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EFFECT OF ANNEALING TEMPERATURES AND DURATIONS ON THE OPTICAL AND ELECTRICAL PROPERTIES OF ELECTRODEPOSITED CdMnTe

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ABSTRACT

The work explored the effects of varying annealing durations and temperatures on the optical and electrical properties of electrodeposited CdMnTe thin films. A 2-electrode system was used for the deposition and the thin films were grown at a cathodic potential of 1400 mV, pH of 2.0 ± 0.02 at 70 ℃ in an electrolytic bath prepared with CdSO4, $MnSO_4$, and TeO_2. The UV-visible spectrophotometer was used to study the optical properties of the thin films, and the photo-electro-chemical cell measurement was used to determine the electrical conductivity types of the thin films. The absorbance of the film increased f or annealing time of 4 and 6 minutes and for annealing temperatures of 50 and 70 ℃. But for an annealing duration of 6 minutes and annealing temperature of 90 ℃, the absorbance had lower values when compared to the as-deposited. Varying energy band gaps were obtained at different annealing parameters and values. Electrical conductivity type of n-, p- and intrinsic types were obtained.

1. Introduction

Cadmium manganese telluride (CdMnTe) is believed to be a potential candidate for room-temperature radiation detection and other applications due to its excellent properties [1.2]. These properties, which are essential for the fabrication of X-ray and gamma-ray detectors, include segregation coefficient k ≈1 for Mn in CdTe, high resistivity, excellent electron transport, sensitivity of doping rate to band-gap change [2]. CdMnTe has also find applications in solar cells, infrared (IR) detectors, optical isolators, and spintronics devices [3, 4]. CdMnTe has been synthesized using techniques like vertical Bridgman method [3, 5-6], molecular beam epitaxy [7], electrodeposition technique [4] and so on. Defects like impurities, Te inclusions, Cd vacancies and so on, have been reported in as-deposited CdMnTe [8].

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Defects are intrinsic in synthesized materials. Reducing defects in materials improve their crystal quality, and hence their device applications [9]. Thermal annealing is used to achieve high crystalline quality of synthesized thin films and crystals [10, 11]. Different materials have been reported to have enhanced optical properties as a result of thermal annealing. Defects like dislocations and structural defects could be removed through annealing [10]. Aside the reduction of defects, [12] reported that thermal annealing could be used in tailoring the properties of the materials, and parameters like annealing temperature, duration, atmosphere, and pressure could alter the effect of annealing on a material

Annealing has varying effects on different synthesized materials. While the increase in the optical band gap of indium-doped zinc oxide with the increase in annealing temperature was reported by [9] and [11], annealing of CdMnTe in air and with $CdCl_2$ resulted in the reduction of the energy band gap of the film [4]. Optical parameters like reflectance, refractive index, and real part of the complex dielectric function have been reported to increase with increasing annealing time [13]. Variation of the annealing time and temperature for ZnS was reported by [14], their result showed that annealing enhanced the reflectance and transmittance of the material. Band gap increase with increases in annealing time for TiO_2 was also reported by [15]. An increase in optical band gap and transmittance with an increase in annealing time for ZnSe was also reported by [16].

According to [17], thermal annealing is indispensable for solution-based processes to facilitate decomposition and oxidation. Also, [4] grew a CdMnTe at 1400 mV, annealed in air, and also applied chemical treatment before annealing at 400 °C for 10 minutes. Their work does not explore the effects of varying annealing duration and varying annealing temperatures. Since electrodeposition technique utilized in the deposition of CdMnTe is a solution-based technique, this work explores the effect of varying annealing temperatures and annealing durations on the optical and electrical properties of electrodeposited CdMnTe.

2 Materials and Methods

Fluorine doped Tin Oxide (FTO) coated conducting glasses were used as the deposition substrates. The FTOs were thoroughly washed in soap solution, and rinsed in deionized water and methanol. A two-electrode potentiostat, with graphite rods was used for the deposition. The FTO was attached to one of the rods to serve as the working electrode of the system. The CdMnTe thin films were then grown from a bath prepared using 10 grams of $3CdSO_4.8H_2O$ of 99% purity, 2 grams of Manganese (II) sulphate hydrate ($MnSO_4.4H_2O$) dissolved in 400 ml of de-ionised water and 4 ml of dissolved TeO_2. The details of preparing the TeO_2 solution have been reported in [4].

