IOSR Journal Of Applied Physics (IOSR-JAP)
e-ISSN: 2278-4861.Volume 16, Issue 5 Ser. 1 (Sept. – Oct. 2024), PP 01-13
www.Iosrjournals.Org

Effect Of Annealing Temperature On The Optical And Structural Properties Of Zinc-Doped Cd_2SnO_4 Thin Films Prepared By Dip-Coating Method

Zachary O. Osewe, Andrew O. Oduor, George O. Onyinge
Department Of Physics And Materials Science, Maseno University-Kenya.

***Abstract*:**
As demand for solar PV modules steadily increases studies on cheaper alternative TCO materials, with low resistivity and high transmittances in the visible spectrum to replace ITO are been undertaken. Among TCO materials considered as alternative to Indium Tin Oxide (ITO) is Cd_2SnO_4, owing to its availability in large quantities at relatively lower costs. Studies on optical properties of N_2 and F_2 doped Cd_2SnO_4 films have revealed increased transmittance 99%, and reduced band gap 3.3 eV. On the other hand Fe doped films have been observed to exhibit higher refractive indices, extinction and absorption coefficients with lower transmittance and optical band gap. Although studies have been carried out on Zinc doped Cd_2SnO_4 films, the effect of annealing temperature on the properties of the films have not been reported. This study investigated the effect of annealing temperature on the optical and structural properties of Zinc-doped Cd_2SnO_4 films. Thin films of Zinc-doped Cd_2SnO_4 were prepared by mixing 0.1 M Cadmium Acetate with 0.1 M Tin II Chloride in ratio 1:1 to prepare Cd_2SnO_4 which was doped with 0.1 M Zinc Nitrate then dip-coated on clean glass substrates. The coated substrates were dried at room temperature and annealed in air the films annealed at 350 ^{o} C, 400 ^{o} C and 450 ^{o} C for 90 minutes Optical transmittance and reflectance were measured in wavelength range 200-1200 nm and with the results: prominent XRD peak oriented in the (2 0 0) direction, transmittance of 78.7% at 700 nm wavelength, absorption coefficient of 3.891 - 5.591 x 10^4 cm^{-1}, extinction coefficient of 0.1852 - 0.2126, refractive indices of 1.983-2.121 at 588 nm wavelength and band gap values range 3.45-3.65 eV. Annealing was observed to reduce refractive index and does not affect transmittance therefore doesn't enhance suitability of films as TCO materials for Photovoltaic applications.

Keywords: *Zinc- doped Cadmium Stannate, Optical and Structural properties, Annealing temperature.*

Date of Submission: 18-09-2024 Date of Acceptance: 28-09-2024

I. Introduction

The main material used to manufacture solar cells ITO, has a wide band gap of between 3.5-4.3 eV and high transmittance in the visible spectrum, hence its wide use as TCO material in thin film solar cells, (Du et al, 2014).Despite the rise in demand for solar PV modules, the cost of these modules still remain relatively high. The scarcity and mechanical brittleness of Indium, the main material component of ITO, coupled with the complicated manufacturing process is a major contributing factor to the high production costs. (Mazzeo et al, 2013). TCO materials used in thin film solar cells should have a band gap greater than 3.2 eV (Minami, 2005), and thus to reduce the costs of PV modules, extensive research must be undertaken to find cheaper alternative materials with requisite properties of high transmittance in the visible spectrum; 380-700 nm, high reflectance in the infrared and low direct current resistivity, that can replace ITO.

Among other TCO materials, Cd_2SnO_4 has been identified as a potential alternative to the ITO due to its availability in large quantities at relatively lower cost (Krishna et al 2010), (Bhuvaneswari et al, 2013) and (Zhongming et al, 2017). Properties of thin films of Cd_2SnO_4 prepared using different methods including; Sol-Gel Method (Carballeda-Galacia et al, 2000), Spray Pyrolysis Technique (Krishnakumar et al, 2009) and Vacuum Evaporation Technique; (Hashemi et al, 1989) have been studied. Spray pyrolysis has been found to be the most cost effective for dip-coating, which is suited for mass fabrication and is less defective in producing film coatings (Sharonova et al, 2019). Optimizing conditions such as deposition temperature, annealing and doping Cd_2SnO_4 using non-metals like Ar, N_2 and F has been found to improve electrical, electronic, optical and structural properties, in particular doping Cd_2SnO_4 with Fluorine efficiently alters the surface morphology of Cd_2SnO_4 thin films, resulting in smooth surface with a few spherical-shaped grains, (Bhuvaneswari et al, 2013). Further studies on Nitrogen and Fluorine doped Cd_2SnO_4 films have revealed increase in transmittance ~ 99%, band gap ~ 3.3 eV and reflectance ~ 1% (Bhuvaneswari et al, 2013). Optical properties of Fe doped Cd_2SnO_4 have been studied where transmittance of 78.45% and band gap energy of 3.9 eV are realized at the 380 nm spectral region. The Optical constants; refractive indices, extinction and absorption coefficients were found to be enhanced by Iron doping due to the free carriers introduced by the dopant, that absorb more of the incident photons (Ongwen et al, 2019).

Zinc ions are able to easily replace Sn/Cd ions; Zinc ion ($Zn^{2+)}$ with ionic radius of 0.073 nm is similar to that of Tin IV ion (Sn^{4+}) which is 0.071 nm but smaller than the ionic radius of Cadmium II ion (Cd^{2+}) which is 0.095 nm making Zn^{2+} easily incorporated into Cd_2SnO_4. Zinc as a doping material has been found to enhance optical luminescence in the Photoluminescence spectrum of Cadmium Oxide (CdO) films; (Renu and Vipin, 2019), it also enhances gas sensing capabilities of Cd_2SnO_4 films towards the stimulants by changing surface morphology and reducing the number of Oxygen atoms (Patil et al, 2012). Doping Cd_2SnO_4 with Yttrium (Y) on the other hand, enhances electrical properties by increasing the number of charge carriers in the films, (Cristaldi, 2012).

Deposition of Cd_2SnO_4 at high temperature has been discovered to favor the growth of larger crystallites where the out-diffusion reduces the number of oxygen atoms; as deposition temperature is increased from 450 ^{o} C to 550 ^{o}C, with the average crystalline size increasing from 29.07 to 42.12 nm, at higher deposition temperature of 550 ^{o}C, there is increased charge carrier concentration and mobility of the carriers in the Cd_2SnO_4 thin films. Spray pyrolysis produces amorphous Zinc-doped Cd_2SnO_4 thin films of thickness less than 100 nm, with no diffraction peaks corresponding to Zinc in Zinc-doped Cd_2SnO_4, The doping improves gas sensing properties at temperature of 350 ^{o}C, Patil et al (2012).

Annealing temperature changes structure by improving surface roughness and increasing crystalline nature of the films. Temperatures higher than 500 ^{o}C cause nano-crystallization and formation of crystal nuclei due to Rayleigh scattering from the large nano-crystalline centers. As the packing density of the films is increased, so is the refractive index leading to reduced transmittance (Day et al, 1990).

Annealing Zinc-doped Manganese Oxide (MnO_2) thin films from 300 ^{o} C to 800 ^{o}C has been found to increase the extinction coefficient of the films while annealing at 600 °C and 800 °C results in transformation of MnO_2 to Manganese III Oxide (Mn_2O_3) (Pishdadian and Shariati, 2013). Higher extinction coefficient values are realized with increasing annealing temperature due to reduction of the band gap (Adel et al, 2014), an indication of increased absorption of films.

