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The effect on CdS/CdTe solar cell conversion efficiency of the presence of fluorine in the usual CdCl₂ treatment of CdTe

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Abstract

The addition of CdF₂ to the CdCl₂ solution used in the well-known CdCl₂ treatment of CdS/CdTe solar cells has been observed to drastically improve the conversion efficiency of fully fabricated CdS/CdTe solar cells. The observed improvement is as a result of further enhancement of structural and optoelectronic properties of the CdCl₂+CdF₂-treated CdTe layers compared to the CdCl₂-treated CdTe layers. A set of CdS/CdTe samples were grown by electrochemical deposition under different conditions and each sample was divided into two. One set of these parts was treated with only CdCl₂ solution while the other set was treated with the CdCl₂+CdF₂ mixture. Both sets were annealed at 450°C for 15 minutes and the solar cells completed by evaporating Au back contact on the CdTe layers after chemical etching. The results of the device measurements show drastic improvements in all the solar cell parameters (open-circuit voltage, short-circuit current density, fill factor and conversion efficiency) for the devices treated with CdCl₂+CdF₂ mixture compared to those treated with only CdCl₂. The conversion efficiencies increased from (1.0 – 3.0)% with CdCl₂ treatment to about (5.0 – 7.0)% with CdCl₂+CdF₂ treatment. The observed improvements have been attributed to the unique properties of fluorine.

Keywords: chalcogenide; electronic material; semiconductor; thin film; heat treatment; electrochemical technique.

1.1 Introduction

CdCl₂ treatment has been known to drastically improve the solar energy conversion efficiency of CdTe-based solar cells at least since the 1990s [1 -3]. Apart from generally improving the efficiency of CdTe-based solar cells, this treatment has been said to result in the conversion of as-grown n-type CdTe thin films to p-type CdTe [4, 5] and in the improvement of n-type conductivity of CdTe layers [6]. There are also recent reports of conversion of p-type CdTe to n-type [3, 7,5] or at least the conversion of thin outer layer of p-type CdTe grains to n-type [8] and thin outer layer of n-CdTe to p-type [7]. These cases however, depend on the nature of the defect distribution in the as-grown CdTe material [7].

The CdCl₂ treatment process involves covering the surface of as-grown CdTe layer with a layer of CdCl₂ from a solution of CdCl₂ in methanol or in water. Alternatively this is done by evaporating dry CdCl₂ power (or crystal) onto the CdTe layer. In the case of CdCl₂ solution, the solution is allowed to dry afterwards. In any case, the CdTe layer with a layer of dry CdCl₂ is then annealed at temperatures up to 450°C in air atmosphere. After cooling, the dry CdCl₂ residue on CdTe is washed off with de-ionised water or methanol. The solar cell device fabrication is then completed by etching the CdTe surface with suitable etchants (in some cases) and evaporating appropriate back metal contact onto the etched CdTe surface. Some researchers have however carried out this all-important chloride treatment in slightly different ways. For example, Cunningham *et al.* reported the incorporation of chloride into CdTe layers during the electrodeposition process by adding CdCl₂ into the deposition electrolyte and therefore carried out post-deposition annealing of CdTe without applying CdCl₂ on the CdTe surface again [9]. Mazzamuto *et al.* also reported the annealing of CdTe layers in the presence of CHF₂Cl in close-space sublimation chamber and this represented CdCl₂ treatment [10].

From the foregoing, it is clear that the incorporation of chlorine or more generally, halogens, is crucial in obtaining high efficiency solar cells based on CdTe. We have therefore combined the addition of CdCl₂ and CdF₂ into our CdTe electrodeposition electrolyte and the post-deposition annealing of CdTe layers with (CdCl₂+CdF₂) treatment, to achieve enhanced solar cell efficiency of CdTe-based solar cells. The results of a comparative study of the effects of post-deposition (CdCl₂+CdF₂) treatment and the conventional CdCl₂ treatment on the conversion efficiency of CdTe-based solar cells are presented and discussed in this paper.

