

# Grain boundaries in CdTe thin film solar cells

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## Abstract

The current state of knowledge on the impact of grain boundaries in CdTe solar cells is reviewed with emphasis being placed on working cell structures. The role of the chemical composition of grain boundaries as well as growth processes are discussed, along with characterisation techniques such as electron beam induced current (EBIC) and cathodoluminescence (CL) which are capable of extracting information on a level of resolution comparable to the size of the grain boundaries. Work which attempts to relate grain boundaries to device efficiency is also assessed and gaps in the current knowledge are highlighted.

## Introduction

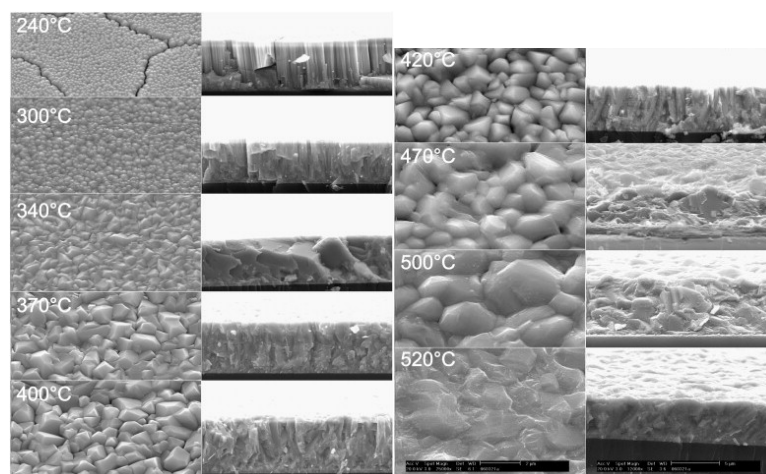
CdTe thin film solar cells have enjoyed a remarkable renaissance in recent years. For over a decade the peak efficiency of CdTe had stalled at 16.5% [1] but recent device development, primarily by First Solar, has seen efficiencies surpass that of multicrystalline Si at over 21%[2]. Despite this there is still great scope for improvement in the technology, with efficiency still some way below the Shockley-Queisser limit due to a comparatively small  $V_{oc}$ . It is often assumed that this  $V_{oc}$  gap seen in CdTe, in comparison to both single crystal GaAs and the theoretical limit, may be attributable to the grain boundaries [3] (GBs) within the material. This certainly seems plausible, one would naturally expect increased defect density as GBs and a resultant increase in recombination which would account for the  $V_{oc}$  loss. Other inorganic PV technologies provide evidence which would seem to support this GB limitation theory: single crystal Si cells outperform multicrystalline ones [4], CZTS[5] and CIGS[6] devices are similarly  $V_{oc}$  limited, while CdTe single crystal device have surpassed 1V[7] and GaAs cells with a similar bandgap to CdTe have achieved in excess of 1.1V [8]. There have however been a number of studies which have suggested not only that GBs are not deleterious to performance but may in fact be beneficial as sources of enhanced carrier collection[9, 10]. Can we therefore really ascribe the performance limitations to GB behaviour or is this simply a red herring and really issues such as low doping density due to self-compensation effects to blame[11]. After all if we consider thin film hybrid perovskite solar cells, which have a small sub-micron grain structure[12], have easily surpassed 1V[13] could we implying the GBs are in fact irrelevant and alternative factors dominate?

The focus of this review is purposefully narrow, concentrating on the functional behaviour on GBs within working cells. There is a vast literature on GB properties in single crystal CdTe but papers in this area are only included when they relate directly to cell structures, such as in the work by Duenow *et al* [14]. The intention is to be selective rather than exhaustive and there are also a number of excellent and more wide ranging reviews which cover other aspects of CdTe solar cells to which the reader is referred [15-19]. This review primarily seeks to answer one simple question: Are grain boundaries in CdTe solar cells a benefit or a hindrance?

## Section 1: Growth effects and recrystallization

There are a wealth of papers devoted to study of CdTe thin film microstructure and indeed most device related papers typically include some microscopic analysis of the grain structure. While the focus of this review is more on the functionality of grain boundaries within working solar cells, some discussion of grain structure in CdTe thin film is necessary as it relates to the deposition and process methods which ultimately define the grain structure. This section will provide a brief background to the growth and processing techniques commonly used for CdTe thin film fabrication. Two factors primarily determine the CdTe thin film grain structure i) the deposition method used and ii) the chloride activation step, with the two being somewhat interrelated. The chloride process in particular has been vastly studied and it is not the intention to review its application here. Instead brief discussion of how these processes relate to grain structure will now be discussed in turn.

### 1.1: Growth techniques

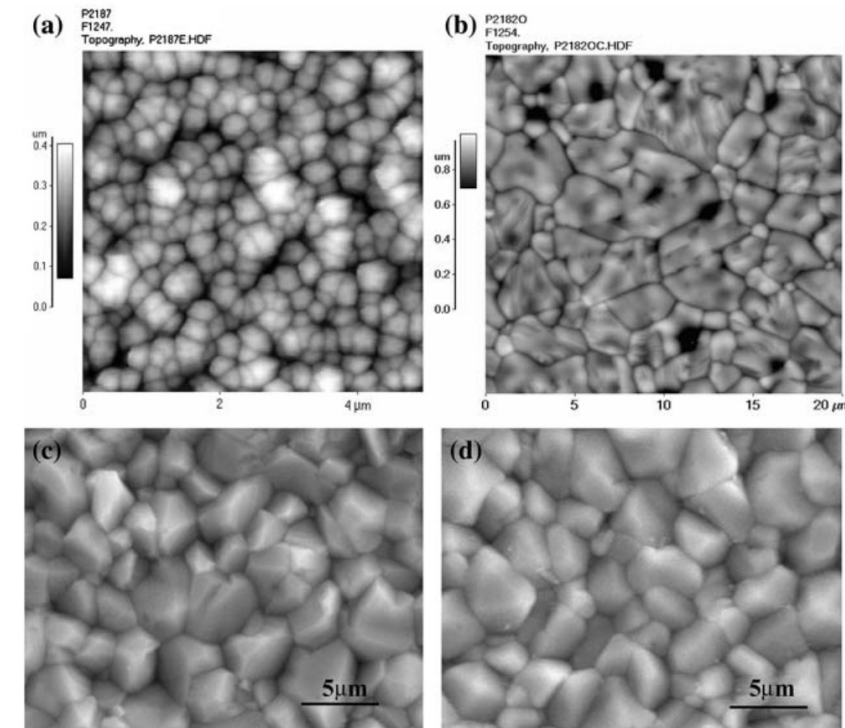


**Figure 1:** Taken from SEM pictures with a 25000× magnification of CdTe films as formed at different substrate temperatures. Left: top view, right: side view. Compact and rather defect free grains are observed at elevated temperatures (520 °C) but also at the transition range between the first and second growth regime (around 340 °C). From J. Luschnitz, et al, CdTe thin film solar cells: Interrelation of nucleation, structure, and performance, *Thin Solid Films*, **517** (2009) 2125-2131.

There are a number of techniques employed to deposit cadmium telluride such as electrodeposition [20], screen printing [21], metal-organic chemical vapour deposition [22, 23], sputtering [24-26], thermal evaporation [27] and close space sublimation (CSS) [28-31]. Each technique will yield a different grain structure, however a broad simplification is that higher temperature techniques or deposition conditions will generate films with a larger grain size [32]. Thus the industrial standard technique of high temperature CSS deposition produces films of a much larger grain size [33] than for low temperature deposition techniques [34] such as, for example, RF sputtering [24]. The reason behind this can be understood through thin-film growth theory [35] and the established mechanism of nucleation followed by grain growth, coalescence and film formation [36]. For higher temperature the critical radius for a stable nucleus (i.e. the size of nucleus stable to re-evaporation) to form will increase [35]. Thus grains have a lower probability of being successfully nucleated at higher temperature and consequentially those grains which do nucleate have reduced density increasing final grain size [37]. A similar effect may be observed through variation in deposition rate; by decreasing the rate at which adatom species arrive at the deposition surface the probability of stable nucleation can similarly be reduced and thus grain size increased (this has been demonstrated for CdTe through the use of elevated deposition pressures [33]). In general it can be considered that

CdTe thin film growth obeys the structure zone model, as demonstrated by Luschnitz *et al* [32, 38] (see figure 1) wherein the grain structure is seen as a progression from needle like growth at low temperatures, to a large well defined grain structure at higher temperatures (or pressures) [38]. It is also worth noting that the thickness of the film will alter the apparent grain size[39], when viewed from the back surface [40, 41], thus thicker films may have a larger apparent grain size although the grain structure at the interface may be unchanged. Clearly the choice of deposition method and the deposition conditions has a significant influence on the grain boundary structure in CdTe solar cells.

