Fluorine-induced improvement of structural and optical properties of CdTe thin films for solar cell efficiency enhancement

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Abstract

CdTe thin films of different thicknesses were electrodeposited and annealed in air after different chemical treatments to study the effects of thickness and the different chemical treatments on these films for photovoltaic applications. The thicknesses of the samples range from 1.1 μm to 2.1 μm and the annealing process was carried out after prior $CdCl_2$ treatment and $CdCl_2$+CdF_2 treatment as well as without any chemical treatment. Detailed optical and structural characterisation of the as-deposited and annealed CdTe thin films using UV-Vis spectrophotometry and x-ray diffraction reveal that incorporating fluorine in the well-known $CdCl_2$ treatment of CdTe produces remarkable improvement in the optical and structural properties of the materials. This $CdCl_2$+CdF_2 treatment produced solar cell with efficiency of 8.3% compared to $CdCl_2$ treatment, with efficiency of 3.3%. The results reveal an alternative method of post-deposition chemical treatment of CdTe which can lead to the production of CdTe-based solar cells with enhanced photovoltaic conversion efficiencies compared to the use of only $CdCl_2$.

Keywords: CdTe; $CdCl_2$; CdF_2; annealing; electrodeposition; solar cell.

1.0   Introduction

CdTe is an important group II-VI semiconductor for applications such as in photovoltaic solar energy conversion [1-5] and radiation detection [6-8]. The most crucial properties of this material for these applications include; optical, structural, chemical composition and electronic properties. These properties have been studied to certain extent to date [9-12]. For photovoltaic application in particular, these studies have mainly concentrated on $CdCl_2$-treated CdTe since $CdCl_2$ treatment is a crucial step in the fabrication of high efficiency CdTe-based solar cells [13-15]. The improvement in solar cell efficiency in this case is attributed to the diffusion of Cl into CdTe. As a modification of the $CdCl_2$ treatment, Mazzamuto *et al.* [14] and Rio-Flores *et al.* [16] have tried to incorporate Cl into CdTe

during post-deposition heat treatment by using a mixture of argon and a Freon gas (CHF$_2$Cl) which contains both Cl and F atoms to achieve improved solar cell efficiency [14]. Recently, authors of the present work have incorporated Cl and F atoms into CdTe through the use of a mixture of CdCl$_2$ and CdF$_2$ in the post-deposition heat treatment of CdTe to obtain improved solar cell efficiency compared to the use of only CdCl$_2$ treatment [17]. This improvement has also been attributed to the higher diffusion property of F compared to Cl. These recent results by the authors' group [17] as well as those of Mazzamuto *et al.* [14] and Rio-Flores *et al.* [16] have necessitated the detailed study of the effects of annealing of CdTe with CdCl$_2$ treatment, CdCl$_2$+CdF$_2$ treatment and without chemical treatment, on the structural and optical properties of electrodeposited CdTe thin films of different thicknesses, in order to further understand how these treatments impact the properties of CdTe for solar cell efficiency improvement. It is pertinent also to observe that although some optical properties of CdTe have been studied at different times [12, 18], comprehensive study of the effect of different annealing conditions (with prior CdCl$_2$ and CdCl$_2$+CdF$_2$ treatments) on the entire optical parameters (transmittance, absorbance, reflectance, absorption coefficient, extinction coefficient, refractive index and dielectric constant) of CdTe has not been reported in a single publication.

The optical parameters of the CdTe thin films of different thicknesses were obtained from normal-incidence transmittance spectra and applying equations (1) - (8) [19-22]. It is well-known that when light is incident on a thin film material, it is either absorbed, transmitted or reflected, and the sum of the fractions of the absorbed, transmitted and reflected light equals unity, assuming no losses due to scattering, so that

$$A + T + R = 1 \qquad\qquad (1)$$

where *A* is absorbance, *T* is transmittance and *R* is reflectance.

The overall response of the material to the incident light is connected to its complex refractive index according to equation (2).

$$N = n + iK \qquad\qquad (2)$$

where *N* is the refractive index of the material, *n* is the real part of the refractive index and *K* is the imaginary part of the refractive index, and also known as the extinction coefficient of the material in question.

The reflectance of the material and the real part of the refractive index are related by equation (3).

$$R = \frac{(n-1)^2}{(n+1)^2} \qquad\qquad (3)$$

The absorption coefficient α, of the material is also related to the extinction coefficient according to equation (4).

