

Annealing and Treatment Effects on Se Diffusion in CdTe Photovoltaics

Jacob F Leaver, Ken Durose, and Jonathan D Major

Stephenson Institute for Renewable Energy, University of Liverpool, Liverpool, L69 7ZF, UK

Abstract—The interdiffusion of CdTe and CdSe at the window layer interface to form alloyed $\text{CdSe}_x\text{Te}_{1-x}$ (CST) layers has been shown to improve the efficiency of CdTe photovoltaic devices, and there is evidence from the literature that Se passivates defects in these devices, particularly at grain boundaries. This work investigates the importance of the Cl treatment by comparing untreated, air-annealed and Cl treated CST devices to determine whether the Cl treatment is required for CST devices. We show that the Cl treatment increases Se diffusion and is still necessary for efficient CST devices, although it is not clear whether the efficiency gains are due to the effects of greater Se diffusion or the usual benefits of the Cl treatment on CdTe photovoltaics.

I. INTRODUCTION

Thin-film CdTe has become established as the most commercially successful alternative to silicon based solar cells, with a total photovoltaic market share of 4.2% in 2019 representing 76% of all thin-film production [1]. It has achieved a lower levelised cost of energy (LCOE) for utility-scale generation and a substantially shorter energy payback time than silicon [2], [3]. However, record efficiencies for CdTe devices are still lower than their mono- and multi-crystalline Si counterparts despite the higher theoretical maximum efficiency for CdTe [4], [5]. Recent improvements in CdTe device efficiencies have mostly focused on improving the short-circuit current density (J_{SC}), through measures to reduce parasitic absorption at 300 nm to 525 nm by thinning or replacing the ubiquitous CdS layer [4]–[7]. As such, the open-circuit voltages (V_{OC}) of the best devices still lag far behind what might be expected from the CdTe bandgap and what has been demonstrated for single crystal devices [8].

In order to achieve reasonable efficiencies, CdTe devices must undergo a “chlorine treatment”. This typically occurs post CdTe deposition and prior to the back-contact processes, and involves heating the device either in air or an inert atmosphere, in the presence of a chloride salt. CdCl_2 is perhaps the most popular choice of chloride, but MgCl_2 has been shown to produce equivalent performance [9]. The exact mechanism through which the chloride treatment improves device efficiency is still not perfectly understood, but it is believed the treatment in part assists recrystallisation of the CdTe and that accumulation of Cl at the grain boundaries passivates defects there. [10]

One of the more recent developments in CdTe photovoltaics has been the inclusion of an alloyed $\text{CdSe}_x\text{Te}_{1-x}$ (CST) layer at the window layer interface, commonly achieved by depositing a thin layer of CdSe before the CdTe and allowing the two to interdiffuse during subsequent device processing

[11]. Due to band-bowing effects the bandgap for the alloyed material is lower than CdTe, resulting in absorption over a wider range of wavelengths and hence an increase in the J_{SC} . This increased current collection from CST devices compared to CdTe-only devices was demonstrated by Paudel *et al.* in 2014 [6], but reduced fill-factor (FF) and V_{OC} meant the efficiencies of the CST devices were still lower. Since then, several groups have demonstrated CST devices with higher efficiencies than their CdTe-only analogues [12]–[14].

As the upper limit on the V_{OC} is set by the built-in voltage, which in turn is derived from the bandgap of the absorber at the pn-junction interface, it is expected that CST devices would have reduced voltages compared to CdTe-only devices. However, observed drops in V_{OC} have not been as severe as predicted from the bandgap alone. Time-resolved photoluminescence (TRPL) studies have shown improved carrier lifetimes for CST compared to CdTe [12], [15], [16], suggesting the inclusion of Se also contributes to defect passivation. Spatially resolved secondary ion mass spectrometry and cathodoluminescence measurements have also suggested Se accumulation and passivation at the grain boundaries [17]. Reduced recombination offsets the V_{OC} losses from the lower bandgap, resulting in devices where the V_{OC} expressed as a percentage of the bandgap is higher for CST than CdTe-only absorbers [18].

So there is evidence that CdSe alloying passivates defects in CdTe, particularly at the grain boundaries, but this is also thought to be the mechanism through which the chloride treatment improves device performance. This work aims to determine whether the chloride treatment is still necessary for CST devices, or whether the inclusion of Se is sufficient to effectively passivate the grain boundaries.