## 1.2: Chloride recrystallization



**Figure 2:** Morphology of CdTe films: (a) LT-CdTe, as-deposited (AFM image); (b) LT-CdTe, CdCl<sub>2</sub>/heat treated at 440C (AFM image); (c) HT-CdTe, as-deposited (SEM image); (d) HT-CdTe, CdCl<sub>2</sub>/heat treated. From: J. Quadros, A.L. Pinto, H.R. Moutinho, R.G. Dhere, L.R. Cruz, *Microtexture of chloride treated CdTe thin films deposited by CSS technique*, *Journal of Materials Science*, **43** (2008) 573-579.

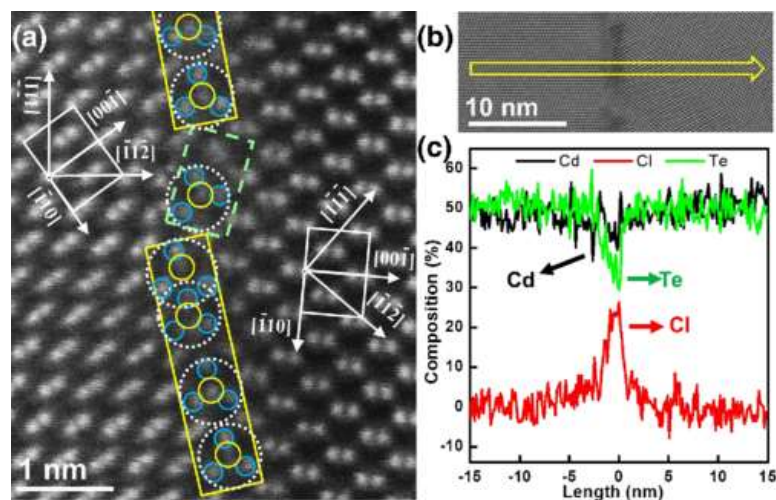
Treatment of CdTe solar cells with chlorine via CdCl<sub>2</sub>, or alternatively with CHF<sub>2</sub>Cl[42, 43] or MgCl<sub>2</sub> [44, 45], is considered vital to production of high efficiency solar cells. While the process has involvement in a myriad of aspects such as *p*-type doping, CdS/CdTe intermixing, junction position and potentially grain boundary passivation, it is often shown to have a large influence on the CdTe grain structure via recrystallization effects. This however predominantly occurs for low temperature deposition where, as discussed above, the as-deposited grain size is small and following chloride treatment the grain size is significantly increased [26, 46-48]. For higher temperature deposition methods the as-deposited grain size is near identical to the treated grain size[34, 49, 50], with the possible exception of some near CdS interface recrystallization[51]. A good example of this effect can be seen in work by Quadros *et al*[52], figure 2. For low temperature deposited CdTe recrystallizes to a much a larger grain size post-CdCl<sub>2</sub> treatment, whereas high temperature deposition produces no change post-annealing. This adds a layer of complexity when considering the grains structure of CdTe solar cells. Comparison between different deposition techniques becomes

highly problematic as the as-grown and treated states will be shifted with respect to one another, in addition to the other changes that occur. In most cases however it is the treated state of the cell that merits analysis, as without treatment device efficiencies are very low.

## Section 2: Chemistry of grain boundaries

One of the primary challenges when assessing the behaviour of CdTe solar cell GBs is to even determine what is the representative chemical composition of a grain boundary? This is a complex issue because of the nature of CdTe solar cells. The purpose of this review is to examine the behaviour of GBs in *functioning* CdTe solar cells, which typically means cells which have been chloride treated and Cu contacted[53]. Untreated cells have doping density around  $10^{13}\text{cm}^{-3}$  [54] but following these activation steps it is closer to  $10^{15}\text{cm}^{-3}$ [31]. In as-grown material both Cd and Te grain boundary cores are observed [55] with first principles calculations [56] suggesting that the Cd core is less deleterious to performance than Te cores but is less easily passivated. The post growth processes are widely established to introduce an array of impurities and dopants into the CdTe which are liable to either reside at GBs, or at least we may expect diffusion to be GB dominated [57-59]. The common impurities we can regularly anticipate in most CdTe cells are copper [60], chlorine [61], sulphur [62] and oxygen [63] (this is not to mention lesser used dopants such as arsenic [64], phosphorous[65], fluorine[42] and impurities such as sodium [66-68]). In this section the current knowledge on grain boundaries will be surveyed to see if there is any understanding as to whether each of the key dopants/impurities is present at the GBs

### 3.1. Chlorine

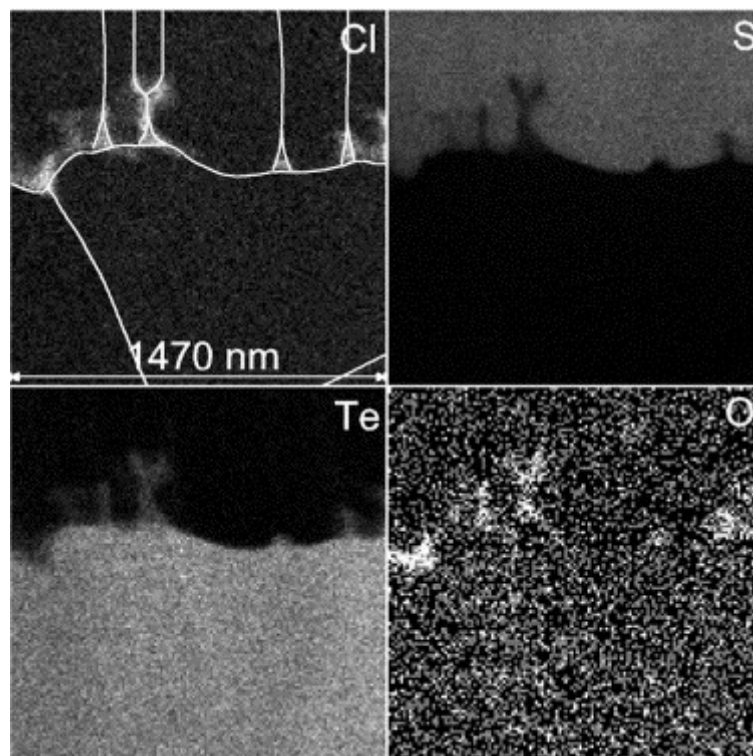


**Figure 3 :** Atomic structure and elemental distribution of the GB. (a) STEM Z-contrast image showing a  $\Sigma 9$  GB with symmetric (yellow boxes) and asymmetric (green dashed box) segments. The basic components of both the symmetric and asymmetric  $\Sigma 9$  GBs are Cd<sub>3</sub>Te dislocation cores (white dashed circles). The small blue and large yellow solid circles indicate single Cd and Te columns, respectively. (b) An EELS line scan was taken along the yellow arrow, and (c) the resulting composition profiles show strong Cl enrichment and Te reduction confined to a 1~2 nm range at the GB. From: Li et al, Grain-Boundary-Enhanced Carrier Collection in CdTe Solar Cells, Physical Review Letters, 112 (2014).

The effect of chlorine treatment on CdTe solar cells is possibly *the* single most studied topic of the field owing to the vast array of structural and electrical changes it induces within the device.

Separating the effect of chlorine alone is somewhat problematic as chloride activation treatments are typically performed in air and often generate intermixing with the CdS layer [39] (although not always[62]). It therefore becomes difficult to truly separate the impact of chlorine from that of oxygen and sulphur. Nevertheless if we focus on the pure GB boundary behaviour we see a weight of evidence that shows chlorine clearly segregates at the GBs throughout the film thickness. This has been demonstrated numerous times by methods such as time of flight secondary ion mass spectrometry (TOF-SIMS)[61, 69, 70], scanning microwave impedance microscopy (sMIM)[71, 72], or through TEM studies coupled to EXD/EELS analysis [9, 73-76]. The first such report of this type from Terheggen *et al* [76] found that Cl replaced Cd at the boundaries resulting in the formation of  $\text{TeCl}_2$  regions whilst more recent work by Li *et al* has also shown both replacement of Te [9] and of Cd [74] with Cl at the GBs. There are additionally some reports of Cl accumulation at the CdS/CdTe interface region [73, 74] but GB accumulation seems more pronounced. Of the many effects that the chloride activation treatment generates within the cell, from a chemical composition standpoint the segregation of chlorine at the grain boundaries is the dominant one. Although it is difficult to isolate it from the effects of both sulphur and oxygen it seems clear that chlorine is the prevalent GB impurity and there seems little evidence at present that chlorine is anything other than beneficial to GB behaviour.