2.1 Experimental Procedure

The CdS and CdTe thin films used in this work were both electrodeposited from acidic aqueous electrolytes using simple two-electrode system with carbon and platinum counter electrodes respectively. The electrolyte for the deposition of CdS contains 0.3M CdCl₂.H₂O and 0.03M Na₂S₂O₃.5H₂O in 800 ml of de-ionised water. Both chemicals were laboratory reagent grade purchased from Fisher Scientific, UK. Prior to the deposition of CdS, the aqueous solution containing only 0.3M CdCl₂.H₂O was electro-purified for 48 hours at a cathodic potential slightly lower than that for the deposition of Cd. These voltage values were established from a cyclic voltammogram obtained for this solution also using the two-electrode system with a computerised GillAC potentiostat. After electro-purification, 0.03M Na₂S₂O₃.5H₂O was then added and the resulting electrolyte was stirred for 24 h. The pH of the electrolyte was adjusted to 1.80±0.02 using dilute HCl and NH₄OH after which another cyclic voltammogram was recorded to determine the cathodic deposition potential range for CdS. The substrate used for all voltammetry and electro-purification in this work was cleaned glass/FTO supplied by Pilkington Group Ltd, UK. After depositing some CdS samples on glass/FTO substrates across the identified deposition voltage range and characterising them using optical absorption, X-ray diffraction (XRD), photoelectrochemical (PEC) cell and scanning electron microscopy (SEM), the best cathodic deposition voltage of 1450 mV was

established. Using this growth voltage, a set of CdS layers was then deposited on different substrates and annealed at 400°C for 20 minutes after CdCl₂ treatment. The substrates used were glass/FTO, glass/FTO/Al-ZnO and glass/ITO/i-ZnO all supplied by Pilkington Group Ltd, UK.

For CdTe deposition, the electrolyte contains 1M CdSO₄ (99% purity), 1mM TeO₂ (99.999%), 1000 ppm CdCl₂ (99.999%) and 1000 ppm CdF₂ (99.999%) all purchased from Sigma-Aldrich, UK. The aqueous solution containing only 1M CdSO₄ was first electro-purified (due to its relative low purity level) following similar steps as in the case of CdS above. From the solution containing only CdSO₄ and TeO₂ at a pH of 2.00±0.02, the cathodic deposition voltage range for CdTe was obtained from cyclic voltammograms recorded using the GillAC computerised potentiostat in two-electrode configuration with Platinum counter electrode. CdCl₂ and CdF₂ were then added as sources of Cl and F for n-type doping of CdTe. After depositing some samples on glass/FTO substrates across the identified deposition voltage range and characterising them using optical absorption, X-ray diffraction (XRD), photoelectrochemical (PEC) cell and scanning electron microscopy (SEM), the best cathodic deposition voltage for CdTe was established as 2038 mV with respect to Pt counter electrode as reported recently [11].

CdTe layers were deposited on the previously annealed CdS layers. Each CdS/CdTe structure was then divided into two halves. One set of these halves was dipped in a saturated solution of CdCl₂ in 50 ml of de-ionised water and allowed to dry. The other set was dipped in the same CdCl₂ solution but also containing about 0.1g of CdF₂ and then allowed to dry. Both sets of samples were then annealed in air at 450°C for 15 min using a furnace. After cooling, these samples were etched in a dilute aqueous solution of (K₂Cr₂O₇ + H₂SO₄) for 5 s, rinsed in de-ionised water, etched again in a warm aqueous solution containing 0.5g each of NaOH and Na₂S₂O₃ for 2 min and rinsed in de-ionised water. After drying in a stream of N₂, the solar cell fabrication was completed by vacuum-evaporating 100 nm-thick Au back metal contacts of 2 mm diameter on the etched CdTe surfaces. Further details of these processes are contained in a recent publication [11].

The resulting solar cells were assessed for their performance using current-voltage (I-V) characteristics obtained using a Keithly 619 Electrometer/Multimeter and a solar simulator with a power density of 100 mWcm⁻². The results of the materials characterisation and device assessment are presented and discussed in the next section.

3.1 Results and Discussion

Figure 1 shows typical XRD pattern and optical absorption spectrum of the electrodeposited CdS layer annealed at 400°C for 20 minutes after CdCl₂ treatment. Figure 1 (a) shows the polycrystalline nature of the CdS layers with preferred crystallite orientation along the (002) crystal plane. Figure 1 (b) shows the absorption edge of this material as well as the characteristic high absorption coefficient of CdS. The energy bandgap of the layer obtained from $(ah\nu)^2$ vs. $h\nu$ plot is 2.42 eV (Not shown here for brevity). Since the main focus of this

paper is centered on CdTe, the rest of the results and discussion will concentrate on CdTe and the resulting solar cells. However, full characterisation of electrodeposited CdS layers using two-electrode system can be found in a recent publication by Diso et al [12].