II. EXPERIMENTAL

Figure 1 shows the device structure used in this work. 100 nm CdSe was deposited by radio-frequency sputtering on NSG Ltd. TECTMC15M soda lime glass (fluorine-doped SnO_2 (FTO) coated glass with a 100 nm un-doped SnO_2 top-coat). CdTe was then deposited by close-space sublimation (CSS) to a thickness of 3 μm to 5 μm at 5 Torr with a source temperature of 600°C. The samples were then either air-annealed, Cl treated or given no post-deposition treatment. 50 nm Au was evaporated through a mask to form an active contact area of 0.24 cm^2 .

Air-annealed samples were heated in air at 430°C for 90 min in a box furnace then removed to cool on the benchtop.

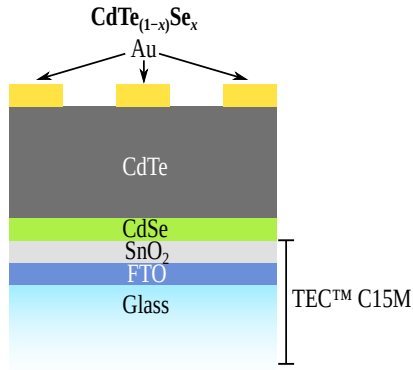


Fig. 1. Schematic of the device structure used in this work.

Cl treated samples were spray-coated with 1 mol dm^{-3} aqueous MgCl_2 solution and heated in air at 430°C for 90 min in a tube furnace, then removed to cool on the benchtop. 430°C was selected as the treatment temperature as previous comparisons between Cl treatments at 410°C , 430°C and 450°C showed the 430°C Cl treatment to result in the highest efficiency for devices with this structure.

Current-voltage measurements were taken with a TS Space Systems solar simulator under an AM1.5 spectrum at 1000 W m^{-2} . External quantum efficiency (EQE) measurements were taken with a Bentham PVE 300 system. The long wavelength onset of the EQE response corresponds to the bandgap of the absorber and was used to assess the degree of interdiffusion in the $\text{CdSe}_x\text{Te}_{1-x}$.

Scanning electron microscopy (SEM) was performed with a JEOL JSM 7001F SEM system. X-ray diffraction (XRD) measurements were taken with a Rigaku Smartlab®X-ray diffractometer.

III. RESULTS

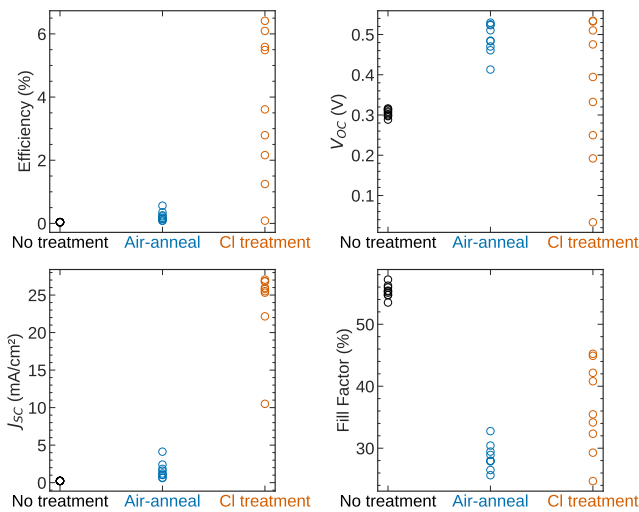


Fig. 2. Performance parameters calculated from current-voltage measurements for each treatment type.

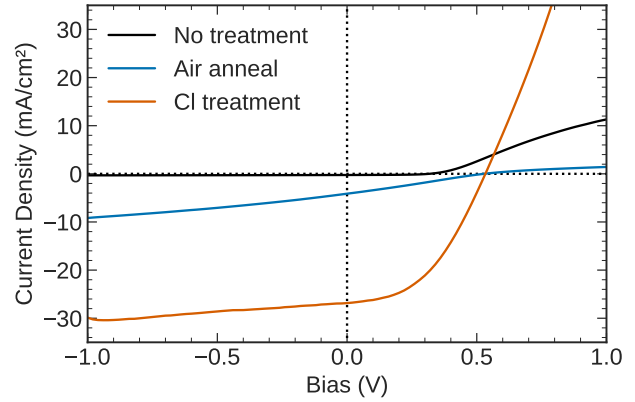


Fig. 3. Current density-voltage curves for the highest efficiency devices for each treatment type.