## 2.2. Oxygen

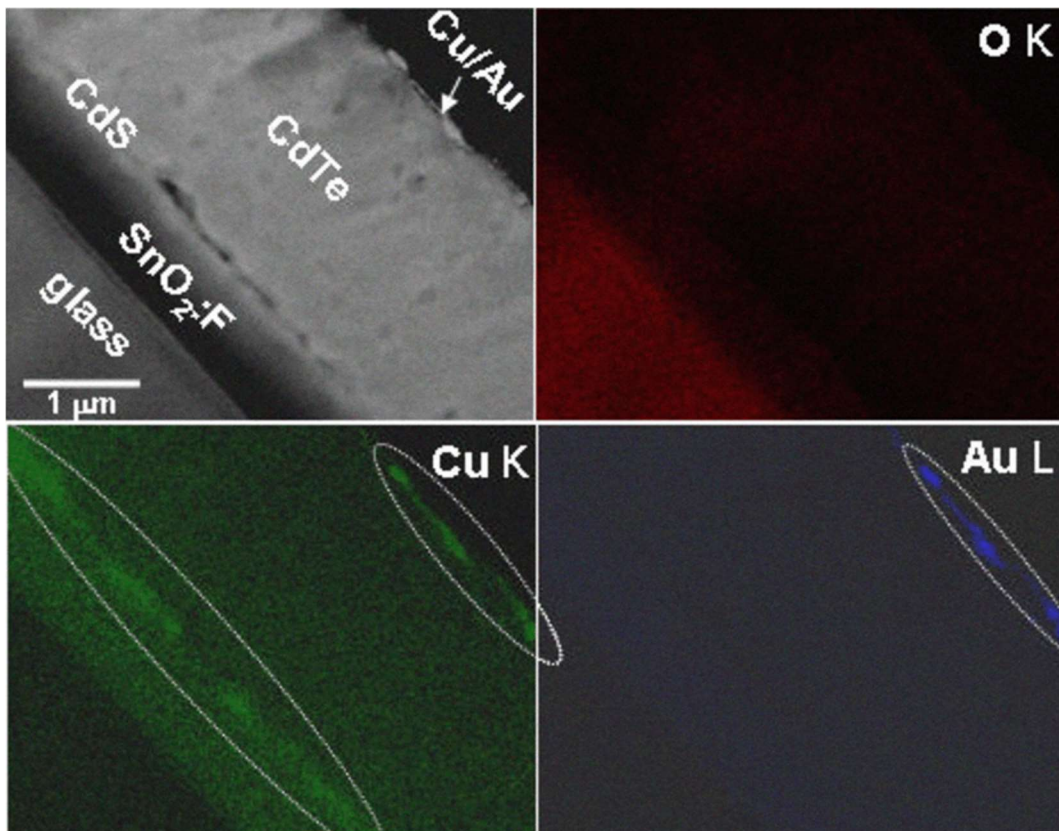


**Figure 4:** EDS mappings of the CdTe/CdS interfacial region. At the interface and along the CdS grain boundaries the concentration of Te, Cl and O is higher. In the Cl map, the grains are outlined along the boundaries for clarity. From: Terheggen *et al*, *Structural and chemical interface characterization of CdTe solar cells by transmission electron microscopy*, *Thin Solid Films*, 431 (2003) 262-266.

The assessment of oxygen's influence on GB behaviour is complicated by the fact that unlike chlorine treatment it may be introduced during multiple steps of the CdTe cell fabrication process. As well as its inclusion post-growth during the chloride activation process [77], oxygen containing ambients are often used during CdTe deposition [78-80]. Additionally there is often significant oxygen content in

the CdS layer, either as a nanostructured CdS:O layers [81, 82], or possibly an oxygen-rich chemical bath deposited (CBD) films [63, 83]. In particular the incorporation during CdTe growth has a dramatic effect on GBs as the resultant CdTe grain structure is hugely modified. Oxygen has been shown to be a nucleation aid [84], reducing the typical CdTe grain size [29, 79, 85, 86] and thus completely changes the balance between GBs and GI. Separating the specific GB related effect of oxygen under these circumstances thus becomes incredibly difficult. Nevertheless, Lv *et al* [87] make a strong effort at separating the effects that result from oxygen incorporation during CdTe. From XPS analysis and temperature dependent JV curves, they postulate that oxygen increases the number of GBs thus reducing mobility. They further postulate that oxygen content at GBs, via Te-O bond formation, increases downward band bending at the boundary (see section 3.4). A similar problem occurs for oxygen incorporation via the CdS as the presence of oxygen modifies the CdS grain size [81, 82] and thus the rate of intermixing [63, 88], making isolation of its effect on GBs nearly impossible. The only route to effectively study the impact of oxygen on GBs would therefore seem to be via post growth annealing. This type of work has been reported alongside chlorine in-diffusion and there are some reports of oxygen segregation at GBs as a result [74, 76], but even in these cases oxygen is only present at the near-CdS interface (see figure 4) or at chlorine-rich precipitates. Loginov *et al* [89] did observe CdO formation following air annealing from TEM electron diffraction patterns but the location of the CdO formation is somewhat unclear. Overall despite the wide assumptions. Interestingly despite wide spread assumption that oxygen resides at grain boundaries and there appears to be no work reported demonstrating the presence of oxygen at typical GBs. Additionally it is rarely separated from the impact of chloride treatment despite it being known that modest performance improvements can be achieved in such a manner [90]. Such studies would allow the GB specific behaviour of oxygen to be characterised and more generally the true impact of oxygen to be established. There seems to be little to suggest oxygen is anything other than beneficial to cell performance but its true presence and impact on the GBs, and indeed GIs, is unclear.

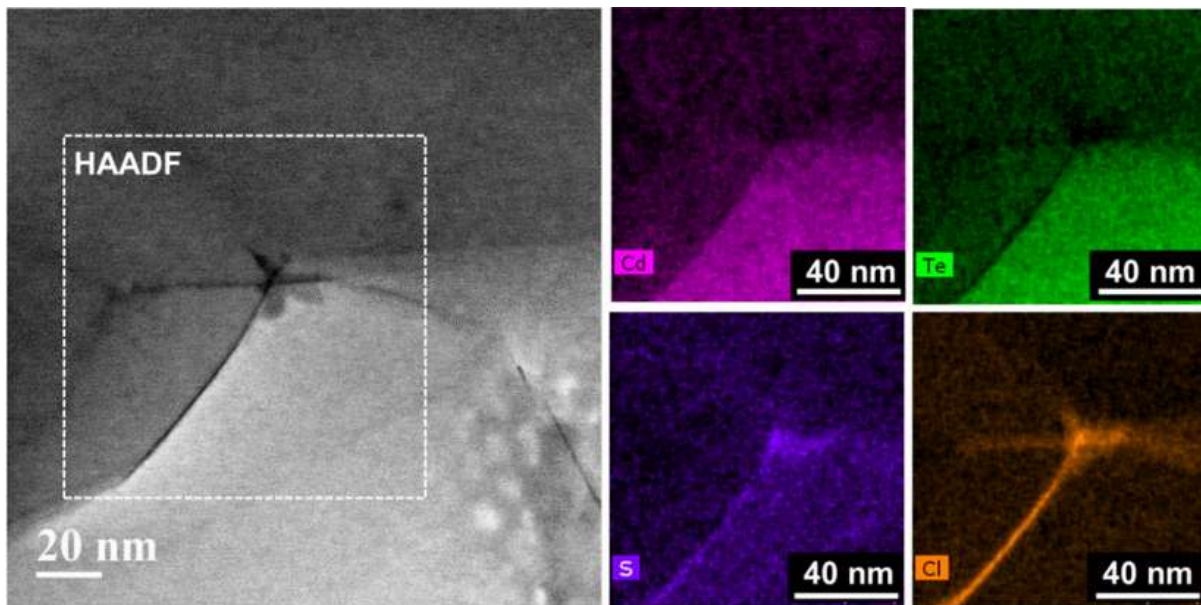
### 2.3. Copper



**Figure 5:** Cross-sectional HAADF image and EDX mapping of Cu, Au and O on the same area. Brightness in the mappings indicates the intensity of Cu Formula, Au Formula and O K signal. From: Liu *et al*, XRF and High Resolution TEM Studies of Cu at the Back Contact in Sputtered CdS/CdTe Solar Cells, in: 33rd IEEE Photovoltaic Specialists Conference, 2008, 29-32.