Zinc-doped Cd_2SnO_4 films sample of concentration 7% of 0.1 M Zn $(NO)_3$ were annealed at temperatures; 350^o C, 400 ^{o}C and 450 ^{o}C and the effect of annealing temperature on optical and structural properties of films investigated.

II. Literature Review

Ongwen et al (2019) doped Cd_2SnO_4 using Iron and employed spray pyrolysis method to prepare thin films. He then studied the effect of concentration of Iron (Fe), Tin II Chloride ($SnCl_2$) and Cadmium Acetate and also deposition temperatures 350 ^{o}C, 400 ^{o}C and 450 ^{o}C on the optical characteristics of the films.

Using spectrometer in the U/Vis/NIR region, he noted reduction in extinction and absorption coefficients and the refractive index but band gap energy and transmittance increased due to increase in concentration of the materials used which was attributed to the rise in crystalline nature of the films formed. Doping with Iron (Fe) amplified refractive index, extinction and absorption coefficients but lowered transmittance and the optical band gap; this was attributed to the rise in the number of mobile charge carriers. At the 380nm wavelength region of the spectrum the following were realized:- absorption coefficient of (4.022 to 5.522) x 10^4 m^{-1}, maximum transmittance of 78.45%, refractive indices in the range 1.77 to 2.12, extinction coefficient of between 0.188 to 0.258 and band gap energy between 3.5 eV to 3.9 eV. Ongwen et al (2019) successfully doped Cd_2SnO_4 using a metal Fe and not Zinc, they varied concentrations of all the reactants used and not the concentration of the dopant only as done with Zinc doped Cd_2SnO_4 in this study. They also considered pre-heating the substrates during deposition process at 350 ^{o}C, 400 ^{o}C and 450 ^{o}C whereas this study did deposition and drying at room temperature before post deposition annealing at 350 ^{o}C, 400 ^{o}C and 450 ^{o}C in air.

Zhongming et al (2017) prepared gas (Argon-Oxygen) sputtered Cd_2SnO_4 thin films on a substrate from 10 cm by 10 cm Corning 7059 glass using a hot-pressed ceramic target, diameter 76 mm. The chamber was evacuated to a low pressure of 5 x 10^{-4} Pa. The Argon (Ar): Oxygen (O_2) ratio was maintained at 8:2; where the distance between the target-substrate distances was 7 cm.

Films varying in thicknesses were made in Ar and Ar-O_2 mixture. The substrates were divided in quarters and annealing in N_2 at temperatures between 560 ^{o}C and 635 ^{o}C for 30 minutes. CTO films of thickness 172 nm and 388 nm were subjected to treatment in dry air/Cadmium chloride ($CdCl_2$) atmosphere maintained at 400 ^{o}C for 60 minutes.

Transmittance and reflectance were measured using a Cary 5000 U/Vis/NIR spectrometer; annealing was noted to significantly improve transmittance when sputtered in atmosphere containing Oxygen. Ar-O_2 sputtered films had sudden edge alteration which was accredited to enlargement of the band gap. N_2 doping enlarged the band gap from 2.83 eV to 3.32 eV but annealing in N_2 did not cause significant change in the band gap energy though there was increase in transmittance and decrease in absorption coefficient but reflectance was not affected.

Series 1 Bruker D8 Advance X-Ray Diffractometer was used to measure X-ray diffraction patterns within 2θ (the angle of detector position from the incident X-ray beam) values between 20^o to 60^o. Sputtered films were found to be amorphous and crystallization occurred in the films annealed at temperatures of 600 ^{o} C and above. An expansive peak was observed at approximately 32^o which increased when annealing rose to temperature above 580 ^{o} C; demonstrating formation of small crystal grains in the films. However films sputtered without oxygen failed to crystallize even after annealing was done at 635 ^{o} C. This study used a non-metal, N_2 for doping Cd_2SnO_4, employed sputtering technique in deposition which was done in evacuated chamber at low pressure. The ambient used for annealing in this study was N_2.

Eman, (2014) employed Vacuum Evaporation Technique to deposit Cd_2SnO_4 on 7059 corning glass slides at room temperature and studied electrical and optical behavior of the thin films. UV/Vis/NIR spectrophotometer was used to measure transmittance in the 200 to 1100 nm range of wavelength where a maximum transmittance of 70 % was recorded in the visible spectrum region. Calculations also revealed a band gap of 3.0 eV; an increase in film thickness was found to increase the transmittance to 71.3 % and band gap of the films to 3.47 eV. The increase in transmittance and the band gap were linked to growth in sizes of the grains causing increased crystalline structure of the films.

The films obtained had thickness ranging between 300-600 nm. Using Edwards E306A coating system operating at vacuum pressure of 2 x 10^{-5} mbar, evaporation of the Cd_2SnO_4 was carried out from the powder of Cd_2SnO_4 with purity of 99.999 %. Structural studies using X-ray diffraction studies indicated that the thin films were polycrystalline in nature, having a cubic structure and with strong peaks oriented in (3 1 1) direction. As thickness of the thin films increased from 300 to 600 nm, strength of the peaks also increased which could be as a result of the growth in the size of the grain of the thin films which was between 19.1 to 21.4 nm (Eman, 2014). This study however did not involve doping or annealing, it also considered Vacuum Evaporation Technique for deposition.

Bhuvaneswari et al (2013) used the method of spray pyrolysis to prepare thin films of Cd_2SnO_4 doped with F. To aqueous solutions of 0.16 M Cadmium Acetate and 0.02 M $SnCl_2$ or the Cd_2SnO_4 solution, 0 - 5 w.t % Ammonium Fluoride (NH_4F) was added to obtain Fluoride-doped Cd_2SnO_4 solution which was deposited on 1737 Corning glass substrates maintained at 540 ^{o} C using compressed air at about 6.5 x 10^4 Pa as the carrier gas. The crystal size of the prepared films was estimated using equation (2.26) where sizes ranging from 17.8 - 47.1 nm was obtained, XRD analysis of the Cd_2SnO_4 doped with 3 w.t % Fluorine showed growth in the (2 2 2) direction (Patterson, 1939).

Results from Scanning Electron Microscope (SEM) revealed effective surface morphology modification on Cd_2SnO_4 films as a result of doping with Fluorine, which showed smooth surface with a few spherical-shaped grains. Due to 1 w.t % Fluorine doping, average optical transmittance in the visible region (between 500 nm to 850 nm) increased from about 79% to about 89 %. Fluorescence emission spectra of Cd_2SnO_4 doped with 1wt% and 3 w.t% of Fluorine showed a change of fluorescence intensity from 200 counts to 500 counts at 601 nm wavelengths, carrier concentration ~ 9.5 x 10^{19} cm^{-3}, mobility ~ 42 cm^2/Vs and resistivity ~ 1.5 x 10^{-3}. In this study, Spray Pyrolysis method was used for deposition at 540 ^{o} C with compressed air at about 6.5 x 10^4 Pa as the carrier gas. Fluorine (non-metal) was used for doping and not Zinc.

Cristaldi et al (2012) doped Cd_2SnO_4 using metal Yttrium (Y) and proceeded to deposit the final solution by spray pyrolysis technique. The films formed were analyzed to ascertain the effects of Yttrium doping on the structural qualities of the films formed. Characterization of the Yttrium-doped Cd_2SnO_4 thin films was done using X-Ray diffraction, AFM and XPS which showed that the films formed were crystalline, with orthorhombic structure. Doping was done in this study and spray pyrolysis technique used for deposition. However, the study did not record any factors considered during deposition and whether some temperatures were involved, no discussion was recorded on how doping influenced optical properties of the films.