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$$\alpha = \frac{4\pi K}{\lambda} \tag{4}$$

where λ is the photon wavelength.

The complex dielectric constant ε, is related to n and K according to equation (5).

$$\varepsilon = (n + iK)^2 = \varepsilon_r + \varepsilon_i \tag{5}$$

where ε_r and ε_i are the real and imaginary parts of the dielectric constant of the material respectively.

The absorbance of the thin film is related to its transmittance according to equation (6).

$$A = \log_{10}\left(\frac{1}{T}\right) \tag{6}$$

The absorption coefficient is also related to the transmittance by

$$\alpha = -\frac{1}{d}\ln T \tag{7}$$

where d is the thickness of the film.

Finally, for a direct bandgap semiconductor, the absorption coefficient is related to the energy hv, of the absorbed photons and the energy bandgap E_g, of the semiconductor by

$$\alpha = \frac{C(hv - E_g)^{1/2}}{hv} \tag{8}$$

where C is a constant, h is Planck's constant and v is the frequency of the incident photon.

2.0   Experimental Procedure

The CdTe thin films used in this work were potentiostatically electrodeposited from an aqueous electrolyte containing 1 M $CdSO_4$ of 99% purity and 1 mM TeO_2 of 99.999% (with 1000 ppm of high-purity $CdCl_2$ and CdF_2 as dopants) using a two-electrode deposition set-up. A high-purity platinum plate was used as the anode (counter electrode) and glass/fluorine-doped tin oxide (FTO) as the cathode (working electrode). Because of its low purity, the $CdSO_4$ chemical was first electro-purified for 48 h at a cathodic potential slightly lower than the potential for the deposition of Cd using glass/FTO substrate. These potentials were determined from a cyclic voltammogram recorded for the 1 M $CdSO_4$ solution in de-ionised water, using a Gill AC computerised potentiostat (ACM Instruments Cumbria, UK). After the electro-purification, 1 mM TeO_2 was then added to make up the CdTe deposition electrolyte. The pH of the electrolyte was adjusted to 2.0 ± 0.02 and CdTe layers were electrodeposited at a cathodic voltage of 2038 mV and temperature of $85.0\pm2.0°C$. Full details of the

electrodeposition of CdTe thin films using two-electrode system is reported in recent publications [23, 24].

Four samples of CdTe with thicknesses were electrodeposited on glass/FTO substrates. The thicknesses of the samples were determined using a UBM Microfocus optical thickness profilometer (UBM, Messetechnik GmbH, Ettlingen, Germany). Each of the four samples with area of 2 cm × 4 cm, was divided into four pieces of area 1 cm × 2 cm each. One set of these pieces was treated with $CdCl_2$ by dipping them in a saturated $CdCl_2$ solution in deionised water and allowed to dry. Another set was treated with a saturated $CdCl_2$ solution containing about 0.1 g of CdF_2. The $CdCl_2$ and CdF_2 chemicals were both of 99.999% purity. All chemicals used in the work were purchased from Sigma Aldrich, UK. The remaining two sets of samples were left without chemical treatment. Afterwards, the samples treated with $CdCl_2$ and $CdCl_2+CdF_2$ together with one set of the samples without chemical treatment were annealed in air at a temperature of 450°C for 15 minutes in a programmable Carbolite furnace. The last set of samples without chemical treatment was left as-deposited.

Optical characterisation of all the annealed and as-deposited CdTe samples was carried out using a Cary 50 UV-VIS Spectrophotometer (Varian, Australia) by recording the normal-incidence transmittance spectra in the photon wavelength range of (750 − 1000) nm. Using equations (1) – (8), the rest of the optical parameters were obtained from the transmittance spectra. For structural characterisation, x-ray diffraction (XRD) patterns of the 16 samples were obtained using a Philips X'pert Pro diffractometer (Philips Analytical, The Netherlands) with Cu-Kα excitation wavelength of 1.5406 Å for 2θ angles from 20° to 70°. The applied tension and current were 40 kV and 40 mA respectively. Solar cells were fabricated using CdTe treated with $CdCl_2$ and $CdCl_2+CdF_2$ and assessed following the procedure reported earlier [17]. The results of the structural and optical characterisation of these samples are presented in the next section.