Figure 2 shows the performance parameters calculated from the current-voltage measurements of nine contacts per post-deposition treatment, with the current density-voltage curves of the highest efficiency device for each treatment shown in Figure 3. Both air-annealing and Cl treatment gave similar improvements in V_{OC} compared to un-treated devices, which contrasts with previous work on air annealing of CdTe-only devices that found no significant V_{OC} increase for air annealing [19]. However, current collection was still poor for air-annealed devices and they were found to have high series resistances. Only the Cl treatment gave reasonable device efficiencies.

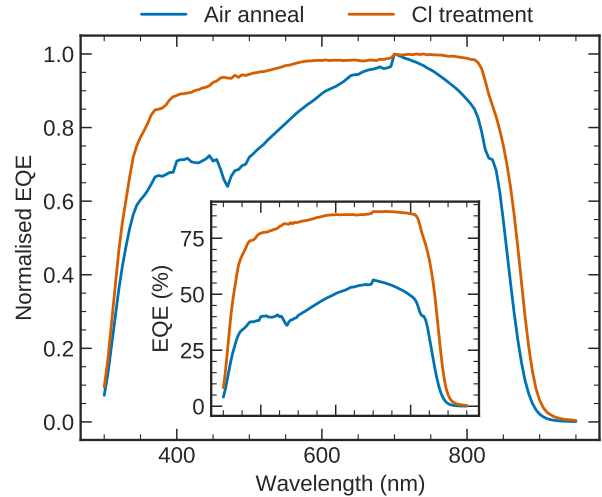


Fig. 4. Normalised EQE results for the highest efficiency devices from the Cl treated and air annealed samples (non-normalised results in inset).

The EQE results for the highest-efficiency air-annealed and Cl treated devices are shown in Figure 4. The un-treated devices did not generate enough photocurrent to be measured. The slight discontinuity in the spectra at 700 nm was due to the

lamp change at this wavelength. As expected from the current-voltage measurements, the EQE for the air-annealed device was significantly lower than for the Cl treated device, with a more substantial drop at roughly 475 nm that was reproduced upon repeat measurements and for other devices from the same sample set. Given that this drop occurs at an energy which does not correspond to any of the device layers, the origin of this discontinuity in the EQE spectrum is unclear. From the normalised spectra we can see that the absorption onset for the Cl treated device was red-shifted compared to the air annealed device, which would suggest an increase in Se diffusion.

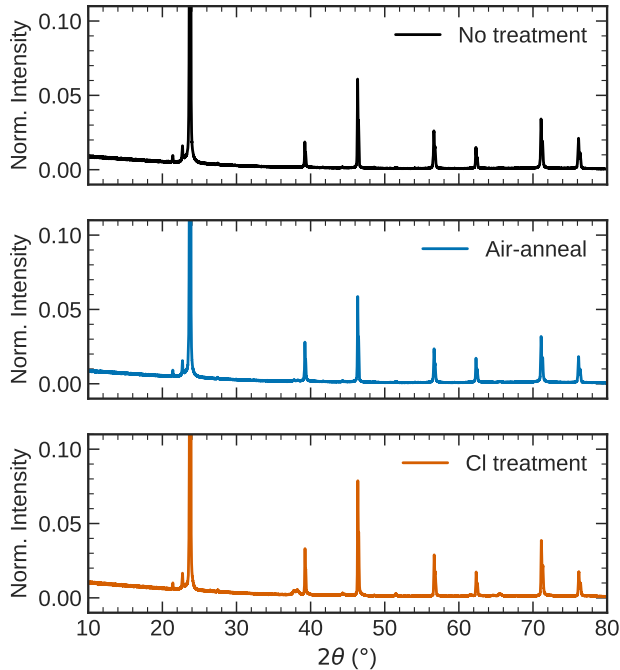


Fig. 5. X-ray diffraction patterns measured for each treatment type, normalised to the intensity of the (111) peak.