The CdMnTe thin films were synthesized at were pH = 2.0 ± 0.02, cathodic deposition voltage of 1400 mV, growth temperature of 70 °C and growth duration of 10 min. Annealing was carried out in air at 70 °C for 4, 6 and 8 minutes annealing time to determine the optimal annealing duration. Another set the films were annealed at 50 °C, 70 °C, and 90 °C for 4 minutes each to identify the optimal annealing temperature. The thin films were studied using the UV-Visible spectrophotometer for their optical properties. The photoelectrochemical cell measurement was used to determine the electrical conductivity type of the films.

Results and Discussion

Optical properties of post-electrodeposited heat-treated (HT) CdMnTe

The thin films annealed for 4 and 6 minutes and the thin films annealed at 50 and 70 °C had good adherence to the substrates. Annealing time of 8 minutes and annealing temperature of 90 °C showed signs of peeling off from the substrate.

Figure 1 and 2 show the absorbance spectra for the heat-treated (HT) and as-deposited (ED) thin films for varying annealing duration and temperature respectively. The graphs show that the absorbance for the heat-treated samples, both for varying time and temperature, decreased with increasing photon wavelength. The absorbance of the samples annealed at 4 and 6 minutes (Figure 1), as well as the films annealed at 50 and 70 °C (Figure 2) were higher than the as-deposited samples. But the samples annealed at 8 minutes (Figure 1) and at 90 °C (Figure 2) had almost constant absorbance which is more than the as-deposited samples in the visible to near infrared region. The improvement in absorbance level after annealing in air according to [18] results from thermally induced re–crystallization and a total reaction between unreacted Cd, Mn and Te atoms to form CdMnTe. It was also observed that average absorbance decreased with an increase in annealing time and increase in annealing temperature as seen in Table 1.

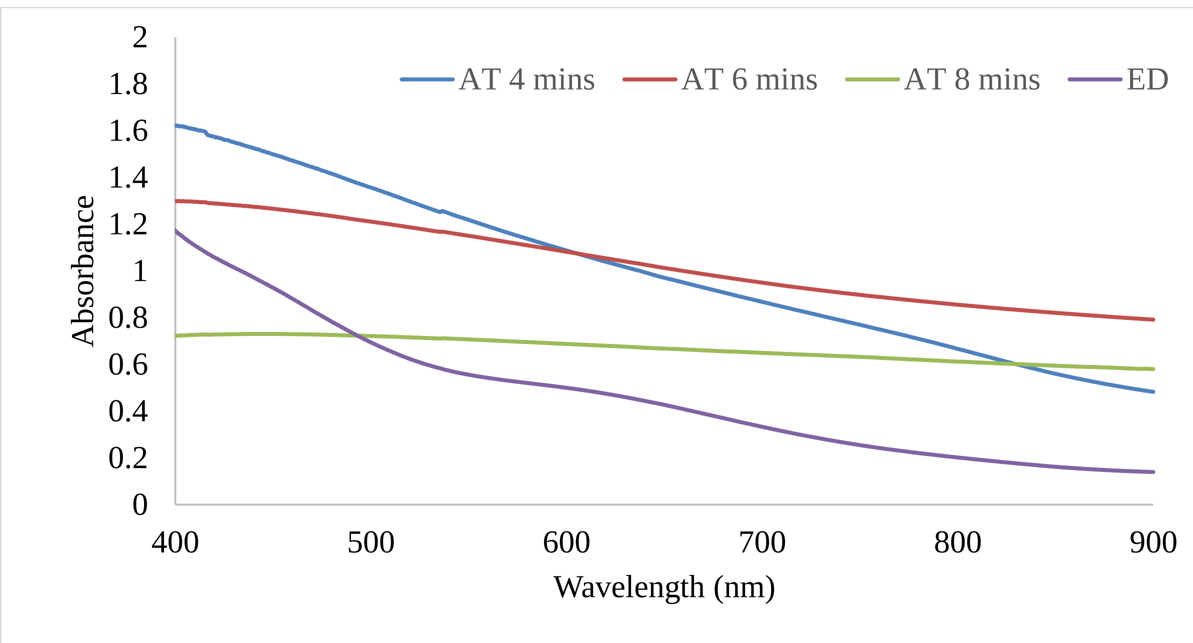

Figure 1: Absorbance spectra of the CdMnTe thin films at different annealing time intervals