3.0   Results and Discussion

3.1   Structural characterisation – X-ray diffraction

Figures 1 (a), (b), (c) and (d) show the x-ray diffraction patterns of the 1.1 μm-thick CdTe thin film sample under different annealing conditions. From these results, the material displays preferential orientation of the crystallites in the (111) crystal plane in all four conditions. Figures 1(b), (c) and (d) however show that annealing with or without $CdCl_2$ or $CdCl_2+CdF_2$ treatment generally improves the (111) preferential orientation of crystallites. This improvement is however seen to be more pronounce for the sample treated with $CdCl_2+CdF_2$ (fig. 1(d)) compared to the one treated with only $CdCl_2$ (fig. 1(c)) and the sample without any chemical treatment (fig.1 (b)).

Figures 2 (a), (b), (c) and (d) show similar XRD patterns for the 1.3 μm CdTe layers under the same annealing conditions as in figure 1 above. Again a similar trend is observed as in the case of 1.1 μm samples in figure1. The sample treated with $CdCl_2+CdF_2$ also shows a more preferential crystallite orientation in the (111) plane compared to the rest of the samples.

Figures 3 (a), (b), (c) and (d) show the XRD results of the 1.8 μm sample under different treatment conditions. In general, the preferential crystallite orientation increases with annealing. Strikingly too, the situation begins to change at this thickness for the samples treated with $CdCl_2+CdF_2$ as is seen by the emergence of two additional XRD peaks corresponding to the (220) and (311) crystal planes of the cubic phase with the intensity of the (111) peak slightly decreasing below that of the sample treated with only $CdCl_2$. Thus the highly preferential orientation in the (111) plane begins to reduce with substantial intensity arising from the (220) and (311) planes, thereby making the material crystallites more randomly oriented. This result suggests a structural transformation of CdTe starting from around this particular thickness of 1.8 μm.

In figures 4 (a), (b), (c) and (d), the XRD patterns of the 2.1 μm sample under different treatment conditions are presented. Again, the (111) preferential orientation improved with annealing for the sample without chemical treatment and the one treated with only $CdCl_2$. For the sample treated with $CdCl_2+CdF_2$, the story changes completely with the (111) peak decreasing drastically in intensity, this time, below that of the as-deposited sample. As a result, one extra peak corresponding to the (331) crystal plane of the cubic phase appears in addition to the (220) and (311) peaks that came up in the corresponding 1.8 μm sample. Not only does one see a total of four XRD peaks, but the peaks corresponding to the (220) and (311) planes increased considerably in intensity, indicating further population of these crystal planes by crystallites. The material layer therefore has more randomly oriented crystallites. The results of figures 1, 2, 3 and 4 suggest a threshold thickness of the electrodeposited CdTe thin film (in the neighbourhood of 1.8 μm) beyond which the crystallites in the material become more randomly oriented with a resultant polycrystalline material.

Again, the results suggest that treating CdTe with $CdCl_2+CdF_2$ prior to annealing facilitates this structural transformation more than the conventional $CdCl_2$ treatment does. Most of the high-efficiency CdTe-based solar cells reported in the literature have employed CdTe materials with randomly oriented crystallites depicted by the type of XRD pattern shown in figure 4(d) [14, 25, 26]. The CdTe samples treated with $CdCl_2+CdF_2$ should therefore produce CdTe solar cells with improved efficiency compared to those treated with only $CdCl_2$. Structural parameters obtained from analysis of the (111) peak of all the samples show that the lattice constant (*a*) and interplaner spacing (d-spacing) are always higher in value and closer to those of the reference material for the samples treated with $CdCl_2+CdF_2$ in comparison with those treated with only $CdCl_2$ or untreated at all. These results are shown in tables 1, 2, 3 and 4 for comparison. The closest reference material with diffraction peaks matching the samples under study has the Joint Committee on Powder Diffractions and Standards (JCPDS) file No: 00-015-0770 with $2\theta = 23.8°$, d-spacing, $d = 3.7420$ Å and latice constant, $a = 6.4810$ Å for the (111) diffraction peak. There is no clear correlation of the structural parameters with thickness of the samples. However, the observed large values of *a* and *d* for the $CdCl_2+CdF_2$-treated samples suggest that with this treatment, CdTe material closer in quality to the standard CdTe in the JCPDS file can easily be obtained by employing this treatment.

