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# The activation of thin film CdTe solar cells using alternative chlorine containing compounds



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## ABSTRACT

The re-crystallisation of thin film cadmium telluride (CdTe) using cadmium chloride (CdCl<sub>2</sub>) is a vital process for obtaining high efficiency photovoltaic devices. However, the precise micro-structural mechanisms involved are not well understood. In this study, we have used alternative chlorine-containing compounds to determine if these can also assist the re-crystallisation of the CdTe layer and to understand the separate roles of cadmium and chlorine during the activation. The compounds used were: tellurium tetrachloride (TeCl<sub>4</sub>), cadmium acetate (Cd(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>), hydrochloric acid (HCl) and zinc chloride (ZnCl<sub>2</sub>). TeCl<sub>4</sub> was used to assess the role of Cl and the formation of a Te-rich outer layer which may assist the formation of the back contact. Cd(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub> and HCl were used to distinguish between the roles of cadmium and chlorine in the process. Finally, ZnCl<sub>2</sub> was employed as an alternative to CdCl<sub>2</sub>. We report on the efficacy of using these alternative Cl-containing compounds to remove the high density of planar defects present in untreated CdTe.

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## 1. Introduction

The leading thin film photovoltaic technology as measured by annual production is thin film cadmium telluride (CdTe). Thin film CdTe modules are manufactured in high volume on an industrial scale and have the lowest production cost of any solar module technology. The module efficiency is currently lower than crystalline silicon [1], but the cell record efficiency has recently increased markedly. The record for a laboratory cell efficiency is 20.4% [1] and a commercial module record efficiency of above 17.0% has been reported by First Solar Inc.

As deposited thin film CdTe solar cells do not perform well and it is necessary to use a cadmium chloride (CdCl<sub>2</sub>) activation process to obtain high efficiencies. Although this process is used in module manufacture, the precise mechanisms involved in the cell activation process are not fully understood. In this paper, we report on the use of different chlorine containing compounds to treat the CdTe/CdS stacks. The effects of the treatments on the electrical performance and the material properties have been analysed. The compounds used include: tellurium tetrachloride (TeCl<sub>4</sub>), cadmium acetate (Cd(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>), hydrochloric acid (HCl) and zinc chloride (ZnCl<sub>2</sub>). TeCl<sub>4</sub> was used to assess the role of chlorine and the formation of Te(0) on the surface, which might assist the back contact. Cd(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub> and HCl were used to investigate the separate roles of Cd and Cl. Also, HCl does not contain any elements present in the CdTe/CdS stack. Finally, ZnCl<sub>2</sub> was studied as a possible

alternative to CdCl<sub>2</sub>, since Zn has the same electronic configuration and oxidation state as cadmium when bonded with chlorine.

## 2. Methodology

Many alternative methods of application can be used for the activation process of CdTe [2–5]. This paper is focused on the use of a wet treatment to analyse the effect of various chlorine containing compounds on CdTe solar cells. Close-space sublimation (CSS) was used to deposit both the CdS and the CdTe layers. The cells were deposited in superstrate configuration on TEC 10 fluorine doped tin oxide coated on 3 mm soda lime glass. The superstrate was passed through the deposition chambers at 0.1 Pa (mixture of N<sub>2</sub> and O<sub>2</sub>) held a few millimetres above graphite boats. The boats were heated to 650 °C and the films were sublimed on to the superstrate surface. A thin n-type CdS layer was deposited followed by ~3 μm layer of CdTe.

The variable process parameters used in the wet activation treatment were as follows: the concentration of the solution, deposition time, annealing temperature and annealing time. All the compounds used are soluble in methanol, so the temperature of the solution was not a critical parameter. The annealing temperature was varied between 300 °C and 425 °C. The concentration of the solutions was then varied to obtain the best result. Percentages were used to identify concentrations where 1% = 0.054 M, based on molecular molar mass. The range chosen depended on the compound used, but was generally between 0.1% and 2.5% (higher concentrations were used for HCl). The annealing and deposition times were varied between 5 min and 25 min. All the compounds were in powder form (Sigma Aldrich®), except HCl which

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was already in solution. The powders were dissolved in methanol using stirring. Samples were immersed in the solution for a specified time and then transferred to a ventilated oven for the annealing procedure.