Copper may be viewed as both a help and a hindrance in CdTe. In most CdTe cell production processes copper is in-diffused from the back surface (or into some partner layer such as ZnTe [91, 92]) in order to enable the formation of an ohmic back contact[93]. However because copper is a fast diffuser in CdTe[94] and it's presence away from the back surface causes long-term performance degradation [95] being attributed to Cu related deep levels[96], accumulation at the CdS/CdTe interface [97] and a reduction in carrier lifetime [98]. CdTe grain structure is expected to assist copper diffusion [99] and the segregation of excess copper at the GBs has been predicted as a mechanism[100], an idea backed up by theoretical predictions [56]. However despite this, direct evidence is somewhat difficult to come by and some authors have suggest that GBs do not in fact assist Cu diffusion [60]. Whilst there have been observations of Cu precipitates at the near back surface [101] and within the CdS layer [102, 103] it would appear there is no direct evidence of the presence of copper populating the GBs. EBIC work of Poplawsky *et al* [9] (figure 7) would seem to imply that, whilst copper treatment has a more uniform and less GB specific effect than CdCl<sub>2</sub> treatment, the GB behaviour as observed by this techniques is certainly modified by copper. It may be that due to its fast diffuser nature, copper resides there in quantities below the detection limit. However the general conclusion is that there is no little direct evidence for the presence of copper at CdTe grain boundaries away from the near back surface and CdS interface.

## 2.4. Sulphur



**Figure 6:** STEM-EDX maps show that S and Cl enrich while Cd and Te reduce at the GB. From Li *et al*, *S-Te Interdiffusion within Grains and Grain Boundaries in CdTe Solar Cells*, *IEEE J. Photovolt.*, 4 (2014) 1636-1643.

Sulphur out diffusion from the CdS is a well established phenomenon and may be observed on a bulk scale via a number of routes such as external quantum efficiency [104], X-ray diffraction [105], with energy-dispersive X-ray spectrometry [106], photoluminescence [107] or ellipsometry analysis [108]. Similar to both copper and oxygen diffusion it is presumed to propagate via GBs [58], and while attaining direct evidence is rather challenging due to the nature of such analysis, the evidence for GB assisted Sulphur diffusion is much more convincing than for copper or oxygen. Yan *et al* [109] found significant sulphur diffusion along GBs but interestingly only when CdTe was deposited in the absence of oxygen. For growth ambients which contained oxygen sulphur diffusion was suppressed. They ascribed this to the formation of CdO phases but were unable to detect these directly. This influence of the CdTe deposition conditions on sulphur GB diffusion is seen by other researchers. Taylor *et al* [62] found that for high temperature deposition conditions significant sulphur diffusion occurred during deposition and there was minimal variation following subsequent CdCl<sub>2</sub> treatment. They additionally found from cathodoluminescence analysis that sulphur diffusion was indeed grain boundary enhanced. In contrast Terheggen [76] found no significant sulphur diffusion as-deposited, irrespective of temperature, but did find sulphur diffusion post-CdCl<sub>2</sub> treatment and not preferentially at GBs. This work by Terheggen seems to be the outlier with most other work such as that by Herndon *et al* [110] identifying sulphur at the grain boundaries. In the case of work by Li *et al* [74] this was additionally linked to a decrease in Te concentration at the boundary (see figure 6). Possibly the best demonstration of sulphur diffusion via GB comes from work on inverted “substrate” geometry cells by Kranz *et al* [111]. Using a combination of atom probe tomography and secondary ion mass spectrometry they demonstrate clear sulphur diffusion via the GBs (as well as chlorine diffusion), with sulphur content being significantly higher at the near interface. The caveat to this is that the Kranz work utilises an inverted “substrate” cell structure, so direct reference to the standard superstrate cell configuration must be treated with some caution. Substrate cells though may offer a better route to effectively studying the impact of sulphur at GBs as despite the number of papers that show sulphur diffusion occurs and that it is GB dominated there is no clear



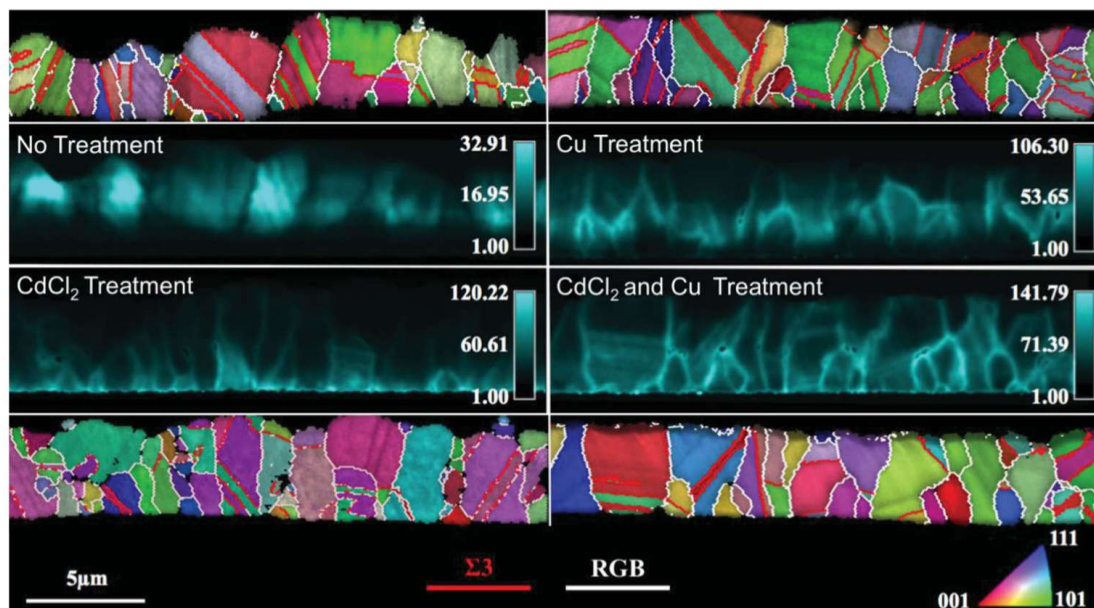
understanding of the role it plays there. This again is primarily due to the difficulty of untangling its impact from the impact of the chlorine treatment.

From this brief review of the chemical composition of grain boundaries we may determine that in a typical activated CdTe solar cell, chlorine resides at the GBs throughout whilst sulphur is present predominately at near-interfacial GBs. Oxygen and copper's presence at GBs is unclear with there being no evidence that the latter resides there at all away from the back surface or at the CdS interface.

### Section 3: Functional microscopy of grain boundaries

In order to directly ascertain the behaviour of GBs it is necessary to measure their properties with a resolution comparable to their size. This means that only high resolution techniques such as electron microscopy or scanning probe techniques are able to truly quantify the GB behaviour. This type of work is incredibly challenging and technological development to allow this is comparatively recent, hence the literature is not vast. This section provides a selective review of the current knowledge of functional microscopy techniques, i.e. those which are capable of extracting quantifiable data related to GB functionality.

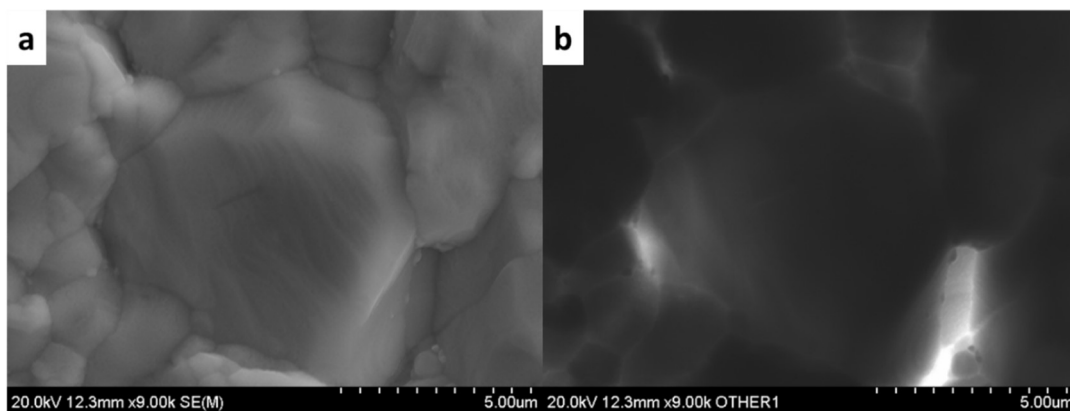
#### 3.1. Electron beam induced current analysis



**Figure 7:** EBIC and EBSD maps of untreated, CdCl<sub>2</sub> treated, Cu treated and CdCl<sub>2</sub>/Cu treated CdTe solar cells. From: Poplawsky et al *Direct Imaging of Cl- and Cu-Induced Short-Circuit Efficiency Changes in CdTe Solar Cells*, *Advanced Energy Materials*, 4 (2014).