X-ray diffraction patterns of the devices measured in this work are shown in Figure 5, normalised to the (111) peak. All the samples show preferred (111) orientation, with much greater intensity for the (111) peak than any others. The Cl treated sample shows slightly increased intensity for the other peaks than the un-treated or air annealed samples, indicating more recrystallisation has occurred, but this effect is very minor.

Figure 6 shows the SEM images taken of the back surfaces of the devices in this study. There appears to be no significant change in the grain sizes between the un-treated and air annealed devices. The more significant change is the formation of voids in the air annealed device, which could provide shunting pathways if they extend all the way through the absorber layer. The Cl treatment has had a greater impact on

recrystallisation, with larger grain sizes and a clear difference in the structure of the grains compared to no treatment and air annealing, although some voids can also be seen. However, conclusions drawn from images of the back surface may not be reliable when considering Se diffusion, as the recrystallisation may be greater near the CdSe/CdTe interface where the as-deposited CdTe grain size is likely to be smaller.

IV. DISCUSSION

The results from XRD and SEM in Figures 5 and 6 show limited additional recrystallisation for the Cl treatment over no treatment and air annealing. This coupled with the increase in Se diffusion observed for the Cl treatment from the EQE in Figure 4 could suggest that this higher recrystallisation allows Se to diffuse further into the bulk material and penetrate the grain interiors. However, since both Se and Cl are known to segregate to the grain boundaries it is also possible that they compete for occupation of grain boundary sites and that this could result in greater Se diffusion to the grain interiors.

It is unfortunate that the un-treated devices were not photoactive enough for measurements of their EQE, as this makes it hard to ascertain the extent of Se diffusion due to air annealing. The ~ 1.5 eV direct bandgap of CdTe [20] would be expected to produce an absorption onset at around 830 nm, whereas the air-annealed device has an onset (taken as the point at which the normalised EQE is equal to 0.5) close to 850 nm, possibly indicating a small bandgap shift and some degree of Se diffusion. However, some or all of this diffusion may be due to conditions during the CdTe deposition or other steps in the device fabrication. Whilst one would expect air annealing to result in more Se diffusion than no treatment, we do not have convincing evidence to assert this.

We propose that the shape of the EQE curve for the air annealed device could be due to parasitic absorption by an interfacial layer of un-consumed CdSe. Taking the bandgap of CdSe as 1.74 eV [20], we would predict an absorption onset at approximately 710 nm, which corresponds to the beginning of a decrease in the EQE. At low wavelength the penetration depth of the light is very small and it is possible that the bump in EQE at low wavelength is caused by photogeneration close enough to the window layer that the carriers can be extracted before they have the chance to recombine.

From Figures 2 and 3 it is clear that the Cl treatment is needed for reasonable device efficiencies, as is the case for CdTe devices without Se alloying. Whilst the Cl treatment has been found to result in increased Se diffusion, it is not clear whether the improvement in device performance is a result of this increased Se diffusion or a direct consequence of the Cl treatment, or a combination of both effects. A small increase in the J_{SC} would be expected from the shift in EQE onset, but the improvements in the fill factor and V_{OC} and the increase in the EQE across the spectrum are harder to explain. They could be due to recrystallisation and increased grain size, passivation of the grain boundaries by Cl and/or Se, Se passivation of defects in the bulk or removal of a defect-laden interface caused by unconsumed CdSe. The limited amount