The back contact was deposited on the cells following the wet treatment to allow the electrical performance of the device to be measured. A thickness of ~50 nm of sputtered gold was used for the back contact. No optimisation of the back contact was carried out. No copper was added and no etching procedure was performed so that only the effect of the activation treatment could be determined.

The electrical performance was studied using current density–voltage (J–V) curves, measured with the solar cell exposed under 1000 W/m<sup>2</sup> illumination and using an AM 1.5 filter. The values presented are averaged from a range of treated cells. Additional analysis was performed using the spectral response technique to investigate the external quantum efficiency (EQE) of a representative cell from each category [6]. Band gap values were calculated from the EQE measurements [7]. Surface chemical analysis was performed by X-ray Photoelectron Spectroscopy (XPS) using a Thermo Scientific K-Alpha Surface Analysis system. The samples were etched with argon ions for 30 s at 1 keV prior to analysis, this was done to remove any surface contamination. A flood gun was used to minimise peak shifting from charging of the sample during analysis, the area of analysis was 200 μm using monochromated copper X-rays. The composition was calculated using sensitivity factors and the peaks were fitted using Avantage software. Scanning Electron Microscopy (SEM) images were obtained using a FEI Nova 600 Nanolab using an acceleration voltage of 10 kV, which was also equipped with a Focussed Ion Beam (FIB), to prepare TEM samples using a standard in-situ lift-out method. Transmission Electron Microscopy (TEM) images were obtained with a Jeol JEM 2000FX operating at 200 kV. Chemical point analysis was carried out using an FEI Tecnai F20 Scanning TEM ((S)TEM) operating at 200 kV, equipped with an Oxford Instruments X-max 80 Energy Dispersive X-ray (EDX) detector.

### 3. Results and discussion

#### 3.1. CdCl<sub>2</sub>

As a reference, TEM images of untreated and standard CdCl<sub>2</sub> wet treated CdS/CdTe are presented in Fig. 1. After the treatment, the CdTe has large grains, without a region of smaller grains near the CdS interface. The grain boundary volume was reduced and the planar defect density inside the grains decreased following the treatment. Defects present in the untreated cells were identified as stacking faults and twins, using atomic scale high resolution-TEM [8]. The stacking faults are completely removed by the activation treatment [9]. The CdS layer was also affected by the treatment with grain enlargement and less sharp grain boundaries.

#### 3.2. TeCl<sub>4</sub>

The process parameters for the TeCl<sub>4</sub> assisted activation treatment were tested and the best conditions were found to be annealing at a temperature of 350 °C for 15 min using a solution concentration of 2% for 15 min dipping time. The best performing cell produced open circuit voltage (V<sub>oc</sub>) = 594 mV, short circuit current (J<sub>sc</sub>) = 17.91 mA/cm<sup>2</sup>, and Fill Factor (FF) = 0.43 with a cell efficiency of 4.58%. These optimised process parameters differ from those of the standard CdCl<sub>2</sub> treatment. TeCl<sub>4</sub> is a volatile compared with CdCl<sub>2</sub> and it has a lower melting point (224 °C) and a lower boiling point (380 °C). This might lead to additional reactions during the annealing procedure. It is possible that the process may lead to the formation of a surface layer that could affect the contact and lower the Fill Factor (FF). XPS analysis showed the presence of CdCl<sub>2</sub>, TeO<sub>2</sub> and Te(0) on the surface. An improvement in the V<sub>oc</sub> and J<sub>sc</sub> was observed compared with the performance of the untreated cell. Recrystallization of the CdTe layer resulted in larger grains with reduced intragranular defect density. The grains were approximately uniform in size unlike the untreated samples