Table 1: Results of XRD study of As-deposited CdTe layers of different thicknesses.

Sample thickness (μm)	2θ (°)	(111) peak intensity	d-spacing d (Å)	Lattice constant a (Å)	FWHM β (°)	Crystallite size D (nm)
1.1	24.0	7041	3.711	6.428	0.1299	63
1.3	24.0	7380	3.707	6.421	0.1299	63
1.8	24.0	13373	3.705	6.418	0.1624	50
2.1	24.0	9546	3.714	6.434	0.1624	50

Table 2: Results of XRD study of CdTe layers of different thicknesses annealed without chemical treatment at 450°C for 15 minutes.

Sample thickness (μm)	2θ (°)	(111) peak intensity	d-spacing d (Å)	Lattice constant a (Å)	FWHM β (°)	Crystallite size D (nm)
1.1	23.8	7949	3.746	6.488	0.1299	63
1.3	24.1	8171	3.697	6.404	0.1299	63
1.8	24.0	13681	3.712	6.430	0.1299	63
2.1	24.0	15066	3.708	6.424	0.1299	63

Table 3: Results of XRD study of CdTe layers of different thicknesses annealed with $CdCl_2$ at 450°C for 15 minutes.

Sample thickness (μm)	2θ (°)	(111) peak intensity	d-spacing d (Å)	Lattice constant a (Å)	FWHM β (°)	Crystallite size D (nm)
1.1	24.0	16668	3.707	6.422	0.1299	63
1.3	24.1	10055	3.696	6.403	0.1299	63
1.8	24.1	15605	3.696	6.403	0.1299	63
2.1	24.0	15528	3.715	6.434	0.1299	63

Table 4: Results of XRD study of CdTe layers of different thicknesses annealed with $CdCl_2+CdF_2$ at 450°C for 15 minutes.

Sample thickness (μm)	2θ (°)	(111) peak intensity	d-spacing d (Å)	Lattice constant a (Å)	FWHM β (°)	Crystallite size D (nm)
1.1	24.0	26855	3.715	6.434	0.1299	63
1.3	24.0	22606	3.714	6.434	0.1299	63
1.8	24.0	14557	3.714	6.433	0.1624	50
2.1	24.0	5311	3.726	6.454	0.1299	63

Since these same samples were also subjected to the conventional $CdCl_2$ treatment, the possible reason for the observed structural improvements can only be linked to the presence of F. Fluorine is also a halogen like Cl, but with smaller atomic size as well as higher diffusivity compared to Cl [27-30]. This therefore means that F diffuses more into CdTe during the annealing process unlike Cl. It can therefore act more as a fluxing agent, compared to Cl, to bring about re-crystallisation and passivation of grain boundaries in CdTe resulting in the observed structural transformation. This actually should be part of the sources of improvement in solar cell conversion efficiency when these CdTe materials are used. Tables 1 – 4 also show that there is no significant effect on crystallite size in all the samples before and after annealing. This observed constancy in crystallite size may be as a result of the limitations of the XRD instrumentation or the Sherrer equation in estimating crystallite sizes larger than 63 nm.

3.2   Optical characterisation – Spectrophotometry

The percentage transmittance spectra of the CdTe samples of different thicknesses with different annealing conditions, in the wavelength range (750 – 1000) nm, are shown in figures 5 (a), (b), (c) and (d).

In the as-deposited samples of different thicknesses (fig. 1(a)), the transmittance edges are poorly defined and fall in the range (780 – 800) nm with a wide spread of the near infrared (NIR) transmittance in the range (20 – 70) %. After annealing without chemical treatment (fig. 1 (b)), and with $CdCl_2$ treatment (fig. 1 (c)), the gradient of the transmittance edge slightly improved, falling in the range (790 – 800) nm with a narrowing of the percentage NIR transmittance in the range (30 – 60) %. For the samples treated with $CdCl_2$+CdF_2, a further improvement in the transmittance edge is observed with the transmittance edges of all the samples experiencing a redshift to ~820 nm wavelength. A further reduction in the percentage transmittance and narrowing of the NIR transmittance in the range (35 – 50) % is also observed. This property is desirable for applications such as in photovoltaic solar cells. In this NIR region, it is also observed that there is no clear correlation between the percentage transmittance and film thickness except for the 2.1 µm sample whose % transmittance remained fairly lowest under all annealing conditions.