The electron microscopy based technique of electron beam induced current (EBIC) analysis is of particular interest for the study of grain boundary functionality. EBIC monitors the current collected by a solar cell following electron hole pair generation due to excitation from an electron beam incident on the surface. In essence EBIC allows the identification of specifically where PV junctions exist within a solar cell with the resolution of an electron microscope. This is particularly powerful for the characterisation of grain boundaries, as it allows their electronic behaviour to be directly visualised. However, despite EBIC having been an established technique for some time [46] it is only relatively recently that the behaviour of grain boundary behaviour has truly been fully explored

using it. EBIC may be applied at a variety of positions within the CdTe cell structure, at the device back surface [112], at the front surface (i.e. near to the CdS/CdTe interface) [112] or in cross section [113]. Back surface analysis whilst the easiest to perform can be rather frustrating to interpret in relation to GB behaviour, as the region furthest from the junction is the one being probed. A beam voltage sufficient to probe the depletion region will likely mask the GB behaviour through lower spatial resolution caused by the large generation volume. This back surface measurement technique typically yields GB with bright contrast [114-116], perhaps indicative of improved carrier collection. It is however important to consider the topography of the sample with this measurement though, as for unpolished “rough” samples (see figure 8 [117]) the grain boundaries may appear “bright” simply by virtue of being closer to the junction in the geometry of the measurement. Indeed such contrast may be removed via careful polishing to smooth the samples [46] so it is rather difficult to draw any definitive conclusions from this form of EBIC GB analysis. The “front wall” EBIC techniques [112, 118], wherein the beam is again incident in plan view but directly on the PV junction region, offers the opportunity for analysis of the GB behaviour in the near junction region and utilising lower beam voltages. This technique is rarely applied though due to the relative difficulty of sample preparation, involving the use of hydrofluoric acid to remove glass and careful masking to protect layers [112, 118]. It is however capable of yielding significant GB insight though free from the topographical restrictions of the back surface measurement. Edwards *et al* [118] and Galloway *et al* [112] found distinct differences in the GI and GB EBIC signals, which were shown to vary with both CdCl<sub>2</sub> treatment and with injection level. From this the authors concluded that the GBs were passivated by chloride treatment and that any contrast observed was not due to recombination. Furthermore they suggest this was indicative of upward band bending at the GBs (leading to minority carrier repulsion [112]) as a result of increased *p*-type doping at the GBs related to CdCl<sub>2</sub> treatment.

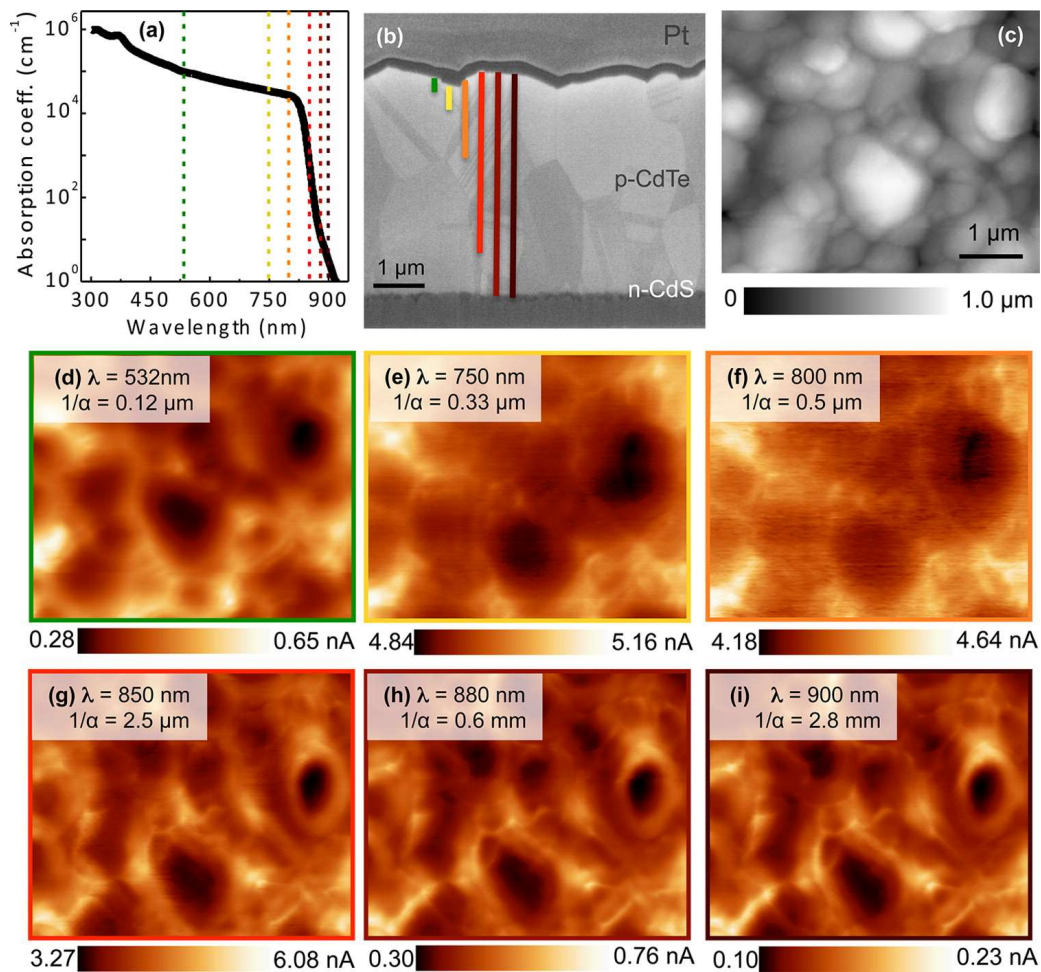


**Figure 8:** Back surface EBIC analysis of an unpolished CdTe solar cell showing a) secondary electron and b) EBIC current images. From: Major *et al*, Back surface EBIC analysis of CdTe solar cells, unpublished work, 2016.

The cross sectional EBIC technique is possibly the most relevant to device operation as it allows direct determination of the both the main junction position within the cell [119] and analysis of the GBs as they traverse front-to-back through the CdTe [9]. However, similarly to back surface EBIC measurements, analysis is particularly sensitive to surface topography [116], thus high quality analysis requires a smooth surface to be produced. This may be produced by chemical etching/polishing processes, but the development of focussed ion beam (FIB) milling techniques has allowed the production of much smoother device cross sections without the requirement for chemical etchants [51]. This has led to a number of studies in recent years using this technique which focus on grain boundary behaviour and which all demonstrate a common, and somewhat

unexpected, result, an improvement in collection manifest through bright EBIC contrast at the GBs [9, 75, 115, 116, 120, 121]. The implication from this finding being that either current collection is improved at GBs [9, 75] or at least recombination is reduced [115, 116], with the GBs instead enhancing current “flow” [115]. The results are consistent with the downward model of band bending at the GBs (see section 3.4), with Li *et al* [9] and Yan *et al* [120] suggesting the GB cores may in fact be n-type, producing localised p-n regions and thus the enhanced collection observed. Additional information relating to the role of the CdCl<sub>2</sub> treatment on GB performance was also extracted from the EBIC work via the comparison of treated and untreated cells [9, 75, 121]. For untreated cells GB contrast is dark, indicative of high recombination, which then becomes bright contrast following treatment (see figure 7). By linking this to evidence of Cl segregation at the GBs from STEM/EELS analysis [9, 75] this shows the clear role of Cl to passivate the CdTe GBs and thus modify their electrical behaviour. Additionally Cu was shown by Poplawsky *et al* [75] to have a distinctly different impact on the GBs in comparison to CdCl<sub>2</sub>, see figure 7. These EBIC results are highly significant finding as they offer the tangible evidence for the role of post-growth treatments on the GB behaviour. The difference in GB contrast between as-deposited and CdCl<sub>2</sub> treated being particularly striking, showing that the chloride treatment has a major impact on GB functionality. Additionally the finding of an improvement beyond the GI level particularly interesting, as stated in the introduction to this review common wisdom suggests grain boundaries should have a negative impact. We must though be careful not to overplay these findings though as the geometry of the measurement needs to be considered, along the nature of the material. Whilst this cross-sectional analysis is compelling, this does not measure the cell in its standard operating condition. We could realistically envisage significant changes in both grain boundary and junction behaviour under non-localised excitation through the front surface. Additionally the electron beams used to probe the GB function have low accelerating voltage (3kV [75]) and thus also we need to consider the fact that surface recombination effects may dominate what is observed. Overall however EBIC analysis provides a strong case to the beneficial effect of GBs within CdTe.