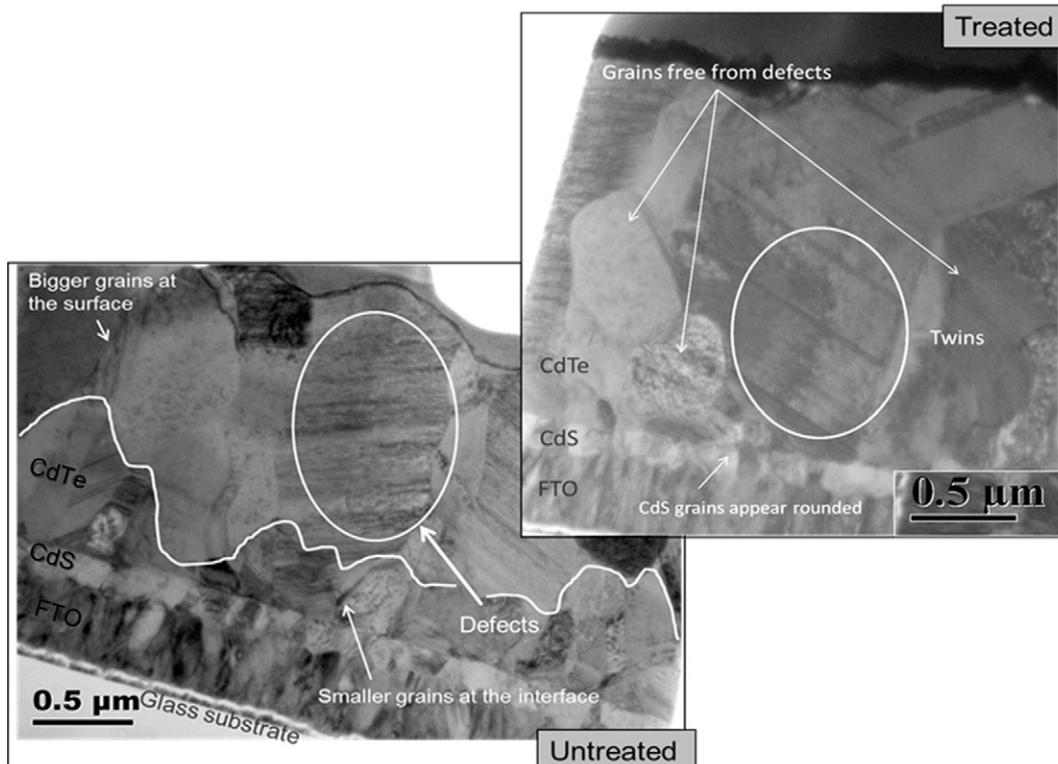


Fig. 1. TEM images of untreated and standard CdCl<sub>2</sub> treated CdS/CdTe.

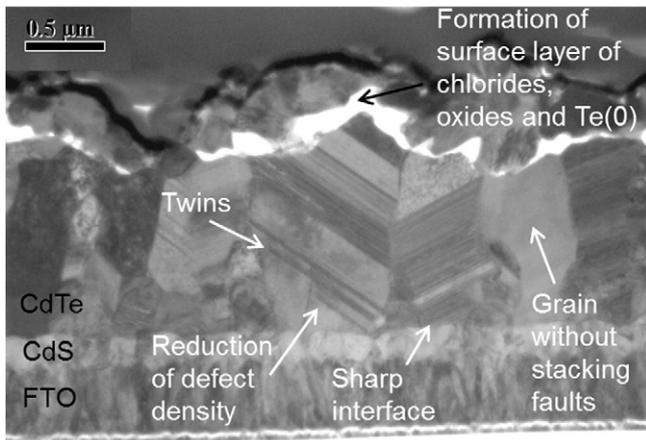


Fig. 2. TEM images of CdS/CdTe treated with  $\text{TeCl}_4$ .

which contain small grains at the CdS interface and larger grains at the surface. The reduction in the density of planar defects and the improvement of the grain boundaries results in enhanced electrical performance. However, the J–V curves did reveal shunting problems.