Patil et al (2012) prepared films from un-doped and Zinc doped Cd_2SnO_4 using spray pyrolysis technique both for gas sensing studies. They added equal volume of 0.1 M Cadmium nitrate; $Cd(NO_3)$ and 0.1 M Tin IV Chloride (ratio 1:1). 1-3 vol % of $Zn (NO_3)$ was added into equal proportions of solution mixture after which each solution was sprayed for 300 seconds then fired at a temperature of 500 ^{o} C for 1 hour to obtain the thin films before commencing characterization and gas sensing studies.

X-Ray diffractogram showed the films had amorphous nature and the patterns shown by X-Ray diffraction showed no peaks that correspond to Zinc in Zinc-doped Cd_2SnO_4 which was associated within inadequate Zinc atoms added to Cd_2SnO_4 during doping. All thin films obtained in this study had a thickness of less than 100 nm. Both the un-doped and Zinc-doped Cd_2SnO_4 thin films were exposed to stimulants used in chemical warfare agents. The Study showed that Zinc-doped Cd_2SnO_4 films have better gas sensing properties than the un-doped Cd_2SnO_4 films at an opening temperature of 350 ^{o} C. Zinc was successfully used as a dopant to Cd_2SnO_4 in this study but optical of properties were not discussed. The study also considered deposition at specific temperatures but not post deposition annealing.

Jayaram et al (2011) studied morphological, electrical and structural properties of un-doped and Magnesium (Mg) doped Cd_2SnO_4 films prepared using spray pyrolysis method. XRD revealed neat crystalline structure with the particles diameter being calculated from the data. Uniform film thickness and uniform grain growth of all the films were observed using Atomic Force Microscopy. Un-doped Cd_2SnO_4 had a thickness of 725 nm which decreased to 285 nm due to Mg doping. Indirect band gap energy 2.97 eV for Mg doped Cd_2SnO_4 was realized from the UV/Vis spectrum. The doping affected electrical properties of Cd_2SnO_4 but not its structural properties. Spray pyrolysis was used for deposition but no mention of conditions under which deposition was done and whether there was annealing. Even though there was doping of Cd_2SnO_4, study did not discuss the optical properties of the films formed.

Krishna et al (2010) used Cadmium Acetate and Tin II Chloride solutions, which were mixed in different mole ratios, i.e.; 2:1, 4:1 and 6:1 then added 3 ml of 2M HCl to form a clear solution of Cd_2SnO_4. The different concentrations of Cd_2SnO_4 were deposited on substrates kept at 400 ^oC, 450 ^oC and 500 ^oC using cheap improvised spray pyrolysis machine for solar photovoltaic cells application. The variables kept constant were; carrier gas whose pressure was 6.5 x 10^4 Pa had a flow rate kept at 6 liters/minute, the angle at which the spray struck the substrate surface was maintained at 45° and nozzle-substrate distance was 35 cm.

The different substrate temperatures had some effects on the properties of the thin films. The films obtained at 400 ^oC substrate were amorphous in nature, whereas the ones obtained at 450 ^oC had orthorhombic structure and exhibited growth along (1 1 1) direction. Sheet resistance of single layer thin films was found to be 160 Ω/□ while forming additional layer on the films led to reduction of sheet resistance to 15 Ω/□. However, addition of layers had no influence on the structural and optical properties of the thin films. For the films obtained at 450 ^oC, transmittance of ranging between 91.7 % and 99.8 % was obtained for amorphous films of 160 nm thickness in the wavelength lying between 770 nm and 795 nm.

A band gap of 2.9 eV was found for all the films without any treatments after deposition, this finding is consistent with the findings by (Eman, 2014). By using gravimetric method, thickness of the film was approximated and the X-Ray diffraction analysis done by Computer controlled Phillips X-Pert Pro; Cu- Kα radiation whose wavelength is 1.5405 Ǻ and Shimadzu UV-1601 was used to record optical spectrum in the 300-1100 nm wavelength range. In this study, deposition was done at specific temperatures, post deposition annealing was not considered. Doping was not done on Cd_2SnO_4.

Alnaimi and Al-Dileamy (2007) used thermos- chemical spray pyrolysis technique to prepare Cd_2SnO_4 thin films. Tin II Chloride dehydrate dissolved in Acetic Acid and Cd Cl_2 pent hydrate dissolved in ethanol and at a mole ratio of 1:2 were the precursor solutions used. The final solution was left for 72 hours to form a uniform mixture then sprayed onto glass substrates heated between temperatures of 300 K and 600 K. The resultant films were targeted to be used in solar photovoltaic cells, thermal and ordinary mirrors and highly specialized filters. Structural analysis was done using XRD technique and the films were found to be amorphous which agreed with the results obtained by (Clark, 1980). Film thicknesses determined by mass method were found to be in the range of 300-600 nm. By looking at the UV/Vis spectrum, the type of electronic transition was observed in the 400-700 nm wavelength range. A band gap of 2.8 - 3.3 eV whose values reduced with increase in film thickness and a transmittance of 90% were realized. They found out that the value of the band gap decreased as the film thickness increased. The findings agreed with the work that was done later by (Krishna et al, 2010). Nothing was mentioned as per deposition temperature and annealing are concerned. In this study, doping was not done to Cd_2SnO_4.

From the above review it is evident that spray pyrolysis technique has been the most dominant method used for depositing the precursor solutions for both doped and un-doped Cd_2SnO_4 thin films. Non-metal Nitrogen and Fluorine as well as metal Iron, Zinc, Magnesium and Yttrium have been used to dope Cd_2SnO_4 but only optical properties of Magnesium and Iron doped Cd_2SnO_4 have been reported, hence the need to study structural and optical properties of Zinc dope Cd_2SnO_4. Past studies have shown that Zn as a doping material enhances optical properties of Cadmium Oxide (CdO) films; Zinc doping was confirmed to enhance luminescence property in the Photoluminescence spectrum (Renu and Vipin, 2019). Zinc doping enhanced gas sensing capabilities of Zinc dope Cd_2SnO_4 by changing surface morphology and reducing the number of Oxygen atoms (Patil et al, 2012). This could be as a result of Zinc ions being able to easily replace Sn/Cd ions; Zinc ion ($Zn^{2+)}$ with ionic radius of 0.073 nm is similar to that of Tin IV ion (Sn^{4+}) which is 0.071 nm but smaller than the ionic radius of Cadmium II ion (Cd^{2+}) which is 0.095 nm making Zn^{2+} easily incorporated into Cd_2SnO_4. In this study, the cost effective method of dip-coating was employed while depositing un-doped and Zinc doped Cd_2SnO_4 precursors before studying their structural and optical properties; dip-coating method has been suitable in mass fabrication while being less defective in producing film coatings (Sharonova et al, 2019).

III. Experimental Details

Zinc Nitrate dehydrate

Using the Relative Formula Mass (International Union of Pure and Applied Chemistry, 1980) 189.4 g/mole the required mass of 3.788 g of Zinc Nitrate for the concentration of 0.1 M Zinc Nitrate samples were obtained by dissolving the masses into 100 cm^3 of distilled water.

Tin II Chloride dehydrate

Required concentration of Tin II Chloride dehydrate whose Relative formula mass is 225.64 g/mole was prepared by dissolving 4.5128 g of the substance into 200 cm^3 of water to prepare 0.1 M Tin II Chloride solutions (International Union of Pure and Applied Chemistry, 1980) .