### 3.2. Scanning probe analysis



**Figure 9:** Photocurrent tomography of CdTe solar cell. (a) Absorption coefficient  $\alpha$  as a function of wavelength for CdTe. (b) Cross-section SEM image showing light absorption as a function of the distance to the p–n junction. Pt layer is used to protect the surface of CdTe during the milling process. The lines schematically illustrate the penetration depths ( $1/\alpha$ ) for the corresponding wavelengths. (c) Topography scan using set point = 0.75 to 0.85 V. (d–i) Photocurrent microscopy measurements of the p-CdTe layer under different illumination wavelengths ( $\lambda$ ). The current scale was adjusted to clearly show the contrast between GIs and GBs in all images. Incident laser power = 1.0 nW; NSOM probe = 300 nm. , From Leite *et al*: Nanoscale Imaging of Photo current and Efficiency in CdTe Solar Cells, ACS Nano, 8 (2014) 11883-11890.

Scanning probe methods such as scanning kelvin probe microscopy (SKPM)[122], scanning tunnelling electron microscopy (STEM)[123] or conductive atomic force microscopy (C-AFM) [124] allow highly localised electrical properties to be determined and thus the separation GB and GI behaviour. By moving a highly resolved conductive tip across the sample surface the photocurrent or photovoltage may be mapped as a function of position. Similar to EBIC analysis these measurement techniques do though face a number of challenges in order to provide reliable information. An important consideration is the impact of topography. These measurement techniques are typically applied to the device back surface which has high roughness, but this effect may be circumvented by the simultaneous measurement of the topography to rule this out from observations[124]. The overall view from these types of measurements seems to support the EBIC based supposition that GBs are a positive effect in the cell structure. Work by Visoly-Fisher *et al* [10, 122, 125] utilising SKPM, C-AFM

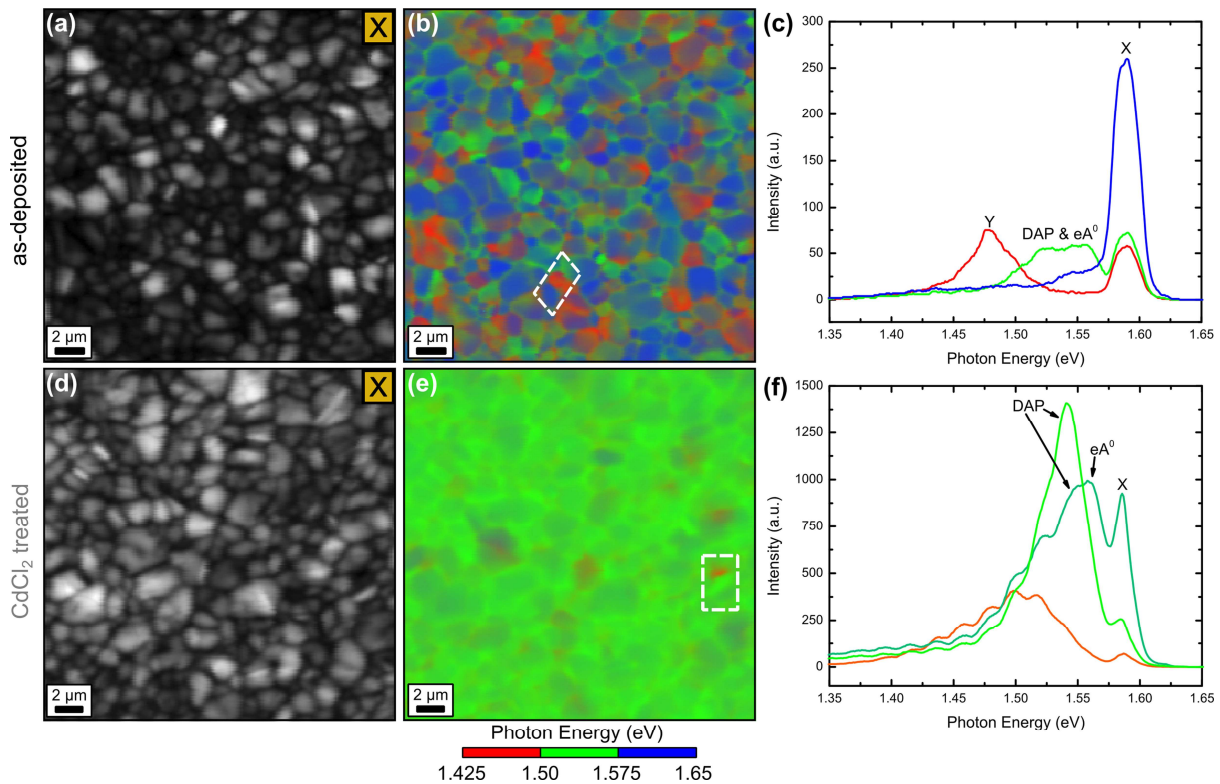
and scanning capacitance microscopy (SCM)[122] strongly supports the concept of beneficial grain boundaries. They observed high photocurrent (i.e. bright current contrast) via these measurements at GB cores, attributed to localised type inversion [125] and lower hole density [122] producing a barrier for hole transport[122]. As a result they suggest the downward band bending model (section 3.4) at the GBs [10, 125], with the boundaries acting as advantageous low resistance electron pathways with a low recombination rate [125]. They further make the suggestion that GBs may additionally act as a sink for impurities which are gettered there during CdCl<sub>2</sub> treatment, in a similar manner that which occurs for Si cells[10]. While there is little direct evidence for this from the work it is an interesting idea nevertheless. Recent work by Li *et al* [126] agrees with the Visoly-Fisher work. By using a range of measurement techniques, SKPM, C-AFM, EBIC, EBSD to study GB behaviour they also observe improvements at GBs and ascribe downward band bending to localised type inversion at the GBs and thus the formation of lateral junction regions with the GIs. Indeed this seems to be the overall consensus from the scanning probe work: GBs are depleted and thus conductive pathways [71, 127, 128], there is greatly reduced recombination at the GBs [71, 125, 126, 129] and localised depletion regions are formed between GB and GIs. There are some suggestions that the upward band bending model may be more appropriate at the boundary [128, 129] but again this doesn't detract from the overall suggestion that GBs are generally beneficial.

An additional subset of scanning probe measurements that may study GB behaviour is optical probe measurements. These clearly differ from those techniques discussed above as there is no direct physical contact with the surface but rather a light spot is used to probe the response. There are a number of variants for the measurement of solar cell photo-response to a localised light source such as optical beam induced current (OBIC) [80, 130], light/laser beam induced current (LBIC) [131-133] or near-field optical scanning microscopy (NSOM)[134]. Whilst OBIC/LBIC techniques have been widely used for analysis of CdTe solar cells they are limited to micron levels of spatial resolution [135] and thus unable to accurately analyse grain boundary performance. This is a particular shame as these measurement techniques operate through the glass and thus are able to probe in a normal working mode. The NSOM technique, although only sparsely used for CdTe solar cells, is capable of generating useful GB related information from an optical probe. Work by Leite *et al* [134] and Smith *et al* [136] shows clear increases in photocurrent at the GBs attributed to improved current collection resulting from localised GB downward band bending, with Leite [134] also supporting the localised junction formation model and additionally performed analysis as a function of excitation wavelength (see figure 9).