The TEM images shown in Fig. 2 of the cell treated with  $\text{TeCl}_4$  reveals the presence of a continuous surface coating between the gold contact layer and the CdTe layer. Some of the grains are free from stacking fault defects and some twins are now discernible. This effect is consistent with observations previously made for cells treated using  $\text{CdCl}_2$  [8,9]. The CdTe/CdS interface appears to be abrupt suggesting little intermixing between the two layers. This observation was supported by a band gap calculation from the EQE data, with  $E_g \sim 1.49$  eV. This band gap has the same value measured for the as-deposited films.

### 3.3. $\text{Cd}(\text{CH}_3\text{CO}_2)_2$ and (HCl)

The highest cell efficiency measured following treatment with  $\text{Cd}(\text{CH}_3\text{CO}_2)_2$  was  $\sim 0.5\%$  ( $V_{oc}$  443 mV,  $J_{sc}$  5.91  $\text{mA}/\text{cm}^2$ , FF 0.19). This cell was treated at 400 °C. The small increase in efficiency resulted from improvements in the current density and voltage. However, these results were similar to those obtained when the sample was simply annealed at the same temperature ( $V_{oc}$  307 mV,  $J_{sc}$  3.18  $\text{mA}/\text{cm}^2$ ). Annealing leads to a reduction in planar defect density when the treatment is applied for extended times [10]. A TEM image of a  $\text{Cd}(\text{CH}_3\text{CO}_2)_2$  treated sample is shown in Fig. 3a. The microstructure of the sample is similar to the untreated sample. Two regions are present in the CdTe layer with smaller grains at the interface and larger grains near the surface. The grains close to the CdS interface are free of planar defects.

Some of the larger grains also show total or partial removal of stacking faults and the presence of twin boundaries. In comparison, samples treated with  $\text{CdCl}_2$  at standard conditions reveal grain enlargement and grain coalescence at the interface.

The performance of the cell treated with HCl (350 °C, 2% concentration, 15 min dipping and annealing time) was as follows;  $V_{oc}$  of 506 mV,  $J_{sc}$  of 10.57  $\text{mA}/\text{cm}^2$ , of FF 0.29, and  $\eta$  of 1.54%. The efficiency is lower than that obtained for the cell treated with  $\text{TeCl}_4$ , with lower current density and Fill Factor. However, these results confirm that chlorine has a major role in the activation process. The use of a higher HCl concentration has an effect on the condition of the surface for contacting. XPS analysis revealed a clean surface following this treatment without the presence of oxide formation. The TEM analysis (Fig. 3b) of the HCl treated cell did not show the presence of small grains at the CdTe/CdS interface. The grains appeared to be enlarged by the re-crystallisation. The planar defect density in the grains is reduced or eliminated by the re-crystallisation process although twin boundaries are observed. Chlorine agglomerates were detected in the CdTe layer using EDX elemental analysis. These agglomerates can cause a reduction in the electrical performance of the device. No change in the band gap was detected as result of the treatment suggesting poor intermixing between the layers. However, chlorine does have a role in the recrystallization process, promoting grain growth from the interface.

### 3.4. $\text{ZnCl}_2$

The optimised electrical performance using  $\text{ZnCl}_2$  was obtained for cells treated at 375 °C for 15 min using a 1% solution and dipping for 15 min. These process parameters are the same as those used for the optimised  $\text{CdCl}_2$  treatment. The best performing  $\text{ZnCl}_2$  treated cell had an overall efficiency of 5.05%, with  $V_{oc} = 494$  mV. The voltage is lower than 726 mV measured for the  $\text{CdCl}_2$  treated sample. However, the current density  $J_{sc}$  for the  $\text{ZnCl}_2$  treated device was  $\sim 2$  mA higher than that obtained for standard  $\text{CdCl}_2$  process (20.8  $\text{mA}/\text{cm}^2$  against 19.1  $\text{mA}/\text{cm}^2$ ). The FF was slightly lower (0.49 against 0.52). The FF and  $V_{oc}$  may be affected by the presence of a surface layer present after the treatment. XPS measurements showed the presence of Zn(0), ZnO, ZnTe and  $\text{CdCl}_2$  on the surface. SEM surface images (Fig. 4b) showed formation of the characteristic ZnO structure above the CdTe grains. A microstructural analysis using TEM revealed a thick additional layer between the CdTe surface and the back contact. This was identified to be ZnO using EDX chemical maps. The CdTe grains appeared to coalesce in a similar way to  $\text{CdCl}_2$  treated samples. The TEM images (Fig. 4a) also showed a reduction in the planar defect density after the treatment. Twins were present in some of the grains similar to  $\text{CdCl}_2$  treated samples. EQE measurements of the  $\text{ZnCl}_2$  treated solar cell