Cadmium Acetate dehydrate

Relative formula mass of Cadmium Acetate dehydrate is 266.53 g/mole (International Union of Pure and Applied Chemistry, 1980), hence 5.3306 g of Cadmium Acetate was dissolved in 200 cm^3 of water to prepare 0.1 M Cadmium Acetate solution.

Accurate masses of each of the above substances were obtained using laboratory electronic balance; *ISOLAB "0,0001g precision"* model. The solids were dissolved in respective volumes of distilled water using clean 500 ml glass beakers.

Cadmium Acetate was mixed with Tin II Chloride while making Cd_2SnO_4 solution instead of the readily available Cd_2SnO_4 so as to be sure of using solutions with the required molarities.

200 cm^3 of 0.1 M Cadmium Acetate and 200 cm^3 of 0.1 M Tin II Chloride giving a white precipitate (Cd_2SnO_4). 20 cm^3 of the Cd_2SnO_4 solution was poured in 16 different conical flasks, each of which was dissolved by adding about 4 ml of 2 M HCl forming a clear liquid 4 (Krishna et al, 2010). The Cd_2SnO_4 solution was placed in four containers; the first container was doped with 0.1 M Zinc Nitrate (7 %) by volume of the Cd_2SnO_4 solution.

The first 20 cm^3 portion of Cd_2SnO_4 solution was un-doped meaning, no volume of Zinc Nitrate was added hence producing un-doped Cd_2SnO_4 thin films.

The second, second, third and fourth 20 cm^3 portion of Cd_2SnO_4 solution were doped using with 7% of 0.1 M Zn $(NO)_3$. The lower percentages/volumes of Zinc Nitrate (dopant) were used to ensure a very low content of Zinc in Cd_2SnO_4, taking into consideration the small band gap in semiconductor materials, since small amounts of impurities drastically modify structural, electrical and optical properties of semi-conductors (Bhatt et al, 2011).

The doped solutions were kept for 72 hours to form homogenous solution and the volumes of the solutions were measured using graduated cylinder.

Substrate Cleaning

The substrates used in this study were Microscope Slides; Diamond White Glass Slides approximately measuring 76.2 mm X 25.4 mm X 1.1 mm, 90° Ground Edges, Plain (bought from Kisumu Equipment and School Supplies-Kisumu). Aqua Regia solution was used in cleaning the new glass slides because it is free from metal traces or solvents and a good surface cleaner (Shugar and Ballinger, 1996). To prepare Aqua Regia solution, 1 M HNO_3 was mixed with 3 M HCl and in the ratio of 1:3, i.e 200 ml Nitric Acid (HNO_3) and 600 ml HCl giving 800 ml final solution. The mixing was done in the fume chamber for safety because the gases are poisonous. The glass substrates were soaked for half a day in the mixture to remove dust and any impurities after which Deionized (DI) water was used to clear the remaining traces of the Aqua Regia solution. Whitman lens cleaning tissues, model number 105 were then used to wipe the glass substrates after which they were stored in the slide holder awaiting deposition (Ongwen et al, 2019).

Deposition of the Precursor

Dip-coating method was used to deposit the precursor solutions of the doped Cd_2SnO_4 solutions onto the glass substrates. For every sample of Zinc-doped Cd_2SnO_4 solution, glass substrates were coated then given time to drip as shown in figure To ensure formation of uniform films; the substrates were immersed and withdrawn at a constant speed in an angle perpendicular to the surface of the solution containing the coating material, they were also left in the solution containing the coating material for 2 minutes to allow the substrate to absorb molecules of the solution for better adhesion.

Annealing

Annealing is the heat treatment to alter physical behavior film coatings. Annealing rearrange the atoms by reducing the number of dislocations (Barbara et al, 2016). Post deposition annealing was done to dried dip-coated substrates by placing them on a heating tray, the oven was pre-heated to the required temperature of 350 ^{o}

C, 400 °C and 450 °C the coated slides annealed for one and half hours in air. After cooling, the substrates were labeled and kept in a slide holding rack before taking measurements and analysis.

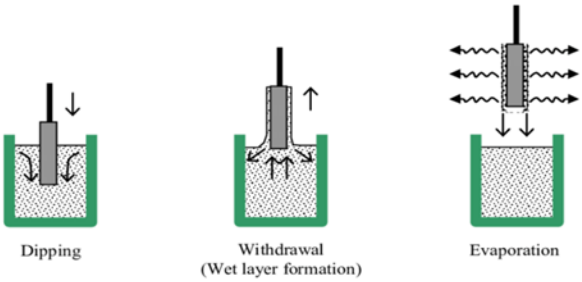

Figure 3.5: Dip-coating method

IV. Results And Discussion

Diffraction Analysis

X-Ray Diffraction characterization was done for the Cd_2SnO_4 films annealed at 350 °C, 400 °C and 450 °C. The samples doped with 7% of 0.1 M Zn $(NO)_3$ produced relatively stronger peaks when annealed at 400 °C. The X-Ray diffraction peaks showed a good fit with card number JCPDS No: 89-0510.

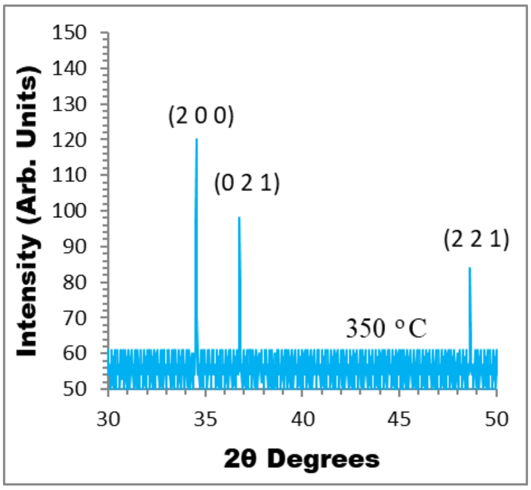

Figure 4.1A: XRD patterns for Cd_2SnO_4 thin films annealed at 350 °C

From figure 4.1A above shows the diffraction patterns for Cd_2SnO_4 thin films annealed at 350 °C; a dominant sharp peak oriented in (2 0 0) direction whose intensity is 120 Arb. Units, together with other peaks were observed.

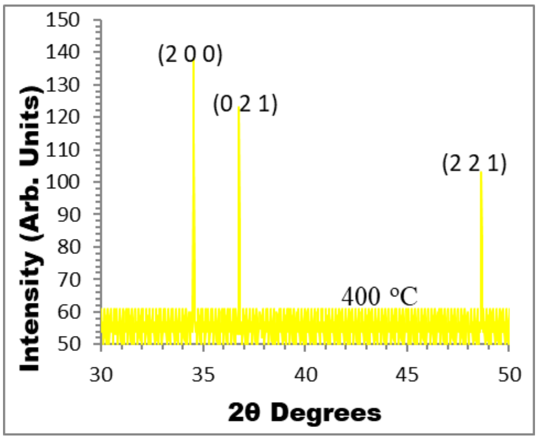

Figure 4.1B: XRD patterns for Cd_2SnO_4 thin films annealed at 400 °C

Figure 4.1B above shows diffraction patterns for films annealed at 400 °C, where it is observed that the intensity improved with the dominant peak being at 138 Arb. Units.