Photoelectrochemical (PEC) cell measurement was used to establish the electrical conductivity type of the CdTe layers deposited on glass/FTO substrates in both as-deposited and annealed conditions. The PEC principle relies on the depletion region formed at solid/liquid junction between the semiconductor (CdTe in this case) and a suitable electrolyte ($\text{Na}_2\text{S}_2\text{O}_3$ in this case). The difference between the open-circuit voltages across this depletion region under illumination (V_L) and under dark condition (V_D) gives the PEC signal. The sign of the PEC signal shows the electrical conductivity type of the semiconductor involved while the magnitude of the PEC signal gives an indication of the suitability of the doping level of the material [13]. The PEC system was calibrated using well-known n-type CdS and p-type ZnTe materials. It is important to mention that standard techniques such as Hall Effect measurement could not be used for this purpose due to the presence of underlying conductive FTO layer. The FTO layer will interfere with the result of Hall Effect measurements since applied electric current will naturally tend to flow through the path of least resistance, which is the FTO in this case. For this reason, PEC measurements become the only available technique for this purpose since again, the electrodeposited CdTe layers are difficult to pull out from the FTO.

Table 1 shows the PEC results of the different CdTe layers in both as-deposited and annealed conditions. The results show that the CdTe layers were all n-type before and after post-deposition heat treatment and before solar cell fabrication.

Table1: Results of PEC measurements on different CdTe layers before and after post-deposition heat treatment.

Sample Condition	Sample No	Thickness (μm)	V_L (mV)	V_D (mV)	PEC signal $V_L - V_D$ (mV)	Conductivity type
As-deposited	A	1.1	-312	-158	-154	n
	B	1.3	-109	-67	-42	n
	C	1.8	-39	-03	-36	n
	D	2.1	-313	-197	-116	n
CdCl_2 -treated	A	1.1	-105	-49	-56	n
	B	1.3	-07	-01	-06	n
	C	1.8	-121	-70	-51	n
	D	2.1	-182	-102	-80	n
$\text{CdCl}_2 + \text{CdF}_2$ -treated	A	1.1	-23	-03	-20	n
	B	1.3	-84	-15	-69	n
	C	1.8	-143	-44	-99	n
	D	2.1	-152	-53	-99	n

Figure 2 shows the XRD patterns of a 2.1 μm -thick CdTe layer in as-deposited and annealed conditions. The annealing was done at 450°C for 15 min after treatment with CdCl_2 and with $\text{CdCl}_2 + \text{CdF}_2$. The as-deposited layer shows preferential orientation along the (111) crystal

plane as is seen in figure 2 (a). After annealing with CdCl_2 treatment, there is obvious increase in the intensity of the (111) XRD peak with associated improvement in the crystallinity of the material as seen in decrease in the full width at half maximum (FWHM) of this peak from 0.16° to 0.13° . However, the layer retains the (111) preferential orientation. After annealing with $\text{CdCl}_2+\text{CdF}_2$, there is a drastic change in the crystallite/grain orientation. The intensity of the (111) diffraction peak decreases significantly and three other peaks emerge from the (220), (311) and (331) crystal planes. This clearly shows that there is a pronounced rearrangement in the orientation of crystallites/grains in this material which is prompted by the presence of fluoride atoms from the $\text{CdCl}_2+\text{CdF}_2$ treatment. The material therefore becomes more polycrystalline in nature. The FWHM of the (111) peak however still remains 0.13° . This could mean that there is no further increase in crystallite size along this plane. Again, it could be as a result of the limitation of the XRD analysis software used in analysing these peaks. In any case, the use of $\text{CdCl}_2+\text{CdF}_2$ treatment prior to post-deposition heat treatment of CdTe layers brings about drastic changes in the structure of the resulting CdTe layers compared to the use of only CdCl_2 .