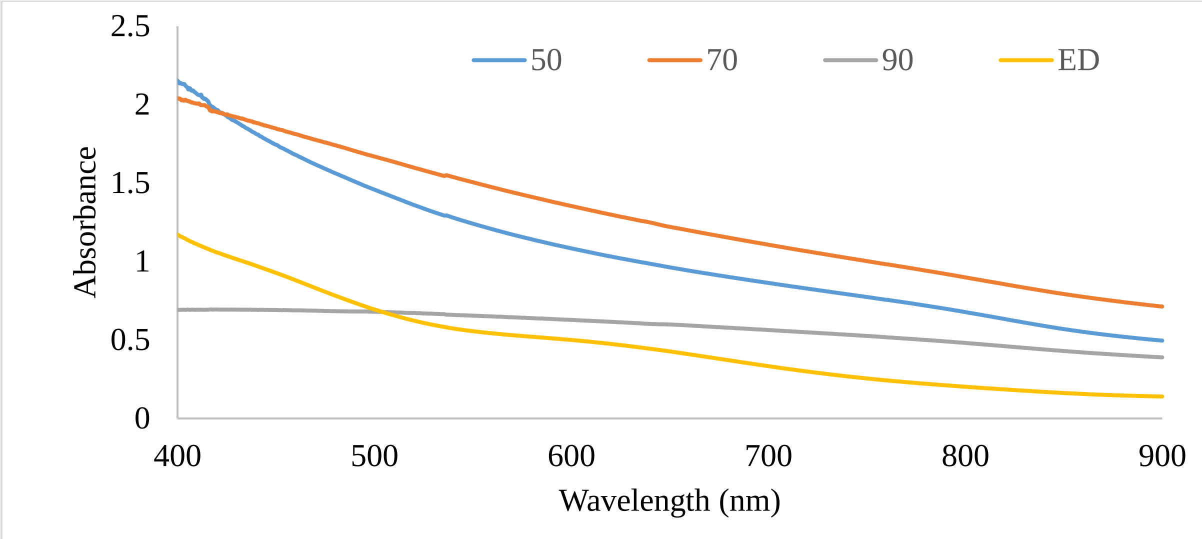

Figure 2: Absorbance spectra of the CdMnTe thin films at different annealing temperature

Table 1: Summary of the optical properties of electrodeposited and heat-treated (HT) CdMnTe thin films

Sample ID	Annealing Parameters	Bandgap energy (ev)	Average transmittance (T)	Average reflectance (R)	Average absorbance (A)	Absorption coefficient t(α)x10 ^{14}(cm-1)	Refractive index (n)	Extinction coefficient (k)	Optical conductivity (σ)x10 ^{14}(s-1)	Dielectric constant (E = Er+ Ei)
E1	4 mins	2.36	0.1112	-0.2319	1.1207	8.01	1.99377	0.343	2.18	5.2196
E2	6 mins	3.84	0.0900	-0.1905	1.1005	8.6	1.3638	0.3868	2.09	2.8734
E3	8 mins	3.70	0.2088	0.1029	0.6883	4.3	2.0076	0.1995	2.01	4.8413
E4	50°C	2.40	0.10449	-0.40404	1.29956	8.935	2.359	0.36688	2.15814	6.74362
E5	70°C	2.00	0.06223	-0.50578	1.44356	11.28	1.5787	0.48386	2.28352	3.67537
E6	90°C	-	0.26132	0.145535	0.59315	3.554	2.610	0.16282	1.58128	7.688
E7	ED	2.85	0.3400	-0.001	0.6609	10.4	2.3621	0.3998	3.36	6.9747

The annealing process significantly impacts the absorption coefficient of the CdMnTe thin films as indicated in Figure 3. The curves of the heat-treated films at varying annealing time show a higher absorption coefficient at a lower photon energy. However, at higher photon energy, the as-deposited film outperformed the heat-treated samples, this fact is corroborated by the average values in Table 1. Nonetheless, there seems to be an optimal annealing time around 6 minutes where the absorption coefficient reaches its maximum values, two times that of 8 minutes annealing time. This suggests that further annealing beyond this point might not lead to significant improvement in the properties of the films.