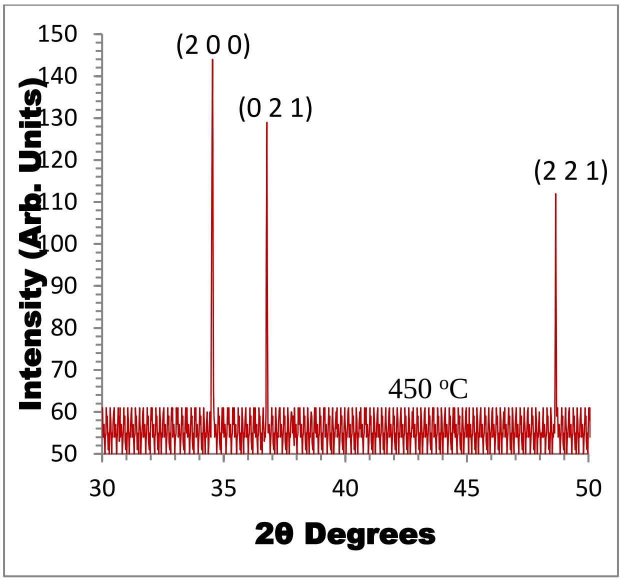

Figure 4.1C: XRD patterns for Cd_2SnO_4 thin films annealed at 450 °C

From figure 4.1C above, the intensity of the most dominant peak rose to 148 Arb. Units due to annealing at 450 °C; Annealing is observed to improve overall intensity of the peak heights, an indication of increased crystallinity of the films with increase in annealing temperature. As annealing temperature increases, the film structure is crystallized hence leading to greater the intensity of the peak heights (Metina et al, 2009). However, annealing did not result into any structural changes in the substance as there were peaks corresponding to (2 0 0), (0 2 1) and (2 2 1) with the position of 2θ = 34.54°, 36.78° and 48.66° respectively for all the annealed films.

Transmittance

Using spectrometer (Spectro 320), transmittance of the films was measured within the 200-1200 nm wavelength and results presented in Figures **4.2A** and **4.2B** below:

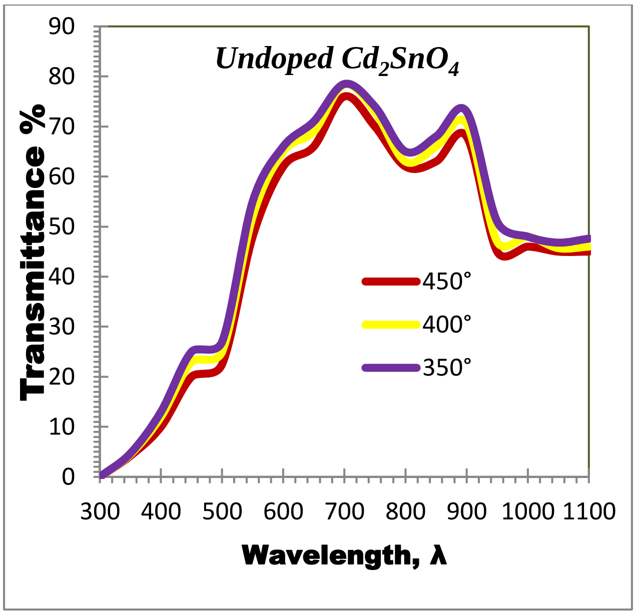

Figure 4.2A: Transmittance graphs for Un-doped Cd_2SnO_4 thin films

Figure 4.2A above shows transmittance of un-doped Cd_2SnO_4 thin films annealed at three different temperatures. Films annealed at 350 °C recorded the highest transmittance of 78.9 % while films annealed at 450 °C recorded the least transmittance of 76.8 % at the lower end of the electromagnetic spectrum.

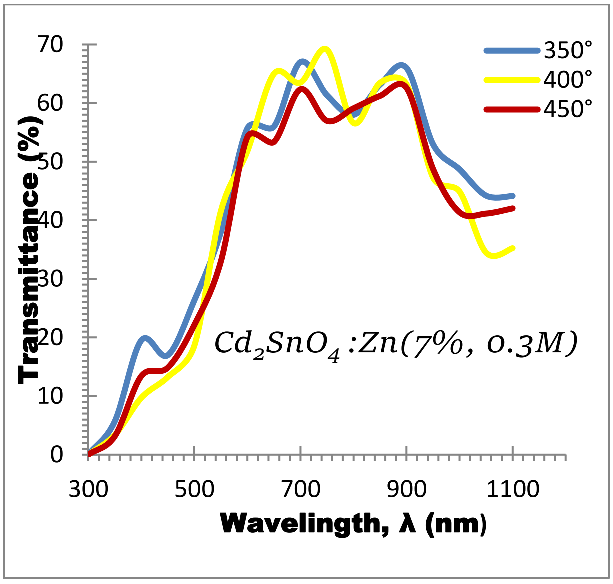

Figure 4.2B: Transmittance graph for Zinc-doped Cd_2SnO_4 thin films.

Transmittance increases with decrease in annealing temperature; this is evident from figure 4.2B. Doped films annealed at 350 °C recorded the highest transmittance of 78.7 % at 700 nm which reduces to 72.4 % when annealing was done at 450 °C. The decrease of transmittance with increase in annealing temperature can be attributed to onset of nano-crystallization and formation of crystal nuclei which is due to increased Reyleigh scattering from the large nano-crystalline scattering centers (Day et al, 1990). Transmittance was also observed to reduce from a maximum of 86.7% at 655 nm wavelengths to 76.2 % at 700 nm wavelengths when Cd_2SnO_4 films were fired in vacuum atmosphere at 400 °C (Cardile et al, 1990). Vacuum annealing shifted the primary optical absorption edge toward the UV from 490 to 430 nm because of increased concentration of free charge carriers. (Ali et al, 2014) while studying how structural and optical qualities of thermally deposited Tin Antimony Sulfide thin films are affected by annealing; they noted that the decrease in transmittances of the thin films when annealing temperature is increased. It was found that annealing at 300 ^{o}C gave the least transmittance whereas 200 ^{o}C annealing of the same films gave the highest transmittance. The optical transmittance spectrum showed that the film transmits well above the visible region of the spectrum and tends to be constant in the far infrared region. The films annealed at 300 ^{o}C had polycrystalline nature making them have less irradiant. RF sputtered Cd_2SnO_4 films were also observed to have a similar effect after heat treatment in H_2 from 300 °C to 800 °C where their transmittance decreased as annealing temperature was raised from 300 °C to 800 °C (Adel et al, 2014).

Absorption coefficient

From the values of, values of absorption coefficient were calculated using equation 4.1 below: (Ahmed, 2016)

$\alpha = \frac{2.303A}{t}$ -- (4.1)

Where A is absorbance and t is film thickness

The Absorption curves for the doped and un-doped films and presented in figures 4.3A and 4.3B below:

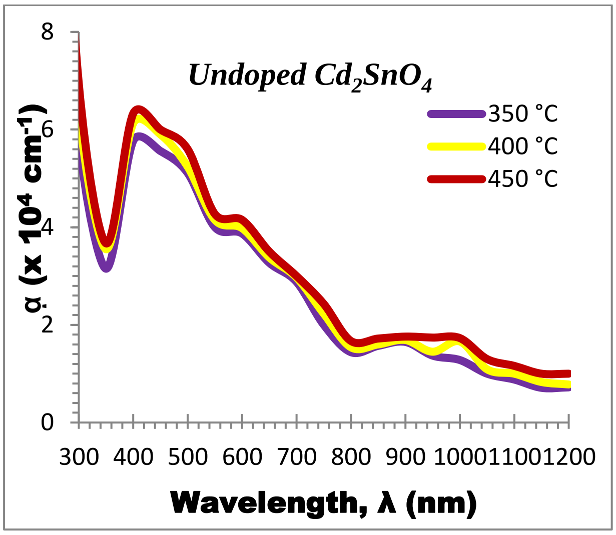

Figure 4.3A: Absorption coefficient graphs for Un-doped Cd_2SnO_4 thin films

Un-doped Cd_2SnO_4 thin films annealed at 350 °C recorded a lower absorption coefficient of 3.946 x 10^4 cm^{-1} compared to 4.215 x 10^4 cm^{-1} obtained from the same films Cd_2SnO_4 of annealed at 450 °C in the 588 nm wavelength region; a clear indication that increasing annealing temperature increases absorption coefficient.