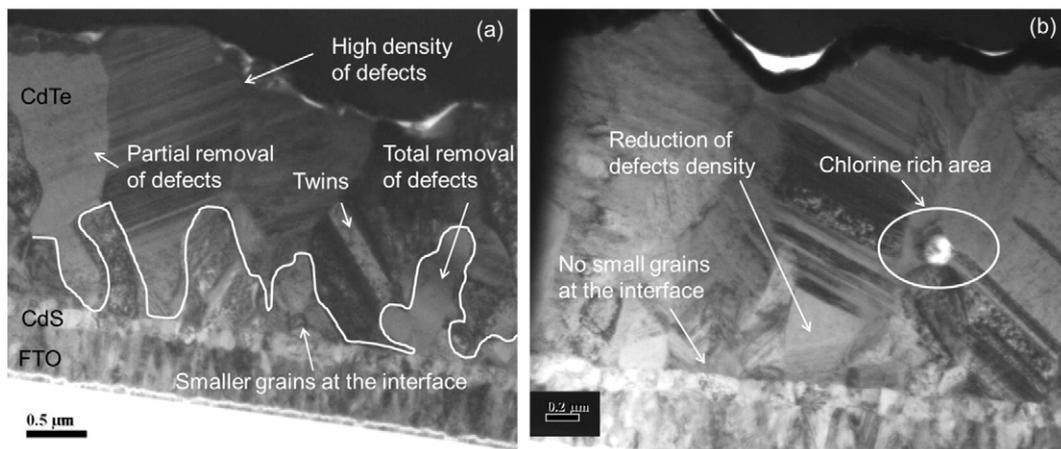


Fig. 3. TEM images of CdS/CdTe treated with  $\text{Cd}(\text{CH}_3\text{CO}_2)_2$  (a) and HCl (b).

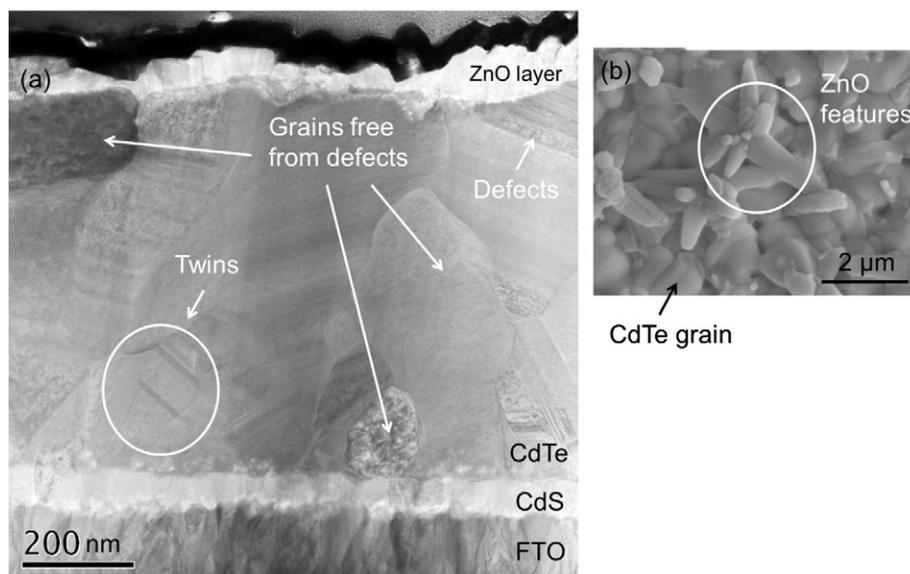


Fig. 4. (a) Cross-section TEM and (b) plan view SEM images at lower and higher magnification of  $\text{ZnCl}_2$  treated samples.

