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PLEASE CITE THE PUBLISHED VERSION

<https://doi.org/10.1109/pvsc45281.2020.9300881>

PUBLISHER

IEEE

VERSION

AM (Accepted Manuscript)

PUBLISHER STATEMENT

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Kornienko, Vladislav, Rachael Greenhalgh, Kerrie Morris, Ali Abbas, Thomas Fiducia, Ryan Maclachlan, Yau Tse, Michael Walls, and Jake Bowers. 2021. "Effects of Successive CdCl₂ Treatments on the Texture of Thin Film Cdte Solar Cells". Loughborough University. <https://hdl.handle.net/2134/13603019.v1>.

Effects of Successive CdCl₂ Treatments on the Texture of Thin Film CdTe Solar Cells

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Abstract — The CdCl₂ activation treatment is required for high efficiency CdTe solar cells. The treatment has many effects including increasing grain size and randomizing texture. Increasing grain size should result in higher efficiencies by minimizing grain boundary recombination. The use of metal-oxide layers to replace cadmium sulphide allows higher activation temperatures to be used resulting in larger grain sizes. However, use of these higher temperatures may affect the concentration of chlorine in the grain boundaries. Here we investigate the use of a first high temperature activation on closed space sublimated (CSS) Au/CdTe/TEC12D devices followed by a second optimized cadmium chloride treatment. We report on the effects on texture and grain size. Electron backscatter diffraction (EBSD) has been carried out using a Plasma Focused Ion Beam (PFIB) equipped with spin milling. Initial results indicate that the first higher temperature activation results in larger grains and a randomized texture.

Keywords—Cadmium Telluride, Solar cells, CdCl₂ treatment, EBSD, Texture, Grain size

I. INTRODUCTION

As-deposited thin film cadmium telluride (CdTe) solar cells have poor conversion efficiency and a cadmium chloride (CdCl₂) activation treatment is essential. The treatment increases grain size, passivates grain boundaries, increases charge carrier lifetimes and removes stacking faults [1]. Chlorine diffuses into the cell via the grain boundaries and there is also evidence that it enters the grain interiors and twin boundaries [2].

In the conventional CdS/CdTe architecture, intermixing occurs at the junction limiting the temperature of the activation treatment to avoid complete consumption of the CdS. Recent improvements have replaced the CdS with transparent metal oxides such as magnesium doped tin oxide (MZO)[3]. These limit intermixing and allow higher activation temperatures to be used. These should result in larger grain sizes, as well as improve the optical bandgap[3].

Previous work has shown that elevated temperatures without the presence of CdCl₂ can lead to the loss of chlorine from the cell and this is associated with a loss in performance[4]. In this paper, we have used TECTM12D supplied by NSG-Pilkington which has an intrinsic tin-oxide layer deposited on the Fluorine

doped tin oxide coated glass. We have investigated the use of a first activation with temperatures up to 480°C in the presence of CdCl₂ and the effect of a second CdCl₂ activation at the optimized temperature of 420°C. We have investigated the effect of these processes on grain size, chlorine distribution and cell performance. Previous studies have reported the increase of reverse saturation current density as well as increased series resistance when the CdCl₂ activation was above 450°C[5].

II. EXPERIMENTAL

CdTe was deposited on TECTM 12D glass by closed spaced sublimation (CSS) for the devices used in this investigation. The CSS temperature was 515°C for the substrate and 630°C at the source. A range of CdCl₂ treatment temperatures between 380°C to 480°C has been carried out for the first activation. After each primary CdCl₂ treatment, a secondary treatment has been carried out at 420°C for each device. The band alignment is unfavorable for the SnO₂/CdTe combination, but the tin oxide layer allows high temperatures to be used. Our focus is not on high cell efficiency but on the microstructure of the CdTe absorber.

We have used electron backscatter diffraction (EBSD) for characterization of texture and measurement of grain size. Surface preparation for EBSD was achieved by spin polishing using a G4 Xenon Plasma Focused Ion beam (PFIB) equipped with an Oxford Symmetry CMOS detector. The stage was tilted to -36° so the ion beam was parallel with the surface. The beam current was 60nA. The beam milled parallel with the sample surface with a beam width of 150µm to remove ~300nm thickness from the relatively rough top surface. The exact depth was not measured, but the same beam current and milling time was used for each device.

The sample platform was rotated by 10° after each milling step for 9 times to prevent a curtaining effect. This produced a smooth flat surface in the center. After the polishing steps, the sample was tilted to 70° and EBSD was carried out with a step size of 0.15µm. The inverse pole figures (IPFs) were produced for direct numerical value of the texture intensity in the growth direction (normal to the surface). The values used are multiples of uniform densities (mud) with a set 5° half width contouring.

The PFIB and the EBSD symmetry camera are state-of-the-art tools that allow rapid sample preparation and analysis. The ion polishing time was approximately 10 minutes with a 5-

minute EBSD scan for the 100x100 μ m usable area. Due to the EBSD detector being connected to the PFIB, the total machine time was only 45-60 minutes per each device, depending on the surface quality.

III. RESULTS

Fig. 1 and Fig. 2 shows IPF maps parallel to the growth direction of the CdTe layer. These include primary CdCl₂ temperatures ranging from 380°C to 480°C alongside the devices which were activated again with a second CdCl₂ treatment at 420°C. The grain boundaries have been underlined for clarity due to multiple grains of similar orientation appearing next to each other.