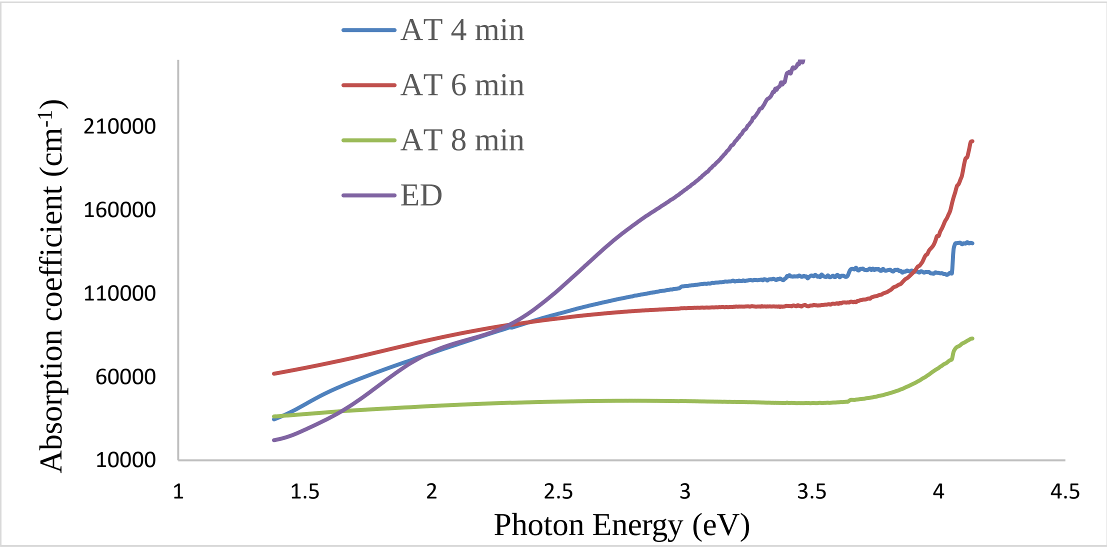

Figure 3: A graph of absorption coefficient (α) against photon energy of the CdMnTe thin films annealed at different time intervals.

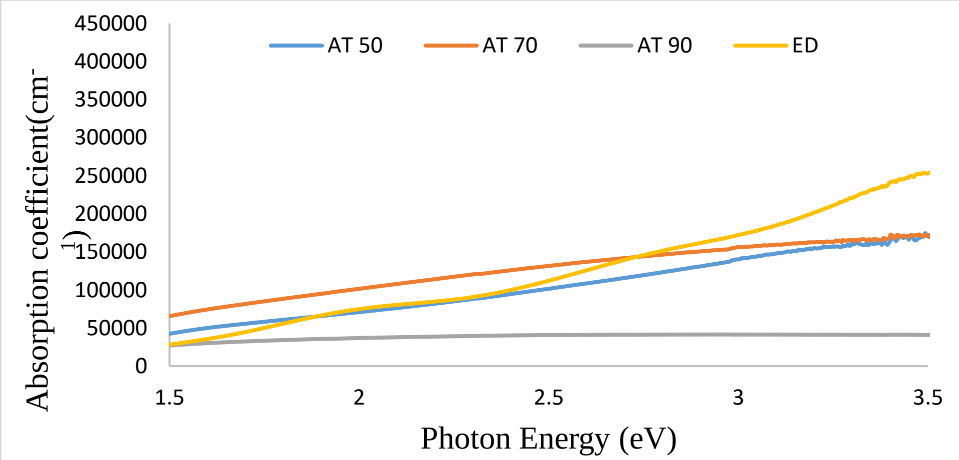

Figure 4: A graph of absorption coefficient (α) against energy of the CdMnTe thin films annealed at different temperature.

The absorption coefficient spectra of the thin films annealed at varying annealing temperature is shown in Figure 4. An increased in the absorption coefficients were observed for the samples annealed at 50 and 70 °C. But at higher photon energy, the as-deposited had higher absorption coefficient. The sample annealed at 90 °C had the lowest absorption coefficient, suggesting that the annealing temperature beyond 70 °C may not improve the properties of the material.

The energy band gaps of the as-deposited and heat-treated films are shown in Figures 5 and 6 respectively. Annealing at 4, 6, and 8 minutes varied the band gaps with these values 2.35 eV, 3.85 eV, and 3.7 eV respectively. While the annealing at different temperatures gave the band gaps of 2.40 eV and 2,0 eV for the thin films grown at 50 and 70 °C. The band gap of the thin film grown at 90 °C could not be extrapolated, maybe due to the poor adherence of the film to the substrate at this annealing temperature.

