Activation of Thin Film CdTe Solar Cells Using a Cadmium Bromide Treatment

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Abstract — **The activation of CdTe with a cadmium chloride annealing treatment is a vital step in the fabrication of high efficiency solar cells. Thin film MZO/CdTe cells have been activated using $CdBr_2$ instead of $CdCl_2$ with a lower activation process temperature. Using this method, $CdBr_2$ does activate the cell as revealed by J-V and EQE measurements. TEM and EDX elemental maps from device cross-sections confirm that bromine is present in the grain boundaries. TEM shows that the treatment removes stacking faults at 425 °C. $CdBr_2$ treatment resulted in a relatively modest conversion efficiency of 5.49% when treated at 375 °C. Nevertheless, the experiments shed further light on the mechanisms involved in the activation.**

Keywords — **CdTe, $CdBr_2$, activation, TEM, EQE, EDX**

I. Introduction

Cadmium telluride (CdTe) is an ideal photovoltaic material due to its bandgap of ~1.5 eV which is close to the maximum theoretical efficiency according to Shockley-Queisser, with a thin film of ~2 μm required to fully absorb the light in the solar spectrum [1].

An activation treatment involving $CdCl_2$ is required to improve the efficiency of CdTe solar cells. The $CdCl_2$ treatment has been observed to recrystallize the CdTe grains, remove planar defects such as stacking faults and decorate grain boundaries [2] , [3]. The CdTe grain boundaries act as recombination centres, and the chlorine passivates these, significantly improving the efficiency of the device [4].

Studies changing the toxic cadmium cation in the process to other chloride sources, including sodium, potassium, magnesium, and hydrogen [5] , [6] have shown that these can be almost as effective in activating CdTe as $CdCl_2$, and are much less toxic. However, little research has been performed on alternatives to the chlorine anion. The introduction of fluorine into the activation process via CdF_2 has been investigated [7], however due to the reactivity of fluorine and

toxicity of CdF_2 this is unsafe and unlikely to be scalable industrially.

Electrically, the chlorine has been theorized to make the grain boundaries less p-type than the grain bulk [8]. This improves carrier collection as grain boundaries may act as a segregated conduction pathway for electrons due to local electric fields [4]. However, the predominant effect of chlorine is passivation of dangling bonds at grain boundaries and removal of planar defects[3], [9].

In this study, the use of $CdBr_2$ during the activation treatment is investigated; and the structural rearrangement caused by $CdBr_2$ and its effect on conversion efficiency. We also report on a preliminary investigation of the effect of varying some processing conditions.

II. Experimental Details

The devices used in this study were produced on 3 mm thick 79 x 91 mm Fluorine doped Tin Oxide (FTO) coated soda lime glass substrates (NSG Pilkington, TEC 10). See Figure 1 for the cell architecture used. The Magnesium doped Zinc Oxide (MZO) buffer layer was deposited by Radio Frequency (RF) - magnetron sputtering [8] and the CdTe layer by close space sublimation [9]. The activation treatments were performed in a graphite box set up in a tube furnace as shown schematically in Figure 2. $CdBr_2$ material (99.9985 % metals basis, ultra-dry Alfa Aesar) was used in a graphite box. The temperature of the source was between 375 °C and 425 °C. This temperature range was chosen because the vapour pressure of $CdBr_2$ at 375 °C is approximately the same as the vapor pressure of $CdCl_2$ at 450 °C [10]. It has been observed that the chlorine in the chlorine doped grain boundaries is easily released above 450 °C [11]. It was assumed that, if $CdBr_2$ had a higher vapour pressure than
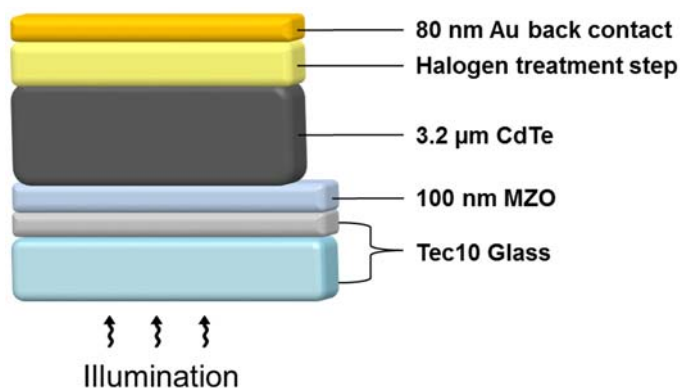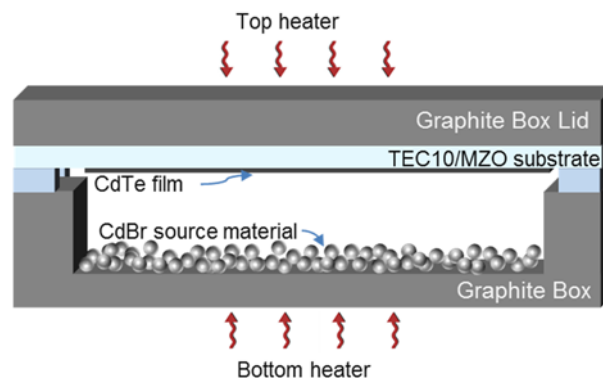