However, at 440°C with and without a second CdCl₂ treatment, the grain size noticeably increases with stronger (111) texture. The primary treated devices at 460°C and 480°C show a clear random texture with increased grain size. The second CdCl₂ treatment had little effect on the texture and grain size at these devices first activated at higher temperatures. The standard deviation also increases with grain size as shown in Table 1. Defects such as voids at the grain boundaries were mostly absent. The grain size increased from untreated at 1.25 μ m to the 3.83 μ m measured at 480°C. The EBSD pattern quality improved at higher activation temperatures indicating the removal of defects, although it is also influenced by the quality of sample preparation. Fig. 3 uses IPF relative intensity values to numerically compare texture changes in the devices. The peak intensity values of (111) decrease from approximately 4.70 at 380°C to 1.63 at 480°C. This implies that the device is more recrystallized at 480°C due to the randomised texture. Table 1 shows all the intensity values recorded.

Fig.1 IPF micrographs of CdTe that show the initial CdCl₂ treatments between 380°C and 480°C and an untreated device for comparison (100x100 μ m scan area).

Fig.2 IPF micrographs of CdTe that show the second CdCl₂ treatments carried out at 420°C as well as an untreated device (100x100 μ m scan area).

As the first activation temperature exceeds 420°C, the texture becomes weaker and the (111) intensity normal to the surface decreases as shown in Fig 1. This is presented numerically by the peak intensity of the IPF triangles shown in Fig. 3. The lower values represent weaker texture intensity. Values close to 1 represent a random texture whereas values much higher indicate a preferred orientation. This is apparent in the IPF in Fig. 1 and Fig.2. The second CdCl₂ treatment at 420°C also decreased the (111) intensity.

After each second CdCl₂ treatment, the grain size increases, but with smaller marginal increases at the higher temperatures. The texture is randomized at higher temperatures; the (101) and (001) appear to grow at the expense of (111) grains. The device activated at 420°C shows a clear and a significant change in the texture compared with those activated at lower temperatures.

Fig 3. IPF texture intensity triangles showing the multiples of uniform density (mud) values for CdCl₂ treated samples at 380°C(a), 440°C(b), 460°C and 480°C(d).

Table 1. Grain size and texture intensities of CdTe devices treated between 380 and 480°C. The 420°C temperature refers to the second CdCl₂ treatment applied.

CdCl ₂ temperatures (°C)	Grain size (μm)	Standard deviation (μm)	Minimum exp. Densities (mud)	Maximum Exp. densities (mud)
Untreated	1.25	0.23	0.35	3.60
380	1.32	0.56	0.25	4.65
380+420	1.51	0.63	0.31	4.71
400	1.29	0.50	0.23	4.70
400+420	1.70	0.76	0.27	4.21
420	1.80	0.93	0.82	1.31
420+420	1.84	0.76	0.72	1.39
440	1.80	0.84	0.35	4.08
440+420	2.02	0.97	0.47	3.15
460	2.65	1.37	0.57	2.44
460+420	2.71	1.45	0.62	1.72
480	3.83	2.03	0.63	1.63

IV. DISCUSSION

Observations have been reported previously where the intensity of the (111) peak decreases with increased CdCl₂ activation temperatures above 450°C using x-ray diffraction (XRD)[6]. However, in this study a gradual increase was visible above 420°C and increased markedly above 460°C. The second CdCl₂ treatment resulted in increased grain growth and randomization of the (111) texture due to incomplete recrystallisation at the lower first activation temperatures. At 460°C and above, the original texture is lost. Note that there is significant lattice strain needed to promote this recrystallisation[7]. This could explain why the grain size did not increase at 460°C with a second treatment at 420°C. Defects in the CdTe layer or other control factors could explain the randomised texture observed at 420°C which then returns to (111) orientation at 440°C.

At higher temperature, the presence of smaller grains of CdTe at the junction can be reduced to create a favourable columnar grain structure that fully extends from the back contact to the interface [8]. Cathodoluminescence (CL) studies have shown an increase in intensity with larger grain sizes up to a CdCl₂ at 420°C and decreasing the characteristic length with higher temperatures which is linked to carrier lifetimes [9]. Stacking faults removed during CdCl₂ treatment have been found to re-appear if the chlorine is removed from the grain boundaries during post annealing without the presence of chlorine [10]. Hence it is important to use transmission electron microscopy (TEM) with EDX mapping to determine if chlorine is present at 480°C with a supply CdCl₂ at the surface. If not, then the second activation treatment is necessary. It may be that the first activation at high temperatures produces large grains and the

second activation at 420°C re-introduces the chlorine and enhances cell efficiency. This exciting combination of EBSD and TEM/EDX studies will be presented in full in the final version of the paper.

Future work will involve using an improved cell architecture using magnesium-doped zinc oxide (MZO) and CdSeTe (CST) in the absorber. We will report on the relationship between HRT materials with CdSeTe/CdTe, the effects of high temperature activation on texture and the processes leading to higher cell efficiencies. The interfacial tensions for different device architectures will likely produce different textures during the CdCl₂ treatments. The CdCl₂ treatment is especially important with CST devices, as it causes the diffusion of the graded layer. This will also affect texture change[11].

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