Figures 3 (a), (b) and (c) show the graphs of optical absorption coefficient (α) vs. photon energy for the as-deposited, CdCl_2 -treated CdTe layers and $\text{CdCl}_2+\text{CdF}_2$ -treated CdTe layers respectively. Again the effect of incorporation of F in the CdCl_2 treatment on the optical absorption behaviour of CdTe can be seen in the improvement of the absorption edge and gradient of the absorption coefficient curve of the material. In the as-deposited material (figure 3 (a)), the absorption edge is extremely weak. There is also a significant absorption of longer wavelength photons with energy below the bandgap of CdTe as can be seen in the absorption coefficient starting from a value close to $10,000 \text{ cm}^{-1}$ in this photon energy range. This is an indication of the presence of high density of defects in this material. The presence of high density of defect levels in CdTe is well known to be responsible for the pronounced Fermi level pinning phenomenon at metal/CdTe interfaces [13 - 16]. After annealing with CdCl_2 treatment, the absorption coefficient edge is improved and absorption of longer wavelength photons decreases as seen in figure 3 (b). However, with $\text{CdCl}_2+\text{CdF}_2$ treatment (figure 3 (c)), further improvement in the absorption edge is observed and a very slight decrease in the absorption of longer wavelength photons is also observed (although this is not pronounced as to be physically observed from the graph).

The improvement in absorption edge of CdTe means improvement in the absorption of photons with energy greater than the energy bandgap by this material. The absorption of photons with energy below the bandgap of CdTe is an indication of the presence of impurity photovoltaic (PV) effect which could result in these low-energy photons effectively creating useful electron-hole pairs that contribute to photogenerated current in a fully fabricated solar cell using these materials [13]. The energy bandgaps of the three CdTe layers in figure 3 obtained from the graph of $(\alpha h\nu)^2$ vs. $h\nu$ (not shown here for brevity) have values of 1.23 eV for the as-deposited sample and 1.48 eV for the samples treated with CdCl_2 and $\text{CdCl}_2+\text{CdF}_2$.

Table 2 shows the summary of solar cell parameters (under AM1.5 condition) obtained for the different solar cell device structures fabricated with both CdCl_2 -treated CdTe layers and $\text{CdCl}_2+\text{CdF}_2$ -treated CdTe layers. Figure 4 shows the I-V characteristics of the same solar

cells under AM1.5 illumination condition. In each case the as-deposited CdS/CdTe bilayer was divided into two halves. One set of these halves was annealed with CdCl₂ treatment and the other set was annealed with CdCl₂+CdF₂ treatment for comparison as mentioned earlier. The results clearly show drastic improvements in the solar cell parameters of the devices with CdCl₂+CdF₂ treatment compared to those with only CdCl₂ treatment.

Table 2: Summary of device parameters (under AM1.5 conditions) obtained for solar cells involving CdCl₂ treatment and CdCl₂+CdF₂ treatment.

Device structure	With CdCl ₂ treatment				With CdCl ₂ +CdF ₂ treatment			
	V _{oc} (mV)	J _{sc} (mAcm ⁻²)	FF	η (%)	V _{oc} (mV)	J _{sc} (mAcm ⁻²)	FF	η (%)
(a) ITO/i-ZnO/CdS/CdTe/Au	500	18.7	0.32	3.0	590	19.3	0.44	5.0
(b) FTO/Al-ZnO/CdS/CdTe/Au	430	10.0	0.28	1.2	610	24.0	0.40	5.8
(c) FTO/CdS/CdTe/Au	490	13.6	0.29	1.9	640	25.0	0.41	6.6
(d) FTO/CdS/CdTe/Au	170	12.8	0.31	0.7	650	22.0	0.47	6.7

The results in Table 2 show that, whatever the device structure used, the effect of CdCl₂+CdF₂ treatment on the solar cell performance is obvious, suggesting that CdCl₂+CdF₂ treatment is more advantageous over the conventional CdCl₂ treatment in producing more efficient CdTe-based solar cells at least based on the n-n heterojunction/Schottky barrier solar cell structure used in this work.

Figure 4 shows the AM1.5 I-V characteristics of these solar cells presented in Table 2 for illustration of the effect of CdCl₂+CdF₂ treatment. It is important to note that the above observed effects of the presence of F are coming mainly from the presence of F in the post-deposition heat treatment and not from the presence of F in the CdTe deposition electrolyte. This result is in agreement with the work reported by Mazzamuto *et al.* [10] in which they used a gas containing both Cl and F (CHF₂Cl) in post-deposition heat treatment of CdTe in a close-spaced sublimation chamber. Although their aim was to incorporate Cl into CdTe through this means, the aim in the present work is to incorporate F into CdTe in addition to the incorporation of Cl. The reason for this F incorporation and the subsequent material and device improvements is derived from the unique properties of fluorine among the halogens. Being the first among the halogens in the periodic table, F has smaller atomic number, smaller atomic radius as well as lower density compared to Cl [17]. F also has higher vapour pressure than Cl at any given temperature [17].