For the absorbance as shown in figures 6 (a), (b), (c) and (d), the best improvement (especially towards the visible region) as well as improvement in the absorbance edge (with redshift) is observed for the samples treated with $CdCl_2$+CdF_2 (fig. 6 (d)). In addition, there is a better correlation between the absorbance and sample thickness with the 1.1 µm sample showing the least absorbance and the 2.1 µm sample showing the greatest absorbance. Again, for the $CdCl_2$+CdF_2-treated samples, there is the least spread in absorbance across the wavelength range under study. In the $CdCl_2$-treated samples, there is an improvement in absorbance compared to the as-deposited samples and the samples without chemical treatment. This improvement however, is not as pronounced as that in the $CdCl_2$+CdF_2-treated samples. The improvement in absorption with increase in thickness and with $CdCl_2$+CdF_2 treatment is desirable for solar cell application and radiation detection.

The percentage reflectance spectra of the samples are also shown in figures 7 (a), (b), (c) and (d). Again, there is an overall redshift in the reflectance edge as well as least spread in reflectance for the samples treated with $CdCl_2+CdF_2$ in comparison with rest of the samples. There is also a fair correlation between the reflectance edge and sample thickness. The higher the thickness of the sample, the more the reflectance edge shifts towards the longer wavelength. The highest observed reflectance for all the samples (in the NIR region) is ~20%, which indicates a fundamental property of these electrodeposited CdTe. This behaviour also manifests in the refractive index and dielectric constant of all the samples showing maximum values as will be seen later.

Figures 8 (a), (b), (c) and (d) present the absorption coefficients (α) of the various samples under different annealing conditions. There is again the best improvement in absorption coefficient and in absorption edges for the samples treated with $CdCl_2+CdF_2$ (fig. 8 (d)) compared to the other samples. For the samples without chemical treatment (fig. 8 (b)), samples treated with only $CdCl_2$ (fig. 8 (c)) and those treated with $CdCl_2+CdF_2$, α displays an inverse relationship with film thickness for photon energies ≥ 1.50 eV, except for the thickest sample (2.1 μm). This may be due to change in stoichiometry in this particular sample during deposition. In the as-deposited samples, α appears to increase with film thickness. The best improvement in absorption coefficient for the samples treated with $CdCl_2+CdF_2$ is worthy of note. This property and the observed least transmittance for the same set of samples suggest that these samples either have more closely packed grains or more passivated grain boundaries or both. This situation, which is favourable to photovoltaic application, must have been initiated by the presence of F in the chemical treatment.

Figures 9 (a), (b), (c) and (d) show the graph of $(\alpha h v)^2$ vs. photon energy for all the samples. Again, the highest absorption $(\alpha h v)^2$ and the best absorption edges are displayed by the samples treated with $CdCl_2+CdF_2$ followed by those treated with only $CdCl_2$ and then by the samples annealed without chemical treatment. These results bring out the overall positive effect of annealing on electrodeposited CdTe. The trend in absorption here, with respect to film thickness follows the same pattern observed for α in figure 8. However, a close observation of figure 9 reveals that the samples annealed with $CdCl_2+CdF_2$ treatment all have the same (narrow) energy bandgap of ~1.48 eV. The samples with only $CdCl_2$ similarly have a common energy bandgap of ~1.50 eV, while the samples annealed without chemical treatment have a common energy bandgap of ~1.52 eV. The as-deposited samples have energy bandgaps in the range (1.47 – 1.50) eV with the thickest sample (2.1 μm) having no defined energy bandgap.

It is important at this point to mention that the as-electrodeposited CdTe layers are not of interest especially in solar cell fabrication as these materials do not produce good solar cells as a result of their poor electronic quality, having been grown at relatively low temperature. It is for this reason that post-deposition heat treatment of CdTe, especially with prior $CdCl_2$ treatment came into practice. This process, which we are now modifying by adding CdF_2, has the advantage of annealing out defects, initiating re-crystallisation and passivating grain boundaries in the CdTe material, thus improving the overall quality of the material for electronic devices application. The major interest in the present work is therefore on the

annealed samples with or without prior chemical treatment.

