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

R.C. Greenhalgh¹, A. Abbas¹, A. H. Munshi², T. M. Shimpi², K.L. Barth², W. S. Sampath², J. W. Bowers¹ and J. M. Walls¹

¹ CREST, Loughborough University, Loughborough, United Kingdom, LE11 3TU
² NSF I/UCRC for Next Generation Photovoltaics, Colorado State University, Fort Collins, CO 80526 United States

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 CdBr₂ instead of CdCl₂ with a lower activation process temperature. Using this method, CdBr₂ 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. CdBr₂ 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, CdBr₂, 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 CdCl₂ is required to improve the efficiency of CdTe solar cells. The CdCl₂ 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 CdCl₂, and are much less toxic. However, little research has been performed on alternatives to the chloride anion. The introduction of fluorine into the activation process via CdF₂ has been investigated [7], however due to the reactivity of fluorine and toxicity of CdF₂ 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 CdBr₂ during the activation treatment is investigated; and the structural rearrangement caused by CdBr₂ 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. CdBr₂ 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 CdBr₂ at 375 °C is approximately the same as the vapor pressure of CdCl₂ 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 CdBr₂ had a higher vapour pressure than
CdCl₂, 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 N₂ 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 CdBr₂. 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 CdBr₂ 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 CdBr₂ treatment, showing minimal diffusion into the CdTe.

The TEM image of the 425 °C CdBr₂ treated cells shown in Fig. 5 structurally resembles the appearance of a device which has been fully treated with CdCl₂. 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 CdCl₂ 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 CdBr₂ 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
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, 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.
CONCLUSIONS

In conclusion, it has been shown that activation with CdBr₂ 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 CdCl₂ can be achieved with CdBr₂. Following this, the authors aim to compare processing temperature and electrical effect of the bromine on the CdTe grain boundaries.

ACKNOWLEDGEMENTS

The Loughborough University authors are grateful to UKERC for financial assistance through the EPSRC Supergen SuperSolar Hub and a studentship with the CDT in New and Sustainable Photovoltaics; and the CSU authors to the NSF I/UCRC for next generation photovoltaics and NSF AIR-RA.

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