These properties give F the advantage of being more diffusive in CdTe with higher probability of forming interstitials as well as diffusing easily through the CdTe grain boundaries compared to Cl. Evidence of higher diffusion coefficient of F relative to Cl and other halogens in general is available in the literature [18-20]. Again, the activation energy for F diffusion is known to be lower than that of Cl diffusion [18-20].

Recent studies of current collection mechanism in CdTe using electron beam induced current (EBIC) technique have revealed high current collection efficiency at the CdTe grain boundaries [8]. This phenomenon together with the overall improvement in the performance of fully fabricated solar cells, have been attributed to Cl diffusion through these grain boundaries during the post-deposition CdCl₂ treatment [8, 7]. This effect should be more pronounced when F is involved in the post-deposition heat treatment of CdTe as has been observed in the present work. This therefore explains the drastic improvement in the overall solar cell device parameters as presented in Table 2 and figure 4. The major ways by which this treatment achieves this improved device performance include the enhancement of the lifetime of photo-generated charge carriers in the CdS/CdTe structure, establishment of optimum doping concentration, and grain boundary passivation [5].

Another major difference in the present work is the intentional use of n-CdTe in the fabrication of the above presented solar cell devices instead of the conventionally reported solar cells based on p-CdTe. As a result, the device structures reported in this work are of the n-n heterojunction + large Schottky barrier type and not a p-n junction type. This is the major reason for adding both CdCl₂ and CdF₂ in the CdTe deposition electrolyte as mentioned in the experimental section.

The n-type conductivity of these CdTe layers was confirmed using PEC measurement as mentioned earlier and it is believed that the presence of F in these materials will enhance the n-type conductivity mode. The selection of etchants used in this work for etching CdTe surfaces prior to back metal contact fabrication helps to pin the Fermi level at the surface of the CdTe layer close to the top of the valence band, in order to achieve large Schottky barriers at the n-CdTe/Au contacts for improved device results [11, 14]. It is also believed that the presence of F in the CdCl₂+CdF₂ post-deposition heat treatment results in the improvement of the qualities (such as carrier transport properties) of these electrodeposited CdTe materials and therefore supports the production of solar cells with improved efficiency in general.

4.1 Conclusion

The effect on the properties of CdTe layers and conversion efficiencies of CdTe-based solar cells, of the presence of Fluorine in the post-deposition heat treatment of CdTe has been studied. The use of a mixture of CdCl₂ and CdF₂ in the post-deposition heat treatment of CdTe layers reveals that this treatment results in profound improvement of the structural and optical properties of CdTe layers as well as the conversion efficiencies of solar cells fabricated using these CdTe layers, compared to the conventional use of only CdCl₂. The CdTe materials tend to become more polycrystalline with improved optoelectronic properties when CdCl₂+CdF₂ treatment is used than when only CdCl₂ treatment is used. Drastic improvement of solar cell parameters and overall conversion efficiency is a clear manifestation of the positive effects of CdCl₂+CdF₂ treatment over CdCl₂ treatment. This remarkable effect of the presence of fluorine is attributed to the size of the fluoride atom as

well as its high diffusivity in comparison to those of the chloride atom. These results show that the conventional CdCl₂ treatment of CdTe in solar cell fabrication could be replaced by CdCl₂+CdF₂ treatment for more rapid improvement of solar cell efficiency.

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Figure 1 : Typical (a) XRD pattern and (b) Optical absorption spectrum of electrodeposited CdS layer annealed at 400°C for 20 min. after CdCl₂ treatment.

Figure 2: XRD patterns of (a) as-deposited, and annealed CdTe with (b) CdCl₂ treatment and (c) CdCl₂+CdF₂ treatment. Annealing was done at 450°C for 15 minutes.

Figure 3: Optical absorption coefficient vs. photon energy of (a) as-deposited, and annealed CdTe with (b) CdCl₂ treatment and (c) CdCl₂+CdF₂ treatment. Annealing was done at 450°C for 15 minutes.

Figure 4: AM1.5 I-V characteristics of solar cells fabricated with CdCl₂-treated CdTe layers (a, b, c and d) and the corresponding solar cells with CdCl₂+CdF₂-treated CdTe layers (e, f, g and h). Each CdS/CdTe sample was divided into two and treated separately with CdCl₂ or CdCl₂+CdF₂ for comparison.