Fig. 1.   The MZO/CdTe Device Architecture

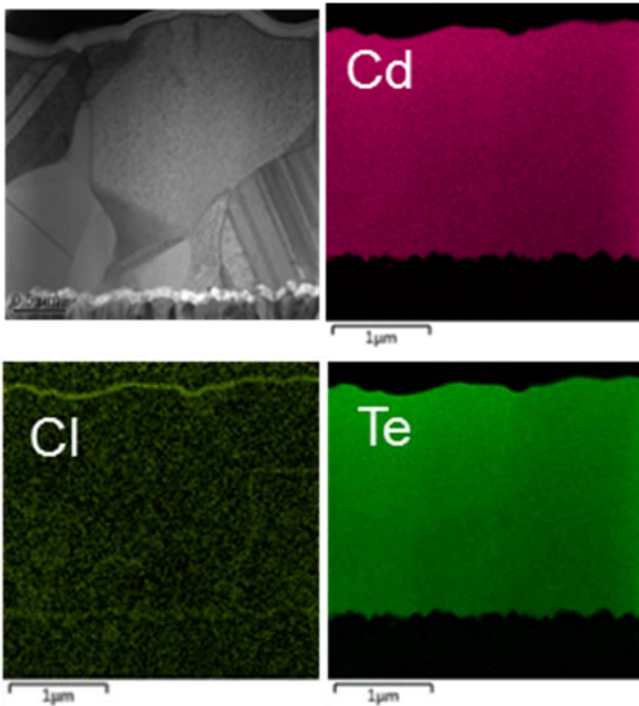Fig. 2.   Activation treatment set up with $CdBr_2$ in a vacuum tube furnace

Fig. 3. TEM images and EDX elemental maps of a CdCl₂ treated device

Fig. 4. EDX elemental map of CdBr₂ treated device

$CdCl_2$, the bromine in the bromine doped CdTe would be more easily released from the CdTe film at a lower temperature, therefore a lower temperature would be preferable.

The tube furnace was pumped down to approximately 100 mTorr. Nitrogen was used to flush the system, the pump and N_2 lines were closed, with the furnace maintained at a 200 Torr. The furnace was heated to 125 °C, pumped and flushed with nitrogen to degas the $CdBr_2$. It was then heated to 300 °C and held for 5 minutes to equilibrate. The temperature was then raised to the specified treatment temperature and dwelled at the specified time. The furnace was then left to cool at a constant pressure of 400 T and the samples removed at 50 °C.

80 nm of gold (wire, 99.999%, Testbourne) was evaporated with an in-house system to form the back electrode. A mask was used to give a contact area of 0.25 cm².

Specimens for Transmission Electron Microscopy (TEM) were prepared by Focused Ion Beam (FIB) milling. TEM was carried out using a FEI Technai F20, equipped with an Oxford Instruments X-max N8 TLE SDD for energy dispersive X-ray Spectroscopy (EDX). The J-V measurements were performed using an in-house solar simulator set up with a xenon arc lamp and AM1.5 filter. The external quantum efficiency (EQE) measurements were acquired with a Bentham PVE300 system. and performed at 0 V bias with an A.M.1.5 white light bias, with a spectral resolution of 5 nm.