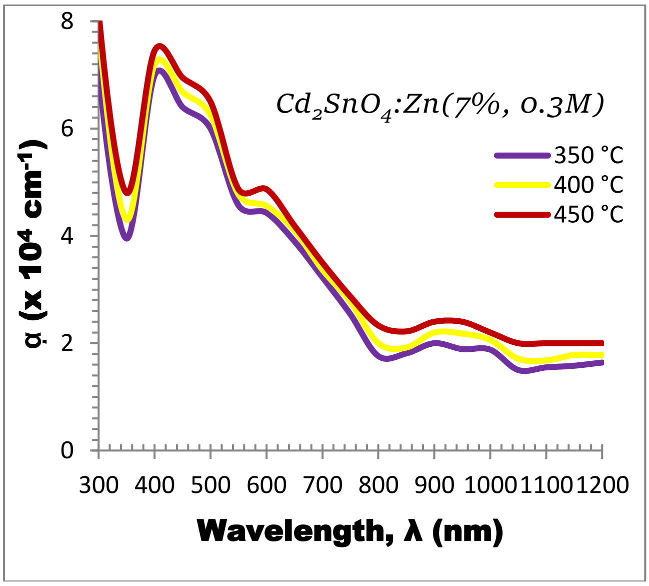

Figure 4.3B: Absorption coefficient for Zinc-doped Cd_2SnO_4 thin films

A similar trend is also observed in figure 4.3B where doped films annealed at 350 °C recorded a lower absorption coefficient of 4.754 x 10^4 cm^{-1} while the largest absorption coefficient obtained was 5.591 x 10^4 cm^{-1} from the films annealed at 450 °C in the 588 nm wavelength. (Adel, 2014) noted that with increase in annealing temperature, absorption coefficient increased and there was a shift of fundamental absorption edge towards the lower energies and longer wavelengths region for Cd O thin films. The shift may be due changes of the quality of the Cd O film with increase in annealing temperature causing improvement of crystallinity of the films.

Extinction coefficient

The extinction coefficient ($\boldsymbol{k}$) is a measure of light quantity that is lost due to absorption and scattering. The values of $\boldsymbol{k}$ were determined by equation 4.2 below:

$$\boldsymbol{k} = \frac{\alpha\lambda}{4\Pi} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.2)$$

where $\alpha = \frac{2.303A}{t}$

The extinction coefficients for the doped and un-doped film annealed at different temperatures have been presented in figures 4.4 A and 4.4B below:

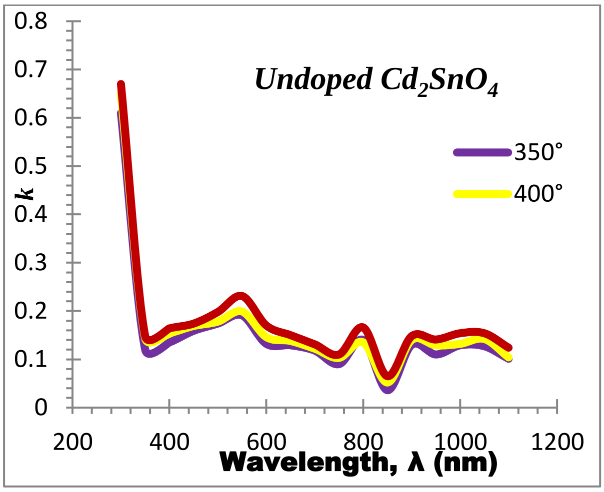

Figure 4.4A: Extinction Coefficients for Un-doped Cd_2SnO_4 thin films

The extinction coefficient of un-doped Cd_2SnO_4 thin films annealed at 350 °C was 0.1852 while the same films annealed at 450 °C recorded extinction coefficient of 0.2126 in the 588 nm wavelength as shown in figure 4.4 A above. The same films were doped with 7% of 0.3 M solution of Zinc Nitrate and annealed at three different temperatures and the results are presented in figure 4.4B below:

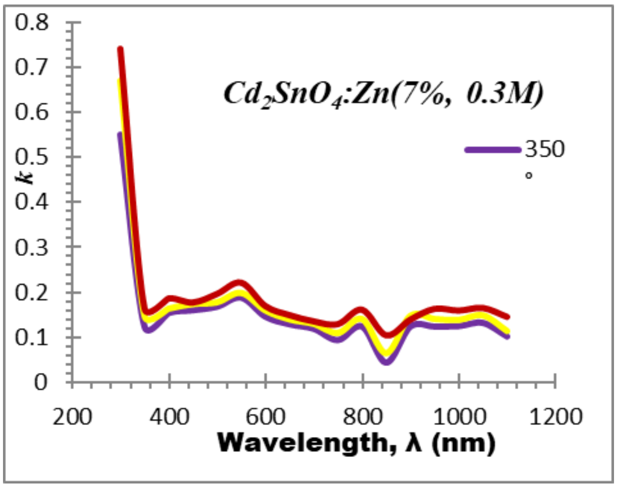

Figure 4.4B: Extinction coefficient for Zinc-doped Cd_2SnO_4 thin films

Increase in extinction coefficient values was realized with increasing annealing temperature, this could be caused by reduction of the band gap (Adel et al, 2014). Figure 4.4B indicates that the highest extinction coefficient of 0.2312 was obtained from films doped with 0.3M solution then annealed at 450 °C whereas thin films at the same concentration annealed at 350 °C recorded extinction coefficient of 0.1942. Annealing Zinc-doped Manganese Oxide (MnO_2) thin films from 300 °C to 800 °C caused an increase in the extinction coefficient of the films while annealing at 600 ° C and 800 ° C resulted in transformation of MnO_2 to Manganese III Oxide (Mn_2O_3) hence their difference in extinction coefficient from the others (Pishdadian and Shariati, 2013). When as-deposited Cd_2SnO_4 thin films were annealed in a 1.33×10^{-2} Pa vacuum at 600 °C for 30 minutes, their extinction coefficient were observed to increase (Kumaravel et al, 2010).

Band Gap Energy

Band gap energy for un-doped Cd_2SnO_4 thin films annealed at 350 ° C, 400 ° C and 450 ° C were determined using the equation 4.3 below:

$(\alpha E)^{1/2} = (E - E_g)$ ………………………………………………………… (4.3)

The optical band gap of thin un-doped and doped Cd_2SnO_4 thin films are presented in figures 4.5A and 4.5B

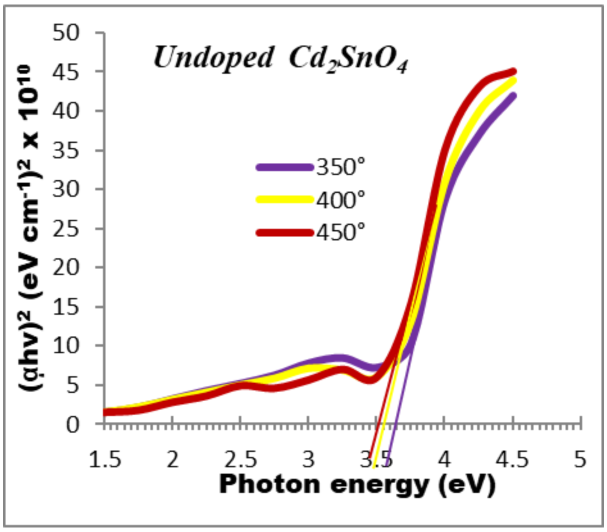

Figure 4.5A: Optical band gap for Un-doped Cd_2SnO_4 thin films

The optical band gap of thin un-doped Cd_2SnO_4 thin films reduced as annealing temperature increased. Un-doped films annealed at 350 °C yielded band gap of 3.7 eV but the same films annealed at a higher temperature of 450 °C recorded a band gap value of 3.5 eV as observed in figure 4.5A. The figure 4.5B below shows band gap for doped Cd_2SnO_4 thin films annealed at 350 °C, 400 °C and 450 °C.