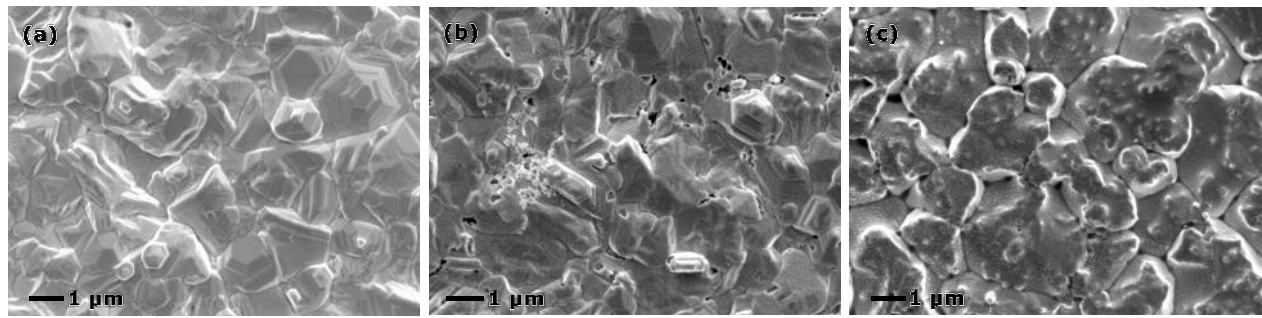


Fig. 6. SEM images of the un-contacted back surface of devices with (a) no treatment, (b) air anneal and (c) Cl treatment.

of additional recrystallisation observed for the Cl treatment from XRD and SEM would suggest this has a limited role in the improvement of the device performance, so it seems more likely to be passivation or the removal of a parasitic interface that is driving the improvement in devices. If Cl and Se both have defect passivating roles in the device the current results give us no way of distinguishing between the two. The improvement in the V_{OC} observed for air annealing over no treatment could suggest some defect passivation by Se, but this alone is not sufficient evidence as there are other factors that affect the V_{OC} . Both air annealed and Cl treated devices were found to have lower shunt resistances than un-treated devices, supporting the prediction of shunt pathways from the SEM images in Figure 6 and potentially explaining the drop in fill factor for the treated devices.

V. CONCLUSION

In conclusion, we have found that the Cl treatment is still a necessary step in device processing for Se-alloyed CdTe photovoltaics, and that it increases the Se diffusion in these devices. It is unclear whether the Cl treatment is needed due to grain boundary passivation by the Cl or increased Se diffusion resulting in defect passivation by Se, although it seems likely that both effects play a role. It is possible that longer and/or hotter annealing without Cl would achieve similar levels of Se diffusion to the Cl treatment, but this would probably need to be done in an oxygen-free atmosphere to prevent excessive oxide formation and would raise the cost and energy required for device production.

Whilst the results presented in this work allow us to gain an understanding of Se diffusion at an aggregate, device-scale level, the distribution of Se within the device, both from front to back contact and between grain boundary and grain interior, is still unknown. We aim to use techniques such as secondary ion mass spectrometry and cross-sectional energy-dispersive X-ray spectroscopy to address this gap in our understanding of the Se diffusion process.

ACKNOWLEDGMENT

This work has been funded by the EPSRC Centre for Doctoral Training in New and Sustainable Photovoltaics, EP/L01551X/1. The authors would like to thank the SEM SRF

Albert Crewe Centre for Electron Microscopy at the University of Liverpool for their support with this research.