III. RESULTS AND DISCUSSION

Fig. 4 shows the EDX maps obtained from the $CdBr_2$ treated cells. The bromine map shows segregation to the grain boundaries as has also been observed with chlorine (see Fig. 3) [3],[12], [13]. This indicates that Cl and Br behave similarly in the CdTe grain boundaries. The zinc and oxygen
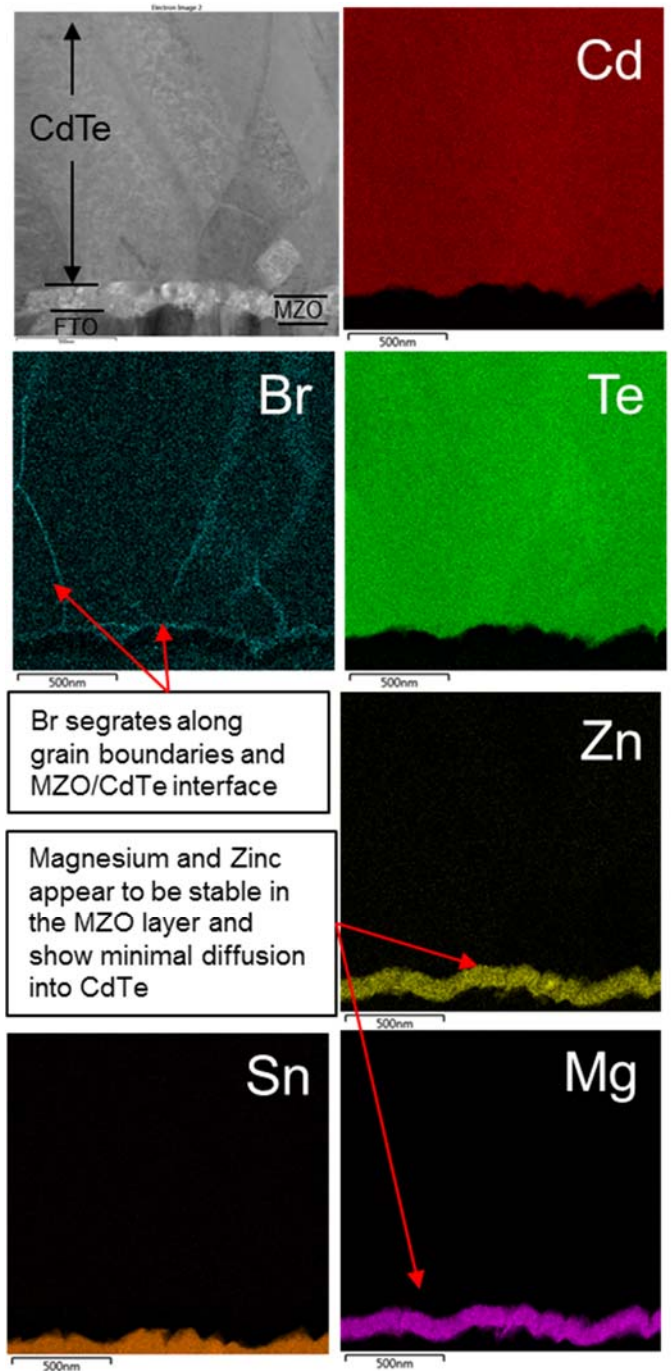
in the MZO appear to be stable following the $CdBr_2$ treatment, showing minimal diffusion into the CdTe.