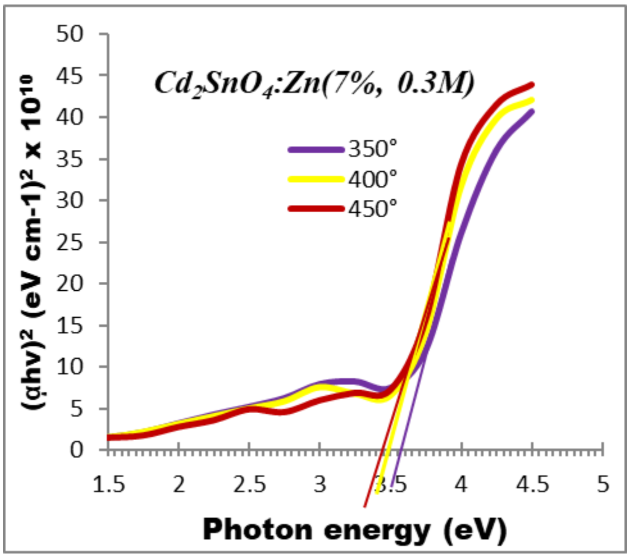

Figure 4.5B: Band gap for Zinc-doped Cd_2SnO_4 thin films

For the films doped with 0.3 M $Zn(NO)_3$ annealed at 350 °C, band gap of 3.55 eV was recorded while 450 °C recorded 3.45 eV as in figure 4.9. (Metina et al, 2009) observed a systematic decrease in band gap of as-deposited films when annealing was done at 823 K and a shift in absorption edge towards longer wavelengths. This is in agreement with (Prabahar and Dhanam, 2005) who noted degradation in optical absorption of the films annealed at 823 K at the forbidden region. Increasing annealing temperature from 350 °C to 800 °C decreased indirect band gap, annealing process not only restricts Oxygen atoms in a material but also eliminates the absence of oxygen (Pishdadian and Ghaleno, 2013). The created O_2 interstitials form secluded band defects in the band gap region, reducing the band gap as annealing temperature is increased (Saturi et al, 2017) and Saipriya et al (2011).

Refractive Index

Refractive index is was determined for both un-doped and doped films after annealing. Refractive index;

$$\boldsymbol{n} = \left[\left\{\frac{4R}{(R+1)^2}\right\} - k^2\right]^{0.5} + \frac{(R+1)}{(R-1)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.4)$$

Where **R** is the reflectance and ***k*** is the extinction coefficient.

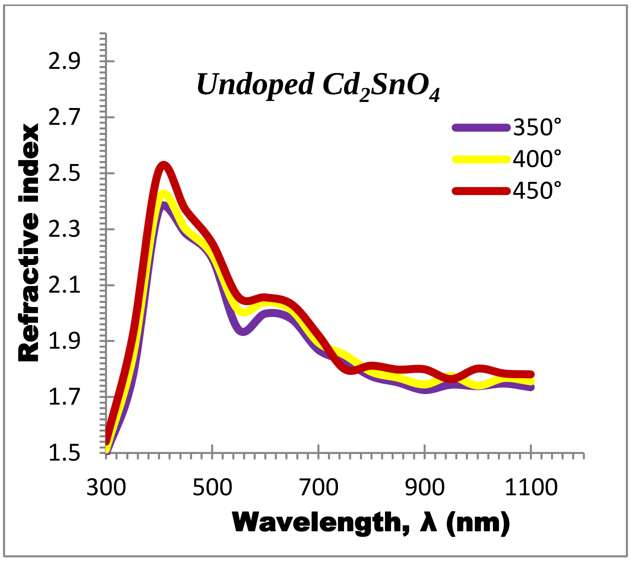

Figure 4.6A: Refractive index for un-doped Cd_2SnO_4 thin films

Refractive index is observed to increase with the rise in the annealing temperature. Films annealed at 450 °C showed higher refractive index compared to those annealed at 350 °C.

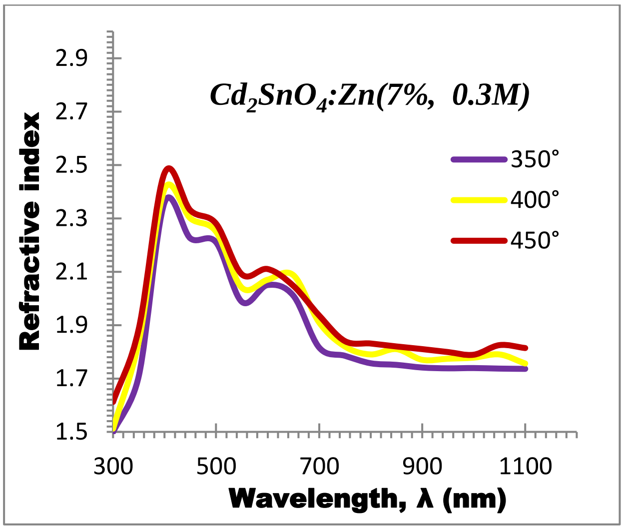

Figure 4.6B: Refractive index for Zinc-doped Cd_2SnO_4 thin films

In figure 4.6B, the films doped with 7% of 0.3 M $Zn(NO)_3$ and then annealed at the highest temperature i.e. 450 °C gave the highest refractive index of 2.121 while ones annealed using the 350 °C temperature had a refractive index of 1.983. Annealing increases the packing density of the films hence the increase in refractive index (Navina et al, 2004). The increase in refractive index with increased annealing temperature could also be due to the change in nano-crystalline size (Shanmugavadivu et al, 2019). All the annealed films had their refractive indices decreasing drastically with increase in wavelengths, meaning little light absorption at longer wavelengths. (Saad et al, 2011) also observed that increase in annealing temperature caused a rise in the refractive index of Chromium III Oxide which they attributed to changes of absorption in the visible and ultraviolet regions due to annealing.

V. Conclusions

Un-doped and Zinc-doped Cd_2SnO_4 thin films were prepared by the relatively less expensive and easy to perform dip-coating method and the films annealed at 350 °C, 400 °C and 450 °C. XRD patterns indicated that the films obtained in this study had good crystallinity, a prominent peak existed along (2 0 0) direction, annealing did not cause any shifting in positions of the peaks. This preparation technique gave good quality of un-doped and Zinc-doped Cd_2SnO_4 thin films as were observed from the results obtained from this study; transmittance of up to 78.9 % at 700 nm for un-doped films, absorption coefficient of up to 5.591×10^4 cm^{-1} and extinction coefficient of 0.1913 - 0.2814 at the 588 nm wavelength as well as high optical band gap of between 3.45 - 3.66 eV. The study produced thin films with high absorption coefficient at low wavelengths, hence suitable for use in front panels of thin film solar photovoltaic cells (Ellingson and Heben, 2011).