REFERENCES

- [1] Fraunhofer ISE, *Photovoltaics Report*, 2020.
- [2] T. E. K. Zidane, M. R. B. Adzman, M. F. N. Tajuddin, S. Mat Zali, and A. Durusu, "Optimal configuration of photovoltaic power plant using grey wolf optimizer: A comparative analysis considering CdTe and c-Si modules," *Solar Energy*, vol. 188, pp. 247–257, 2019.
- [3] F. Liu and J. C. J. M. van den Bergh, "Differences in CO₂ emissions of solar PV production among technologies and regions: Applications to China, EU and USA," *Energy Policy*, vol. 138, p. 111234, 2020.
- [4] M. A. Green, E. D. Dunlop, J. Hohl-Ebinger, M. Yoshita, N. Kopidakis, and A. W. Y. Ho-Baillie, "Solar cell efficiency tables (version 55)," *Progress in Photovoltaics*, vol. 28, no. 1, pp. 3–15, 2019.
- [5] R. M. Geisthardt, M. Topič, and J. R. Sites, "Status and potential of CdTe solar-cell efficiency," *IEEE Journal of Photovoltaics*, vol. 5, no. 4, pp. 1217–1221, 2015.
- [6] N. R. Paudel and Y. Yanfa, "Enhancing the photo-currents of CdTe thin-film solar cells in both short and long wavelength regions," *Applied Physics Letters*, vol. 105, no. 18, p. 183510, 2014.
- [7] J. Britt and C. Ferekides, "Thin-film CdS/CdTe solar cell with 15.8% efficiency," *Applied Physics Letters*, vol. 62, no. 22, pp. 2851–2852, 1993.
- [8] J. M. Burst, J. N. Duenow, D. S. Albin, E. Colegrove, M. O. Reese, J. A. Aguiar, C.-S. Jiang, M. K. Patel, M. M. Al-Jassim, D. Kuciauskas, S. Swain, T. Ablekim, K. G. Lynn, and W. K. Metzger, "CdTe solar cells with open-circuit voltage breaking the 1 V barrier," *Nature Energy*, vol. 1, no. 3, p. 16015, 2016.
- [9] J. D. Major, R. E. Treharne, L. J. Phillips, and K. Durose, "A low-cost non-toxic post-growth activation step for CdTe solar cells," *Nature*, vol. 511, pp. 334–337, 2014.
- [10] J.-H. Yang, W.-J. Yin, J.-S. Park, W. Metzger, and S.-H. Wei, "First-principles study of Cu and Cl in polycrystalline CdTe," *Journal of Applied Physics*, vol. 119, no. 4, p. 045104, 2016.
- [11] T. Baines, G. Zoppi, L. Bowen, T. P. Shalvey, S. Mariotti, K. Durose, and J. D. Major, "Incorporation of CdSe layers into CdTe thin film solar cells," *Solar Energy Materials and Solar Cells*, vol. 180, pp. 196–204, 2018.
- [12] X. Zheng, D. Kuciauskas, J. Moseley, E. Colegrove, D. S. Albin, H. Moutinho, J. N. Duenow, T. Ablekim, S. P. Harvey, A. Ferguson, and W. K. Metzger, "Recombination and bandgap engineering in Cd-_xSeTe/CdTe solar cells," *APL Materials*, vol. 7, no. 7, p. 071112, 2019.
- [13] M. Lingg, A. Spescha, S. G. Haass, R. Carron, S. Buecheler, and A. N. Tiwari, "Structural and electronic properties of CdTe_{1-x}Se_x films and their application in solar cells," *Science and Technology of Advanced Materials*, vol. 19, no. 1, pp. 683–692, 2018.
- [14] D. E. Swanson, J. R. Sites, and W. S. Sampath, "Co-sublimation of CdSe_xTe_{1-x} layers for CdTe solar cells," *Solar Energy Materials & Solar Cells*, vol. 159, pp. 389–394, 2017.
- [15] D. Kuciauskas, J. Moseley, P. Šćajev, and D. Albin, "Radiative efficiency and charge-carrier lifetimes and diffusion length in polycrystalline Cd-_xSeTe heterostructures," *Physica Status Solidi RRL*, vol. 14, p. 1900606, 2020.

- [16] J. M. Kephart, A. Kindvall, D. Williams, D. Kuciauskas, P. Dippo, A. Munshi, and W. S. Sampath, "Sputter-deposited oxides for interface passivation of cdte photovoltaics," *IEEE Journal of Photovoltaics*, vol. 8, no. 2, pp. 587–593, 2018.
- [17] T. A. M. Fiducia, B. G. Mendis, K. Li, C. R. M. Grovenor, A. H. Munshi, K. Barth, W. S. Sampath, L. D. Wright, A. Abbas, J. W. Bowers, and J. M. Walls, "Understanding the role of selenium in defect passivation for highly efficient selenium-alloyed cadmium telluride solar cells," *Nature Energy*, vol. 4, no. 6, pp. 504–511, 2019.
- [18] A. H. Munshi, J. Kephart, A. Abbas, J. Raguse, J.-N. Beaudry, K. Barth, J. Sites, J. Walls, and W. Sampath, "Polycrystalline CdSeTe/CdTe absorber cells with 28 mA/cm² short-circuit current," *IEEE Journal of Photovoltaics*, vol. 8, no. 1, pp. 310–314, 2018.
- [19] J. D. Major, M. Al Turkestani, L. Bowen, M. Brossard, C. Li, P. Lagoudakis, S. J. Pennycook, L. J. Phillips, R. E. Treharne, and K. Durose, "In-depth analysis of chloride treatments for thin-film CdTe solar cells," *Nature Communications*, vol. 7, p. 13231, 2016.
- [20] S. Adachi, *Handbook on Physical Properties of Semiconductors: Volume 3: II–VI Compound Semiconductors*. Boston, MA: Springer US, 2004.