The overall view of these scanning probe measurements is that the GBs are beneficial, there appear to be no obvious dissenting voices to suggest the GBs are hindering device performance. Within the scope of these measurements the GBs are clearly beneficial but there are some considerations to be made when evaluating this type of work in order to allow a true assessment of the GB behaviour. Primarily, what is the impact of the geometry of the measurement? These scanning probe measurements are generally performed on the free back contact surface[10, 71, 122, 124-126, 128, 129, 134, 136] so is the GB behaviour that is observed relevant to the operation of the cell under normal operating conditions? Work by Moutinho *et al* [124] highlights the surface dependent nature of these measurements and shows that surface etching treatments, such as bromine/methanol or nitric-phosphoric acid etches, produce a larger change in the observed GB current behaviour than CdCl<sub>2</sub> treatment. This does tend to imply that the surface conductivity is having a large effect and there is the potential that what is being observed is simply a surface effect. In addition Moutinho *et al* further report cross sectional cell analysis via C-AFM[127], which finds the GBs are conductive throughout the thickness of the film. This would suggest that measurements of the GB behaviour at the back surface are indeed representative of the film GB behaviour.

Furthermore, the fact that all reports suggest improved performance at GBs irrespective of the measurement techniques used and surface treatment is reassuring.

### 3.3. Cathodoluminescence and Photoluminescence



**Figure 10:** CLSI data for the as-deposited film across the top row [(a)–(c)] and the CdCl<sub>2</sub>-treated film across the bottom row [(d)–(f)]. (a) and (d) show grayscale CL intensity images of the excitonic energy window (X ~ 1.575–1.61 eV), which show that exciton emission is sharply reduced at the GBs. (b) and (e) show photon energy maps of the 1.425–1.65 eV energy window. Pixel color in these maps gives the dominant transition energy range (defined by the colour bar below the maps) in the spectra at each location. The spectra (c) and (f) were taken from the areas in white boxes in (b) and (e), respectively. From: Moseley *et al*, Cathodoluminescence Analysis of Grain Boundaries and Grain Interiors in Thin-Film CdTe, *IEEE Journal of Photovoltaics*, 4, 1671-1679 (2014).

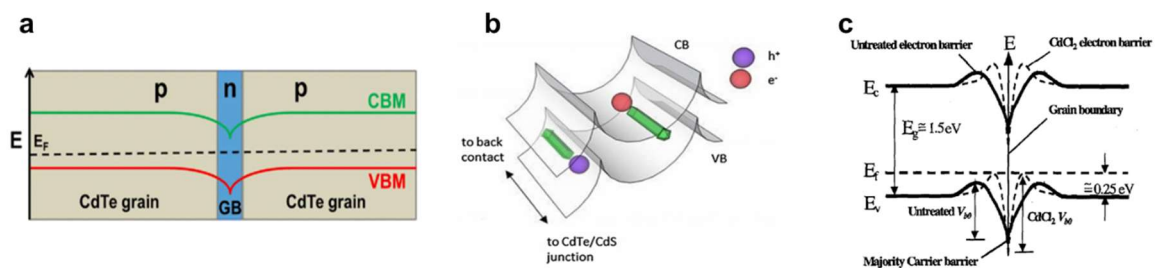
Spatially resolved luminescence techniques such as cathodoluminescence (CL) or photoluminescence (PL) appear to be tailor made to study GB behaviour. These techniques allow visualisation of generation and recombination behaviour at resolutions capable of distinguishing between GB and GI. Most relevantly for GB analysis these techniques allows us to identify areas of non-radiative carrier recombination and thus areas we may expect to be deleterious to device performance. Surveying the CdTe grain boundary luminescence literature as a whole, two key points become apparent. Firstly, these techniques show an increase in non-radiative recombination at the GBs compared to GIs [60, 137-146] and secondly this recombination at GBs is significantly reduced following CdCl<sub>2</sub> treatment [138, 139, 143, 144]. This is typically manifest through a reduction in observed exciton related luminescence at the GBs compared to GIs, with that reduction being minimised following CdCl<sub>2</sub> treatment. This strongly supports the GB passivation theory for CdCl<sub>2</sub>, wherein Cl is accumulating at GB and minimise the recombination impact of deep levels present there in as grown material [147]. This is in essence similar to that observed for EBIC and scanning probe techniques, but crucially as Moseley *et al* [138] note “CdCl<sub>2</sub> treatment is not a perfect fix for

GB recombination, and GB recombination may still be limiting performance in CdCl<sub>2</sub> treated devices.” This is indeed the finding of all the luminescence work that the negative impact of boundaries is simply minimised following CdCl<sub>2</sub> treatment rather than GBs being enhanced beyond the GIs unlike that observed for EBIC and scanning probe analysis. Again the nature of the measurements need to be taken into account though. CL and PL are typically applied to the device back surface (although cross sectional data gives similar results[62]), measurement conditions are naturally in the dark and there is the potential for issues with surface recombination effects (although this is much more effectively separated than for EBIC [137]). Luminescence techniques do though allow far greater extraction of additional spectroscopic information about GBs than either EBIC or scanning probe methods. Additional analysis has shown that carrier lifetime is reduced at the boundary [139] whilst recombination velocity is significantly increased [140], which Kanevce *et al* [141] link to  $V_{oc}$  loss. Comparison with electron back scattered (EBSD) analysis also shows  $\Sigma 3$  twins are typically inert with little enhancement in recombination[142, 144], presumably due to a lack of dangling bonds as posited by Consonni *et al* [148]. Novel PL imaging [146] and time resolved CL techniques [145] have suggested that hole traps at grain boundaries may even provide a conduction pathway for hole transport, at least at low temperatures.

It is interesting to see that, similar to the scanning probe and EBIC fields, luminescence measurements appear to have converged on a single unified answer to the GB question, that grain boundaries are a hindrance. The fact that this unified answer opposes that obtained from these other measurements is highly problematic though. It essentially leaves us in a situation where we would need to appraise which measurement technique is most valid to understand the GB behaviour. This is not something that can easily be done.

### 3.4. Grain boundary band bending models

The analysis discussed in sections 3.1-3.3 clearly indicates that there are pronounced variations in the band structure localised at GBs. These variations in GB performance invariably leads to the prediction for specific models of band bending at the boundaries to account for this phenomena which are summarised in this section.



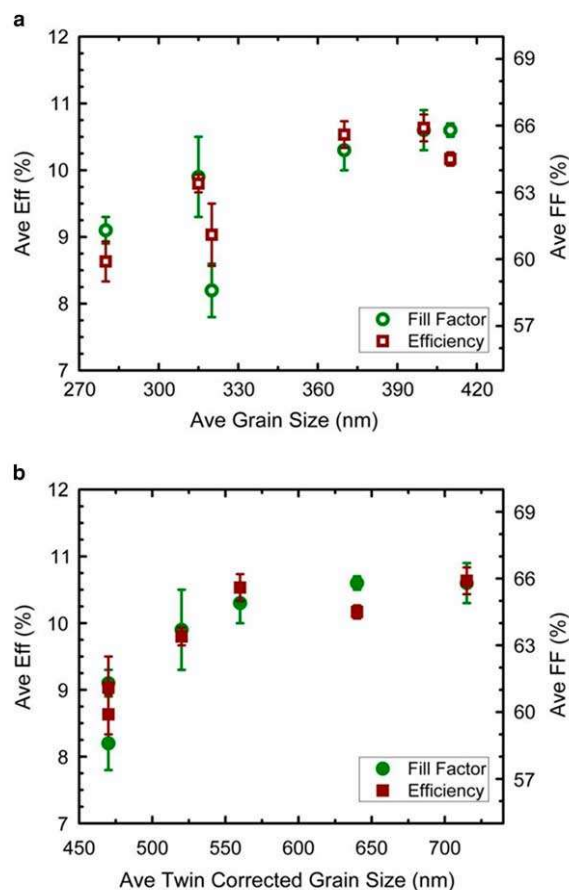
**Figure 11:** Various grain boundary band bending models predicted, a) downward p-n-p model From: Li *et al*, Grain-Boundary-Enhanced Carrier Collection in CdTe Solar Cells, *Physical Review Letters*, 112 (2014), b) upward band bending model from: Brooks *et al* Scanning Kelvin probe measurements on As-doped CdTe solar cells, *Semiconductor Science and Technology*, 28 (2013), c) near boundary barrier model from: Woods *et al*, The effects of CdCl<sub>2</sub> on CdTe electrical properties using a new theory for grain-boundary conduction, *Conference Record of the Twenty-Eighth IEEE Photovoltaic Specialists Conference*, 603-606 (2000).