Annealed un-doped Cd_2SnO_4 thin films exhibited the highest transmittance of 78.9 % and the best refractive index of 2.121 making it the most suitable material for photovoltaic applications. Solar photovoltaic cells are manufactured using thin film coatings of transmittance of ~ 80% and above; Andreas (2012).

References

[1] Adel, H., Omran, A., Imad, A., Disher A., Oday, A.& Chichan A. (2014).Annealing Effect On The Structural And Optical Properties Of Solgel Deposited Nanocrystalline Cdo Thin Films. 34 (1), 2014.

[2] Ahmed, S., Ahmad, M., Babu, S. & Saiqa, I. (2016). Green Synthesis Of Silver Nanoparticles Using Azadirachta Indica Aqueus Leaf Extract. Journal Of Radiation Researchand Apllied Sciences. 9 (1), 1-7.

[3] Ali, N., Ahmed, R., Shaari, A., Rahim, I., Shah, M., Hussain, A., Ahmad, N. & Abbas, S., M. (2014). Annealing Effects On The Structural And Optical Properties Of Thermally Deposited Tin Antimony Sulfide Thin Films .Brazilian Journal Of Physics, 44 (6), 733-738.

[4] Alnaimi, M. & Al-Dileamy, N. (2007). Determination Of Optical Constants Of Cadmium Stannate Films. Doha: University Of Qatar.

[5] Andreas, S. (2012). Transparent Conducting Oxides: An Up-To-Date Overview. Materials, 5, 661-683.

[6] Carballeda-Galacia, D., Castanedo-Perez, R., Jimenez-Sandoval, O. & Jimenez-Sandoval, R. (2000). High Transmittance Cdo Thin Films Obtained By Sol-Gel Method. Thin Solid Films. 371(1-2), 105-108.

[7] Cardile, M., Bowden, E., Koplick, J. & Buckley, G. (1990). Thin Solid Films.186 (1990), L11.

[8] Cristaldi, A., Gulino, A. & Maria, E. (2012). Structural, Electronic And Electrical Properties Of Yttrium-Doped Cadmium Stannate: Journal Of Physical Chemistry, 116 (5), 3363-3368.

[9] Day, R., France, P., Carter, S., Moore, M. & William, R. (1990). Fluoride Fiber For Optical Transmission. 22 (1990), 259-277.

[10] Ellngson, R. & Heben, M. (2011). Sheet Resistance: Measurement And Significance. University Of Toledo. Phys 6/7280:2.

[11] Eman, M., Igbal, N. & Alias, F. (2014). Optical And Electrical Properties Of Cadmium Tin Oxide Films Prepared By Vacuum Evaporation Technique: Research And Reviews In Materials Science And Chemistry, 4(1), 1-16.

[12] Hashemi, T., Al-Dhhan, Z. & Hogarth, C. (1989). A Novel Method Of Producing Dicadmium Stannate In Thin Film Form. Journal Of Materials Science. 24 (1989), 615-617.

[13] International Union Of Pure And Applied Chemistry. (1980). Atomic Weights Of Elements 1979. Pure Appl. Chem. 52(10), 2349-2384.

[14] Jayaram, V., Baldev, R., Krishnan, R., David, C., Dash, S. & Ajikumar, P. (2011). Reactive Pulsed Laser Deposition And Characterization Of Niobium Nitride Thin Films. Surface And Coatings Technology.206 (6), 1196-1202.

[15] Krishna, K., Kamamurthi, K. & Elangovan, E. (2010). Novel Procedure To Prepare Cadmium Stannate Films Using Spray Pyrolysis Technique For Solar Cell Applications. Caparica: New University Of Lisbon.9, 467 – 471.

[16] Krishnakumar, V., Kumaravel, R., Ramamurthi, K. & Santhakumar, K. (2009). Preparation Of Cadmium Stannate Thin Films By Spray Pyrolysis Technique. 9 (2), 467-471.

[17] Mazzeo, M., Mariano, F. & Gigli, G. (2013). High-Efficiency Ito-Free Flexible White Organic Light-Emitting Diodes Based On Multi-Cavity Technology. Organic Electronics, 4 (12), 2840- 2846.

[18] Metina, H., Selma, E., Mehmet, A., Semra, D. & Mehmet, B. (2009). The Effect Of Annealing Temperature On The Structural, Optical, And Electrical Properties Of Cds Films. 1(2009). 189-197.

[19] Minami, T. (2005). Transparent Conducting Oxide Semiconductors For Transparent Electrodes. Semiconductor Science And Technology, 20 (4), 35-44.

[20] Navina, M.,Vinay, G., Kondepudy, S. & Abhai, M. (2004). Effect Of Annealing On Refractive Indices Of Radio-Frequency Magnetron Sputtered Wave Guiding Zinc Oxide Films On Glass. Journal Of Applied Physics. 96 (2004), 3134.

[21] Ongwen, N., Oduor, A. & Ayieta, P. (2019). Effect Of Concentraion Of Reactants And Deposition Temperature On Optical Properties Of Iron-Doped Cadmium Stannate Thin Films Deposted On Glass Substrates By Spray Pyrlysis: Internal Journal Of Scientific And Technical Research In Engineering (Ijstre). Masen Unversity.

[22] Patil, L., Dea, V. & Kaushik, M. (2012). Modified Cadmium Stannatenano Structured Thin Films Prepared By Spraying Technique For Detection Of Chemical Wafers. Pratibha: International Journal Of Science, Spirituality, Business And Technology, 1 (1), 2261-2277.

[23] Pishdadian, S. & Ghaleno, M. (2013). Influences Of Annealing Temperature On The Optical And Structural Properties Of Manganese Oxide Thin Film By Zn Doping From Solgel Technique. 123 (2013), 1-17.

[24] Prabahar, S. & Dhanam, M. (2005). Cds Thin Films From Two Different Chemical Baths—Structural And Optical Analysis. J. Cryst. Growth. 41 (2005), 285.

[25] Renu, K. & Vipin, K. (2019). Impact Of Zinc Doping On Structural, Optical And Electrical Properties Of Cdo Films Prepared By Sol-Gel Screen Printing Mechanism. Journal Of Sol-Gel Science And Technology. 94(2020), 648-657.

[26] Saipriya, S., Sultan, M. & Singh, R. (2011). Effect Of Environment And Heat Treatment On The Optical Properties Of Rf-Sputtered Sno2 Thin Films. Physica B: 406 (2011), 812-817.

[27] Shanmugavadivu, A., Yuvaloshini, J. & Ravi, G. (2019). Effect Of Annealing On The Characteristics Of Nanocrystalline Cds Thin Films Prepared By Chemical Bath Deposition Method. International Journal Of Semiconductor. 3(2), 33-42.

[28] Sharonova, A., Surmeneva, M., Loza, K., Prymak, O.& Surmenev, R.(2019). Surface Functionalization Of Titanium With Silver Nanoparticles. Journal Of Physics: Conference Series, 1145 (1), 012-032.

[29] Shugar, G. & Ballinger, J. (1996). Chemical Technicians' Ready Reference Handbook. New York: Mcgraw-Hill. 4th Edition,972 Pages. Isbn 0- 07-0571 86-4.

[30] Zhongming Du, Xiangxin Liu, Yufen Zhang, Ziyao Zhu. (2017). "High-Quality Cadmium Stannate Annealed In N Atmosphere For Low-Cost Thin Film Solar Cell ", Rsc Advances, 2017.