The TEM image of the 425 °C $CdBr_2$ treated cells shown in Fig. 5 structurally resembles the appearance of a device which has been fully treated with $CdCl_2$. Full depth, 1 micron wide recrystallized grains are observed. These grains are free from stacking faults and twins are present which are also observed in $CdCl_2$ treated cells and are thought to be electrically benign [3],[14]. The untreated device shown in Fig. 5 has stacking faults in almost all of the grains, narrow grains, and smaller grains present near the MZO/CdTe interface; as observed previously in CdTe [3]. The TEM image of the 375 °C $CdBr_2$ treated cell shows twins, a reduced number of stacking faults, and many small grains at the interface, and larger grain sizes than the untreated grains. This
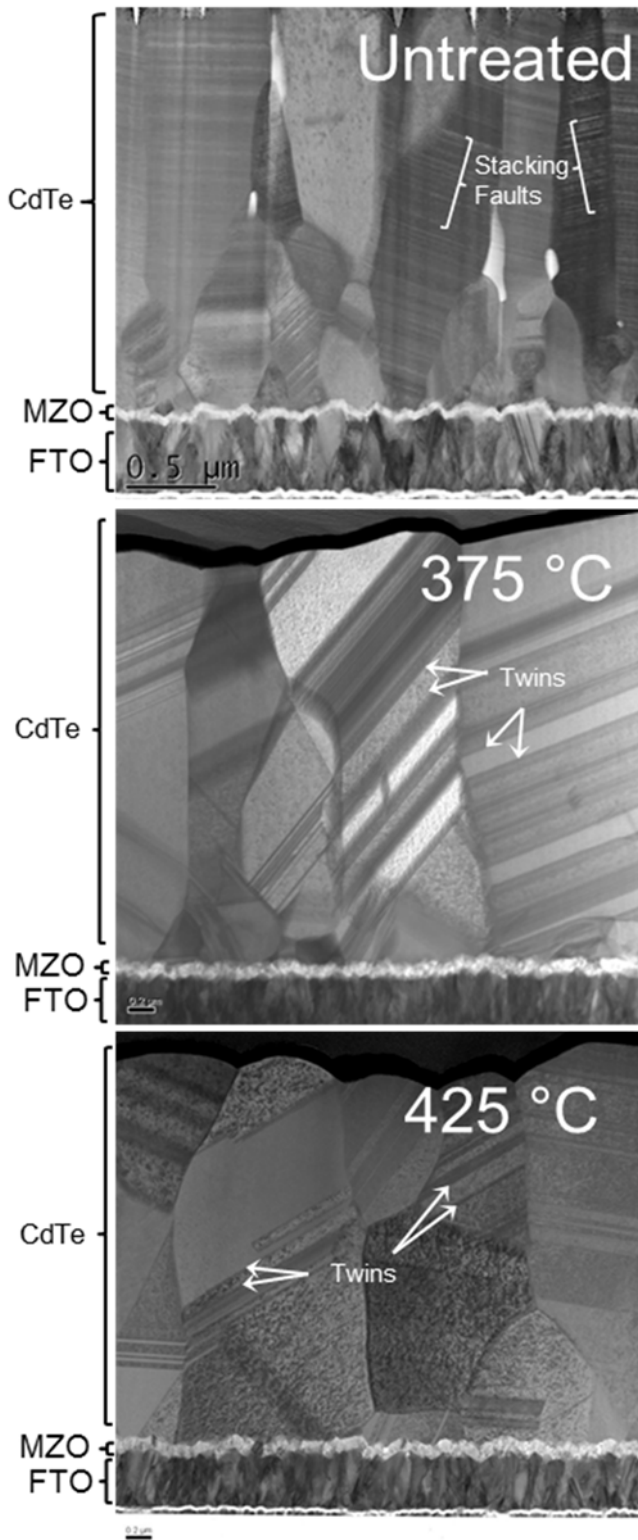
Fig. 5. Dark Field TEM cross-sections of CdTe untreated, treated at 375 °C with CdBr$_2$ for 15 minutes and treated at 425 °C for 15 minutes. The treated cells are free of voids.

indicates partial recrystallization as there is a reduction of defects in the CdBr$_2$ treated device when compared to as-deposited samples. These are preliminary results, and it is expected that the process will improve further with optimization.

The 375 °C CdBr$_2$ treated device in this work has an efficiency of 5.49% (Fig. 7) with just partial recrystallisation,
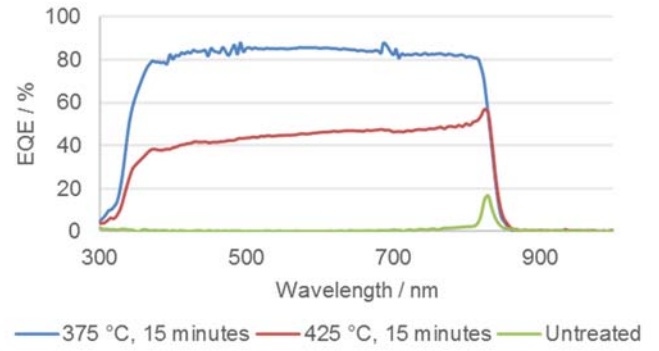