The extinction coefficient of the CdTe layers under study are shown in figures 10 (a), (b), (c) and (d). The extinction coefficient determines the absorption coefficient according to equation (4). The variation of K with photon energy follows similar trend as the absorption coefficient. For the samples treated with only $CdCl_2$ however, two observations can be made. Firstly, the thinnest sample (1.1 μm) in this set has the least values of K. Secondly, the values of K for this entire set of samples is about one order of magnitude higher than those for the samples without chemical treatment (fig. 10 (b)) and with $CdCl_2$+CdF_2 treatment (fig. 10 (d)). The reason for this deviation is not clearly understood at present. However, the treatment with only $CdCl_2$ may be responsible for this. Apart from this deviation, one observes that the spread in the values of K is least for the samples treated with $CdCl_2$+CdF_2.

The refractive indices of the various CdTe samples as a function of photon energy are shown in figures 11 (a), (b), (c) and (d). These graphs are similar to those of reflectance in figure 7, if the reflectance were plotted against photon energy. The least spread in the refractive index is observed for the samples treated with $CdCl_2$+CdF_2. For this set of samples, $n \sim 2.60$ for all the sample thicknesses for photon energies $\leq E_g$ except for the 2.1-μm sample in which n varies from 2.25 to 2.60 in this photon energy range. The reason for this slight deviation in the 2.1 μm-sample may be connected with the rapid structural transformation observed in the sample (fig. 4 (d)) which may have resulted in the reduction in the density of crystallites or grains in one or more of the observed four crystal planes of orientation in the XRD pattern. Consequently, light propagates faster in this material for certain photons with higher energies than others (in the NIR region), since $n = c/v^2$, where c is the speed of light in vacuum and v is the velocity with which light propagates in the sample. Below the bandgap energy, there is no clear dependence of n on film thickness for all the samples under the various annealing conditions. Another possible reason for the observed trend in the values of n for the 2.1-μm sample is due to the presence of large gaps or holes between the randomly oriented crystallites resulting from annealing. Under such situation, large amount of photons (especially, in the NIR region) can transmit through such holes resulting in relatively low n values.

Figures 12 (a), (b), (c) and (d) show the graphs of real part of the dielectric constant vs. photon energy. These graphs are generally similar in feature to the graphs of n vs. photon energy. The samples treated with $CdCl_2$+CdF_2 show the least spread in the values of ε_r. For photon energies $hv \leq E_g$, ε_r is in the range $(6.4 - 7.0)$ for these samples. For the $CdCl_2$-treated samples, ε_r is in the range $(5.2 - 6.9)$ while for the untreated samples (fig. 12 (b)), ε_r is in the range $(6.0 - 7.0)$. The range of values of ε_r is even wider for the as-deposited samples (fig. 12 (a)). There is again no clear correlation between the values of ε_r and film thickness in all the samples irrespective of the annealing condition. The observed values of ε_r suggest that devices fabricated with the $CdCl_2$+CdF_2-treated CdTe samples will display

relatively improved and more stable capacitance and therefore will have longer response time in the infrared photon energy range.

Figures 13 (a), (b), (c) and (d) show the graphs of imaginary part of the dielectric constant ε_i as a function of photon energy. A trend similar to that observed for the extinction coefficient K is seen here. The samples treated with only $CdCl_2$ have values of ε_i that are about one order of magnitude higher than the rest of the samples. The spread in the values of ε_i is the least for the samples treated with $CdCl_2+CdF_2$ compared with the samples treated with only $CdCl_2$ and those without chemical treatment. Apart from the sample with thickness of 2.1 μm, the value of ε_i tends to decrease as the film thickness increases for all the annealed samples. A possible reason for the deviation in the 2.1 μm-sample has been stated earlier. These results and all the previous results discussed so far suggest that samples treated with $CdCl_2+CdF_2$ generally show the best improvement in their quality for solar cell application compared to other samples.