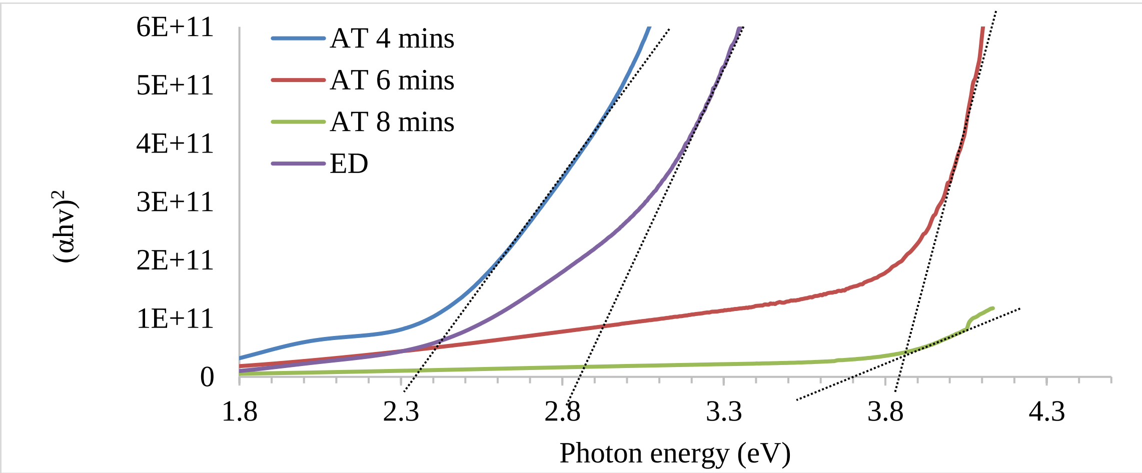

Figure 5: A Tauc plot of the CdMnTe thin films annealed at different time intervals.

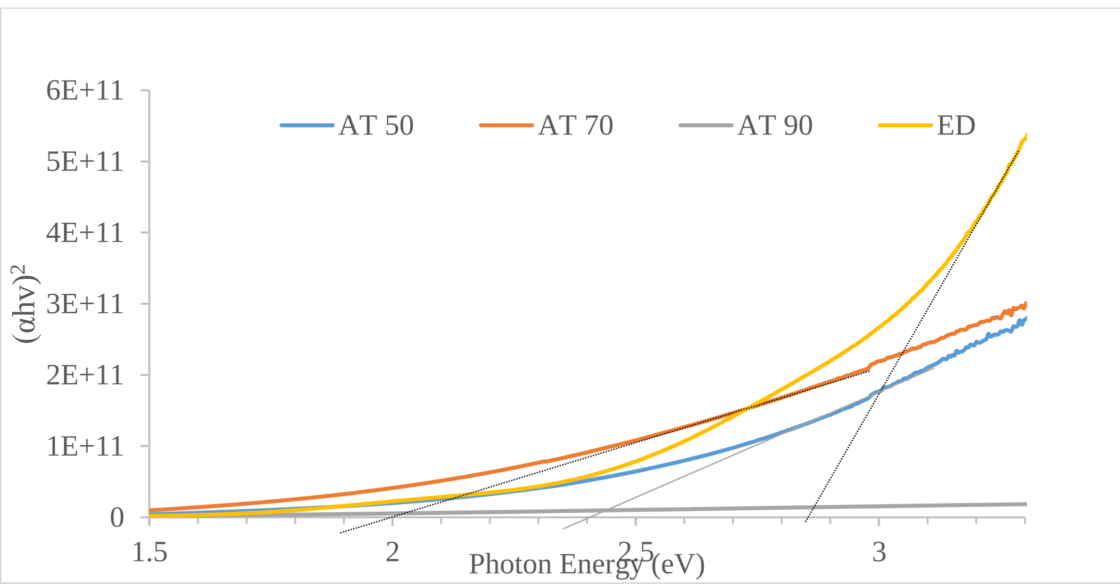

Figure 6: A Tauc plot of the CdMnTe thin films annealed at different temperature

The result of the PEC cell measurements revealing the electrical conductivity type of the as-deposited and annealed CdMnTe thin films are shown in Table 2. The electrical conductivity type of the as-deposited is n-type, and this conductivity type was still retained for the samples annealed at varying annealing times. However, the electrical conductivity type changed for the samples annealed at varying temperatures. The electrical conductivity type for the sample annealed at 50 °C changed to p-type, while the samples annealed at 70 and 90 °C became an intrinsic type. This work partially aligned with [4], who reported that the electrical conductivity type for CdMnTe grown at higher cathodic potentials is n-type, and changes to p-type after annealing in air.

Table 2: PEC results showing the electrical conductivity types of the thin film

Parameters	Values	PEC signal
ED (mV)	1400	-0.20
Annealed at varying time (minutes)	4	-0.10
	6	-0.10
	8	-0.20
Annealed at varying temperature (°C)	50	1
	70	0
	90	0

Conclusion

This work successfully explored the effect of varying annealing durations and temperatures on the optical and electrical properties of the electrodeposited CdMnTe thin films. The result of the optical analysis showed that the absorbance of the CdMnTe thin films for the as-deposited and annealed all decreased with increasing photon wavelength. However, annealing at lower times and temperatures enhanced the absorbance of the material. Annealing at varying durations and temperatures produced energy band gaps in the range of 2.36 – 3.84 eV and 2.00 – 2.40 eV respectively. The electrical conductivity types for the as-deposited and the samples annealed at varying durations were n-type. However, samples annealed at varying temperatures were of p- and intrinsic types.

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