Fig. 6. EQE spectra of the untreated sample and samples treated at 375 °C or 425 °C for 15 minutes

TABLE I
CURRENT DENSITIES OF TREATED AND UNTREATED DEVICES
FROM EQE MEASUREMENTS

TREATMENT	CURRENT DENSITY
375 °C, 15 min	24.48 mA/cm^2
425 °C, 15 min	13.64 mA/cm^2
Untreated	0.39 mA/cm^2

which is greater than the efficiency for the process at 425 °C where a more pronounced structural improvement was observed. This indicates that the bromine may be electrically passivating the grain boundaries similar to chlorine, [3],[4],15]. However, further electrical characterization will be required to explain this observation. The EQE spectra shown in Fig. 6 comparing the treatment at 375 °C with the untreated cell shows a drastic increase in the EQE to 80% between wavelengths 375-816 nm. The untreated cell has a 0% EQE response between 375-715 nm, with a slight increase to 3.6% at 810 nm and a peak at 830 nm. The 375 °C treated device has an EQE response similar to CdCl$_2$ treated MZO/CdTe devices [12]. This is surprising given that it has only undergone a partial recrystallisation, and indicates that bromine is electrically active without the need for full microstructural rearrangement. The 425 °C treated cell which appears to be fully recrystallized has a much lower EQE response, so may be overtreated in terms of bromine in the boundaries and at the junction.

The J$_{sc}$, V$_{oc}$ and Fill Factor (FF) are lower for CdBr$_2$ in this study when compared with optimized CdCl$_2$ treated cells. As an example, an optimized CdCl$_2$ treated MZO/CdTe cell, with a Cu doped optimized back contact has J-V parameters of: J$_{sc}$ = 26.8 mA/cm^2, V$_{oc}$ = 863 mV and FF = 79.2% [16]. The 375 °C CdBr$_2$ treated MZO/CdTe device with an unoptimized gold back contact in this study showed a maximum current density of 24.48 mA/cm^2 from EQE data (See TABLE), a V$_{oc}$ of 570 mV and a FF of 47% from J-V data (Fig. 7). This is a significant improvement on the untreated device with an EQE current density of 0.39 mA/cm^2 and the V$_{oc}$ from J-V of 280 mV and efficiency of 0.07%. Further optimization of the activation process and device finishing should lead to improvements in these parameters. This is a promising start for further research into passivation with bromide compounds.
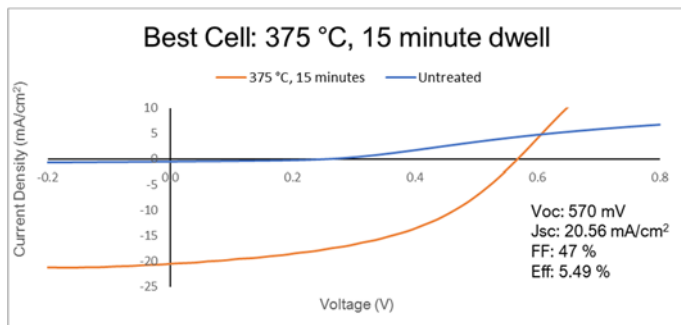
Fig. 7.   J-Vcurve of the 5.49 % efficient CdBr$_2$ device treated at 375 °C with a 15 minute dwell, with an untreated device for comparison

Conclusions

In conclusion, it has been shown that activation with CdBr$_2$ introduces the halogen into the grain boundaries of the MZO/CdTe device. The bromine annealing process causes recrystallization of the CdTe absorber layer and the removal of stacking faults. Efficiencies of 5.49% have been obtained. The experiments show that the passivation effects observed following a chlorine treatment can also be observed following treatment with bromine.   A preliminary study has shown that iodine also causes cell activation.

The focus for further work will be to observe if the full microstructural rearrangement caused by treatment with CdCl$_2$ can be achieved with CdBr$_2$. Following this, the authors aim to compare processing temperature and electrical effect of the bromine on the CdTe grain boundaries.

Acknowledgements

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