Hu et al., "Effects of the substrate temperature on the properties of CdTe thin films deposited by pulsed laser deposition," Surf. Coatings Technol., vol. 213, pp. 84–89, 2012, doi: 10.1016/j.surfcoat.2012.10.022.

[10] A. Ali, N. A. Shah, A. K. S. Aqili, and A. Maqsood, "Impact of evaporation rates of Cd and Te on structural, morphological, optical, and electrical properties of CdTe thin films deposited by a two-sourced evaporation technique," Cryst. Growth Des., vol. 6, no. 9, pp. 2149–2154, 2006, doi: 10.1021/cg060217q.

[11] S. Surabhi, K. Anurag, and S. R. Kumar, "Structural, morphological, electrical and optical properties of Zn doped CdTe thin films," Chalcogenide Lett., vol. 19, no. 2, pp. 143–152, 2022, doi: 10.15251/cl.2022.192.143.

[12] I. M. Dharmadasa et al., "Improvement of composition of CdTe thin films during heat treatment in the presence of CdCl2," J. Mater. Sci. Mater. Electron., vol. 28, no. 3, pp. 2343–2352, 2017, doi: 10.1007/s10854-016-5802-9.

[13] I. M. Dharmadasa and J. Haigh, "Strengths and Advantages of Electrodeposition as a Semiconductor Growth Technique for Applications in Macroelectronic Devices," J. Electrochem. Soc., vol. 153, no. 1, p. G47, 2006, doi: 10.1149/1.2128120.

[14] A. A. Ojo and I. M. Dharmadasa, "Analysis of electrodeposited CdTe thin films grown using cadmium chloride precursor for applications in solar cells," J. Mater. Sci. Mater. Electron., vol. 28, no. 19, pp. 14110–14120, 2017, doi: 10.1007/s10854-017-7264-0.

[15] O. I. Olusola, M. L. Madugu, A. A. Ojo, and I. M. Dharmadasa, "Development of CdMnTe thin films using electroplating technique for opto-electronic device applications," J. Mater. Sci. Mater. Electron., vol. 31, no. 24, pp. 22151–22161, 2020, doi: 10.1007/s10854-020-04717-5.

[16] S. C. Ray and K. Mallick, "Cadmium Telluride (CdTe) Thin Film for Photovoltaic Applications," Int. J. Chem. Eng. Appl., no. January, pp. 183–186, 2013, doi: 10.7763/ijcea. 2013.v4.290.

[17] D. G. Diso, F. Fauzi, O. K. Echendu, O. I. Olusola, and I. M. Dharmadasa, “Optimisation of CdTe electrodeposition voltage for development of CdS/CdTe solar cells,” J. Mater. Sci. Mater. Electron., vol. 27, no. 12, pp. 12464–12472, 2016, doi: 10.1007/s10854-016-4844-3.

[18] S. Mahato, N. Shakti, and A. K. Kar, “Annealing temperature dependent structural and optical properties of electrodeposited CdSe thin films,” Mater. Sci. Semicond. Process., vol. 39, pp. 742–747, 2015, doi: 10.1016/j.mssp.2015.06.019.

[19] S. I. Ozmen and H. M. Gubur, “Synthesis and characterization of CdTe/CdSe thin film on glass/ITO by electrodeposition at room temperature,” Bull. Mater. Sci., vol. 45, no. 2, 2022, doi: 10.1007/s12034-021-02653-6.

[20] N. Amin, M. R. Karim, and Z. A. Alothman, “An In-Depth Analysis of CdTe Thin-Film Deposition on Ultra-Thin Glass Substrates via Close-Spaced Sublimation (CSS),” Coatings, vol. 12, no. 5, 2022, doi: 10.3390/coatings12050589.

[21] H. I. Salim, V. Patel, A. Abbas, J. M. Walls, and I. M. Dharmadasa, “Electrodeposition of CdTe thin films using nitrate precursor for applications in solar cells,” J. Mater. Sci. Mater. Electron., vol. 26, no. 5, pp. 3119–3128, 2015, doi: 10.1007/s10854-015-2805-x.

[22] O. K. Echendu, K. B. Okeoma, C. I. Oriaku, and I. M. Dharmadasa, “Electrochemical deposition of CdTe semiconductor thin films for solar cell application using two-electrode and three-electrode configurations: A comparative study,” Adv. Mater. Sci. Eng., vol. 2016, pp. 10–14, 2016, doi: 10.1155/2016/3581725.

[23] A. A. Ojo, K. A. Olanipekun, B. S. Oluwadare, and T. O. Oni, “Evaluation of the Effect of Deposition pH on the Physico-chemical Properties of Electrochemically Deposited Cadmium Telluride for Photovoltaic Device Applications,” Eur. J. Eng. Technol. Res., vol. 6, no. 6, pp. 1–7, 2021, doi: 10.24018/ejers.2021.6.6.2404.

[24] A. A. Ojo and I. M. Dharmadasa, “Optimisation of pH of cadmium chloride post-growth-treatment in processing CDS/CDTE based thin film solar cells,” J. Mater. Sci. Mater. Electron., vol. 28, no. 10, pp. 7231–7242, 2017, doi: 10.1007/s10854-017-6404-x.

[25] A. Kuddus, A. B. M. Ismail, and J. Hossain, “Design of a highly efficient CdTe-based dual-heterojunction solar cell with 44% predicted efficiency,” Sol. Energy, vol. 221, no. April, pp. 488–501, 2021, doi: 10.1016/j.solener.2021.04.062.