A number of different models have been proposed, which are shown in figure 11, and predict either downward [9, 10, 72, 87, 120, 125, 126, 136] (figure 11a), upward [112, 114, 129, 149, 150] (figure 11b) or in one case downward but with a near boundary barrier [151] (figure 11c). The downward bending model has been used to explain the improvements in collection observed via EBIC and scanning probe analysis. Li *et al* [9] suggest a p-n-p localised junction between GBs and GIs resulting from Cl segregation there, causing improved photogenerated carrier separation. This model is extended somewhat by Lv *et al* [87] who suggest that oxygen may serve to additionally increase the boundary barrier height in this model. This concept of downward band bending and a localised depletion layer supports observations from scanning probe measurements [10, 125, 136] and Visoly-Fisher *et al* [10] additionally propose a channelling effect where holes flow along GBs to the back contact. There are conversely a number of proponents of the upward band bending, typically in instances where lower current collection has been observed to occur at grain boundaries. For example both Galloway *et al* [112] and Brooks *et al* [129] utilise the upward bending model (figure 11b) to explain reduced collection observed for EBIC and SKPM analysis respectively. This is proposed to occur due to increased hole concentration near the boundaries, resulting in minority carrier repulsion. An additional layer of subtlety to these models was suggested by Woods *et al* [151] who made theoretical predictions of downward bending at the boundary but with a minority carrier barrier due to increased p-doping at the near boundary (figure 11c). Whilst this model seems entirely plausible, it also appears almost impossible to verify experimentally due to the level of resolution that would be required.

## **5: Grain boundary relation to device performance**

A true assessment of the impact of grain boundaries in CdTe solar cells needs to be done on cells under normal operating conditions. This is however incredibly challenging. The most obvious route to assessing the true impact of grain boundaries on CdTe solar cells would seem to be a comparison of device performance as a function of CdTe grain size. One would anticipate that as the grain size of the film is increased the contribution of the GBs would be reduced and an assessment on the impact could be made. Unfortunately complete cell structures are not so simple and there are numerous aspects which need to be considered in parallel. Typically altering a deposition process to manipulate grain size via will have knock on effects for intermixing of the CdTe/CdS layers [62] and possibly post-growth chloride processing (making the assumption that Cl-diffusion is GB dominated). Separating these effects from that of the grain size and thus GBs is incredibly challenging and may be the reason why there are so few papers where grain size is able to be directly linked to cell performance.





**Figure 12:** a) Average efficiency and FF versus nontwin-corrected average grain size for CdCl<sub>2</sub>-treated samples. b) Average efficiency and FF versus twin-corrected grain size for CdCl<sub>2</sub>-treated samples. From: Nowell *et al*, *Characterization of Sputtered CdTe Thin Films with Electron Backscatter Diffraction and Correlation with Device Performance, Microscopy and microanalysis*, 21 (2015) 927-935.

The work which has most directly focussed on the interrelation between grain boundaries and device performance has been that by Nowell *et al* [152, 153]. In this work electron back scattered diffraction (EBSD) analysis was used to accurately characterise the CdTe grain size which was varied throughout the sample. The use of EBSD additionally allowed the separation of grain boundary type enabling the separation of normal and twin boundaries. A positive correlation was observed between grain size and device performance (see figure 12), with the authors ascribing the trend to the reduced negative impact of GBs. Interestingly though this trend was much improved after the removal of twin boundaries from their calculations and offers some confirmation of the luminescence analysis of minimal recombination at twin boundaries [142, 144]. A similar performance trend with grain size was observed in Major *et al* [33], where the pressure of nitrogen used during CSS deposition was increased to deposit larger grained CdTe films. An improvement in performance was seen as a function of grain size for all performance parameters up to a limiting point. At this point the benefits of grain boundary minimisation were assumed to be overtaken by other considerations such as contact resistances. Through modification of the CdTe nucleation temperature similar grain size control may be achieved. In the work by Li *et al* [154] the CSS substrate temperature was varied with higher temperatures producing a larger grain size which was in turn linked to an improvement in the cell  $V_{oc}$ . There are additionally a number of papers where the chloride recrystallization effect and deposition conditions are linked to performance such as the

excellent work by Luschitz *et al* [32], however it is incredibly difficult to draw any conclusions about the nature of GBs from these studies owing to the vast complexity of changes that occur during treatment. An example of this complexity can be seen in the recent work by Spalatu *et al* [155] wherein grain structure is initially controlled by deposition temperature, with higher temperatures giving a larger as-deposited grain size. The device performance is shown to be at a peak for a temperature of 450°C, corresponding to a certain grain size as-deposited, but as recrystallization occurs following CdCl<sub>2</sub> treatment the treated grain size is in fact ~1µm for all deposition temperatures. It could be that another factor such as sulphur diffusion during deposition is the dominant factor here but no real conclusions to this effect can be drawn. We may also consider a route of secondary inference via the fact that deposition techniques which produce larger grain sizes, e.g. CSS, have yielded higher efficiencies [1] than techniques such as sputtering [47], MOCVD [156] or thermal evaporation [157]. It is tempting to infer from this that GBs are deleterious but we must then also consider work demonstrating that oxygen inclusion during CSS deposition, which reduces the grain size [85], has also been shown to improve performance [79]. This highlights the problem with such device level analysis. The structures are simply too complex and at present no research has been able to untangle the impact of GBs on device performance from the myriad of other processes. Whilst in general there seems to be some evidence that a reduction in GBs, via an increase in grain size, may improve performance, it is by no means proof and there is still a lack of understanding on a device level. The improvement in performance observed could simply be related to improved chlorine and/or sulphur/oxygen incorporation at the GBs for these deposition conditions. Whilst this is still GB related it is not a fundamental comparison of the nature of the GBs and their limitation on performance.

## Conclusion

An overarching conclusion to be drawn from this review is that there remains a level of complexity to the characterisation of GBs in solar cells that is yet to be fully overcome. All the techniques employed to measure the behaviour have some form of limitation, typically not examining the cells under operating conditions and with the potential of being surface limited. As a result they offer somewhat contrasting results. CL measurements indicate enhanced recombination whilst scanning probe techniques and EBIC tend to imply improved collection. Analysis of device results as a function of grain size only implies the effect of GBs as it is complicated, and thus masked by secondary factors, such as variations in intermixing. Even more than other thin film PV platforms though the GB challenge in CdTe is particularly complex due to the requirement of post-growth treatments to achieve high efficiencies. The behaviour of grain boundaries is so intrinsically linked with the impact of oxygen, sulphur, copper and particularly chlorine, that as Gessert *et al* [158] note, "It is difficult to design experiments that de-couple the effects of O-, Cl-, and Cu-related point defects from each other, and from effects due to grain boundaries". Rather than characterising one simple factor, for functional CdTe solar cell GBs an interpenetrating arrangement of impacts are required to be assessed. What can be said with relative certainty is that GBs in *as-grown* (i.e. untreated) CdTe are certainly a limiting factor to performance. Almost all reports surveyed, irrespective of characterisation technique employed, are in agreement on this point. It further seems that the literature demonstrates to an extent that all of chlorine, oxygen, sulphur and copper play some role in modification of the GBs electrical behaviour but that chlorine is primarily the dominant force in this respect. Whilst sulphur certainly seems to reside at the GBs but there is little clear understanding of its exact role there whilst copper may or may not even be present there at all. In contrast there is a weight of evidence that chlorine passivates the grain boundaries and modifies the conduction barriers that exist there, something which oxygen may also play a role in but the evidence appears less clear cut. The impact of the boundary passivation is undoubtedly beneficial for

device performance but whether it simply lessens the negative impact of the GBs, as suggested by techniques such as CL, or whether it actually improves the collection efficiency to a level beyond the grains themselves, as suggested by EBIC and some of the scanning probe techniques, is still unclear. It is therefore not possible to make a judgment on whether GBs are in fact beneficial or not to device performance. More than this though there still seems to be no clear indication of whether the GB behaviour is linked to the apparent  $p$ -type doping limit and self-compensation effects for CdTe and how, if at all, this is linked to the lower than optimal  $V_{oc}$  values achievable. This is of particular relevance when considered that recent work on phosphor doped single crystal CdTe devices [7, 65] has demonstrated doping levels in excess of  $10^{17} \text{ cm}^{-3}$  and  $V_{oc}$  greater than 1V. To achieve similar  $V_{oc}$  levels in polycrystalline devices we need to answer the question of whether the lack of GBs, the lack of chlorine or a combination of both is responsible for this in these single crystal cells. The key to achieving this will be to better understand the GB physics of CdTe solar cells as they behave under standard operating conditions. Despite the large amount of excellent work that has been done in this area there still remains significant research to be undertaken to determine the true impact of GBs on CdTe solar cells.

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