were different from those measured following treatment with other compounds. The current density measured for these cells was higher than the standard  $\text{CdCl}_2$  wet treated cells. The calculated band gap of  $E_g = 1.47$  eV compared with 1.48 eV for the  $\text{CdCl}_2$  cells suggests a higher level of intermixing between the CdS and CdTe. EDX point analysis confirmed sulphur diffusion into the CdTe close to the interface. The presence of the ZnO layer at the surface was also identified using EDX point analysis and XPS composition–depth profiling. The presence of this layer may explain the low voltage and Fill Factor.

#### 4. Conclusions

In this paper, we report on the effects of using different chlorine containing compounds on the efficiency of thin film CdTe solar cells (See Table 1). The study has confirmed the importance of the presence of chlorine during the treatment. The samples treated using a chlorine-containing compound showed recrystallisation of smaller grains present near the CdS interface into larger grains. This is consistent with microstructural changes observed using a  $\text{CdCl}_2$  treatment [8,9]. We have previously reported that the recrystallisation process for the CdTe starts at the CdS interface and this is very clear with columnar films grown by magnetron sputtering or electrodeposition [11]. Although this phenomenon is less clear for CSS deposited films, this work has provided further evidence that even for large grained material the critical concentration of chlorine required to initiate the process occurs at the junction. This observation is contrary to conclusions made elsewhere [12]. Thermal energy assists the reduction in planar defect density in the smaller grains at the interface while chlorine acts as a fluxing agent to drive the recrystallization of the grains. It is now known using Density Function Theory that certain types of stacking faults act as hole traps and

that these are removed by the recrystallisation process [13]. The highest conversion efficiency always corresponds to the removal of stacking faults in the CdTe absorber layer.

The use of both  $\text{TeCl}_4$  and  $\text{ZnCl}_2$  resulted in improvement in conversion efficiency. Both of these treatments led to the formation of surface oxides which appear to affect the device performance. These problems could be avoided by removing the oxides with a chemical etch. The surface of the treated films was more conductive following either Te or Zn deposition. A controlled deposition of these metals may improve the formation of the back contact. Te(0) was detected on the surfaces of the  $\text{TeCl}_4$  treated samples. This may create a Te-rich layer which can also be obtained using an etching procedure [14]. ZnTe was detected on the surface of the  $\text{ZnCl}_2$  treated samples by XPS. This compound may also benefit the back contact [15].

Chlorine agglomerates were found inside the CdTe layer following the HCl treatment and this affected cell performance. Over treatment with chlorine is known to reduce device efficiency [16,17].

The increase in conversion efficiency using alternative chlorine containing compounds is encouraging since an alternative to the use of toxic cadmium chloride is desirable. Further optimisation of the process is required to fully understand the mechanism of activation process. It is interesting to note that the use of  $\text{MgCl}_2$  has been shown recently to lead to cell efficiencies comparable with those obtained using the conventional  $\text{CdCl}_2$  treatment [18]. This is a viable alternative since  $\text{MgCl}_2$  is both less expensive and non-toxic.

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Table 1

List of microstructural changes and electrical performances for samples treated using different compounds.

	Small grains at CdS/CdTe interface	Surface layer	$E_g$ [eV]	$V_{oc}$ [mV]	$J_{sc}$ [ $\text{mA}/\text{cm}^2$ ]	FF	$\eta$ [%]
Untreated	Yes	No	1.49	173	0.39	0.35	0.02
$\text{CdCl}_2$	No	No	1.48	726	19.1	0.52	7.24
$\text{TeCl}_4$	No	Yes	1.49	594	17.9	0.43	4.58
$\text{Cd}(\text{CH}_3\text{CO}_2)_2$	Yes	Yes	–	443	5.91	0.19	0.51
HCl	No	No	1.49	506	10.57	0.29	1.54
$\text{ZnCl}_2$	No	Yes	1.47	494	20.8	0.49	5.05

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