This combined, more superior improvement, in the structural and optical properties of CdTe layers treated with $CdCl_2+CdF_2$ is expected to produce solar cells with better device performance compared to those treated with $CdCl_2$. In order to substantiate this claim, authors have recently reported preliminary solar cell device results confirming the advantage of this treatment [17]. However, as work progresses towards optimizing growth, chemical treatment and annealing conditions, as well as device fabrication steps, current solar cell results obtained for 2 mm diameter glass/FTO/CdS/CdT/Au cells and presented in figure 14 show drastic improvement in efficiency for solar cell with $CdCl_2+CdF_2$ treatment compared to that with $CdCl_2$ treatment. These cells show efficiencies of 8.3% and 3.3% respectively for $CdCl_2+CdF_2$-treated CdTe and $CdCl_2$-treated CdTe respectively. Other device parameters for the 8.3% cell are: open-circuit voltage (V_{oc}) = 656 mV, short-circuit current density (J_{sc}) = 33.3 mAcm^{-2} and fill factor (FF) = 0.38, while device parameters for the 3.3% cell are: open-circuit voltage (V_{oc}) = 510 mV, short-circuit current density (J_{sc}) = 20.2 mAcm^{-2} and fill factor (FF) = 0.32. These results are better than the earlier reported maximum values of 6.7% and 3.0% for $CdCl_2+CdF_2$ and $CdCl_2$ treatment respectively [17]. The CdTe thickness used for these cells was 2 μm with CdS thickness of 240 nm.

4.0   Conclusion

The effects of post-deposition annealing with different chemical treatments on the structural and optical properties of electrodeposited CdTe thin films have been studied in detail using x-ray diffraction and spectrophotometry. The result of XRD study shows that samples with thicknesses up to 1.8 μm exhibit increased preferential orientation of the crystallites in the (111) plane after annealing relative to the as-deposited material and irrespective of the chemical treatment before annealing. For samples with thicknesses > 1.8 μm, the preferential orientation in the (111) crystal plane tends to decrease below that of the as-deposited material for samples annealed after $CdCl_2+CdF_2$ treatment. However, for samples with thicknesses ≥1.8 μm, the intensity of the (111) XRD peak generally begin to decrease gradually for

CdCl$_2$+CdF$_2$ treatment while XRD peaks corresponding to the (220), (311) and (331) crystal planes begin to emerge. This trend indicates a structural transformation of the samples under this treatment condition. The lattice constant and d-spacing of the materials get closer to those of the standard reference material for these samples treated with CdCl$_2$+CdF$_2$.

The results of optical characterisation show that the absorption property of all the samples increases with increase in film thickness while the transmission decreases with increasing film thickness, irrespective of the annealing condition employed. The optical properties of the materials in general get improved on annealing, with less spread in the optical parameters. However, annealing after CdCl$_2$+CdF$_2$ treatment improves these properties further. The energy bandgaps of the samples annealed with CdCl$_2$+CdF$_2$ treatment become smaller compared to the rest of the samples. This trend also underlines the influence of CdCl$_2$+CdF$_2$ treatment on the optical properties of these electrodeposited CdTe materials for photovoltaic application. Photovoltaic solar cells fabricated with with CdCl2+CdF2-treated CdTe and CdCl2-treated CdTe produced efficiencies of 8.3% and 3.3% respectively showing the advantage of CdCl2+CdF2 treatment over conventional CdCl2 treatment.

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Figure captions

Fig. 1 XRD patterns of 1.1 μm CdTe samples with different annealing conditions

Fig. 2 XRD patterns of 1.3 μm CdTe samples with different annealing conditions

Fig. 3 XRD patterns of 1.8 μm CdTe samples with different annealing conditions

Fig. 4 XRD patterns of 2.1 μm CdTe samples with different annealing conditions

Fig. 5 Optical transmittance vs. photon wavelength for CdTe thin films with different thicknesses under different annealing conditions

Fig. 6 Optical absorbance vs. photon wavelength for CdTe thin films with different thicknesses under different annealing conditions

Fig. 7 Optical reflectance vs. photon wavelength for CdTe thin films with different thicknesses under different annealing conditions

Fig. 8 Optical absorption coefficient vs. photon energy for CdTe thin films with different thicknesses under different annealing conditions

Fig. 9 $(\alpha h v)^2$ vs. photon energy for CdTe thin films with different thicknesses under different annealing conditions

Fig. 10 Extinction coefficient vs. photon energy for CdTe thin films with different thicknesses under different annealing conditions

Fig. 11 Refractive index vs. photon energy for CdTe thin films with different thicknesses under different annealing conditions

Fig. 12 Real dielectric constant vs. photon energy for CdTe thin films with different thicknesses under different annealing conditions

Fig. 13 Imaginary dielectric constant vs. photon energy for CdTe thin films with different thicknesses under different annealing conditions

Fig. 14 Current density-Voltage graphs of solar cells made with CdTe annealed with $CdCl_2$ and $CdCl_2+CdF_2$