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Post deposition annealing on $\text{Cu}_2\text{ZnSnS}_4$ solar cells and the effect of Cu-Zn disorder at high temperatures

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Abstract — Post deposition annealing is a frequently used approach in CZTS(Se) research community to boost the efficiency of the cells. In this study, we investigate the influence of post deposition annealing in air on CZTS devices performance, produced by pulsed laser deposition. There are competing beneficial and detrimental effects depending on the temperature. We suggest that Cu-Zn ordering at 150°C and diffusion of Cd into CZTS from 250°C to higher temperature could be the main beneficial effects that increase the efficiency. A record efficiency for pulsed laser deposition of 5.4% was obtained at 150°C and 15 min post deposition annealing.

I. INTRODUCTION

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS) is a promising p-type solar cell absorber which consists of earth abundant and non-toxic elements. It was proposed as a replacement for other thin film solar materials, such as CIGS and CdTe, with efficiency exceeding 22%, but relying on scarce and toxic elements [1]. However, the CZTS performance is only 11% [2]. The main parameter that is limiting the efficiency is the V_{OC} deficit. There are several suggestions for the V_{OC} deficit. Cu-Zn disorder is one of the candidates that creates charged defects caused by position swapping between Cu and Zn due to their similar radii[3]. Non-optimal band alignment at CdS and CZTS interface is also another possible candidate.

Post deposition annealing (PDA) has been reported to increase all device parameters of CZTS solar cells, i.e., fill factor (FF), V_{OC} and short-circuit current (J_{SC}). PDA in a temperature range varying from 270°C to 330°C has led to a solar conversion efficiency of 11%, which is the highest reported value up to date [2][4]. PDA studies in wide range of temperature have been reported for CZTSe. However, a detailed study of PDA as a function of temperature in CZTS has not been reported yet. Elemental interdiffusion of Cd into CZTS and Cu/Zn into CdS is believed to dominate at high temperature, and can result in a better band alignment at the newly formed interface, and thus a higher solar cell efficiency[2]. However, the elemental interdiffusion at the interface is not the only effect, and there are other possible interrelated effects. One of them could be disorder in the absorber layer. CZTS is fully Cu-Zn disordered above the

critical temperature $T_{\text{C}}=260^\circ\text{C}$. Nonetheless, if CZTS is annealed below 260°C it starts to get more Cu-Zn ordered. The effective temperature for reordering is determined to be 150°C, and 24 hours were required to reach significant reordering[3].

In this work, we perform a systematic study on the effect of PDA on a CZTS cell performance as a function of temperature. We observed an efficiency increase in two different regimes around 150°C and 300°C, correlating with the highest V_{OC} and the highest J_{SC} respectively. At the higher temperature regime of 250°C to 300°C, the performance is likely to be dominated by interdiffusion of elements and Cu-Zn disorder. At the lower temperature regime around 150°C the Cu-Zn ordering might be the most relevant effect. With the aim to mitigate the Cu-Zn disorder effect at high temperatures, a long time re-annealing at 150°C up to 2400 min has also been performed. Raman spectroscopy, PL, and optoelectronic parameters from J-V analyses from full solar cells are discussed in the results.

II. EXPERIMENTAL

CZTS absorber layers were produced by sulfurization of oxide precursors deposited at room temperature by pulsed laser deposition. 2.5x2.5 cm² Mo/soda lime glass (SLG) were used as substrates. Oxide precursor films were deposited by pulsed laser deposition (PLD) using a compound oxide target and a 248 nm KrF excimer laser under vacuum pressure $<5 \times 10^{-6}$ mbar. The multicomponent oxide target (Haldor Topsoe A/S) consists of CuO, ZnO and SnO in a non-stoichiometric ratio of Cu/Sn=1.69, Cu/(Zn+Sn)=0.75 and Zn/Sn=1.24. The precursors were annealed at 575°C for 50 min in a quartz furnace in nitrogen at 250 mbar. The samples were placed in a graphite box with 120 mg of sulfur.

Solar cells were completed by the following steps: i) etching of the absorbers in $(\text{NH}_4)_2\text{S}$ solution at room temperature for 5 minutes; ii) CdS buffer layer deposition (60 nm) by chemical bath deposition, using a CdSO_4 precursor; iii) Transparent top layers of i-ZnO (80 nm) and ZnO:Al (400 nm), deposited by radio-frequency (RF) magnetron sputtering. Finally, $3 \times 3 \text{ mm}^2$

solar cells were mechanically scribed. Neither antireflective coatings nor metallic grids were used.

We performed PDA on a single full cell at temperatures starting from 150°C for 15 min and quenched it to measure IV parameters. The temperature was increased by 25°C after each IV measurement. After reaching 300°C, the cell was re-annealed at 150°C for 15 (0.25), 180 (3), 1200 (20) and 2400 (40) minutes (hours) to decrease the Cu-Zn disorder. All PDA experiments were performed in air.

Near-resonance Raman and photoluminescence (PL) spectra were measured with Renishaw inVia system at room temperature. The laser wavelength and spot size are 785 nm and 5 μm , respectively.

Device characteristics of solar cells were measured using Newport Sol2A Class ABA steady state solar simulator under standard test conditions, calibrated using a Si reference cell.

III. RESULTS

The main Raman modes of CZTS are apparent in each PDA in Fig. 1 at peak positions at 288, 302, 339, 367 and 376 cm^{-1} . Paris et al. showed that normalized Raman modes peak intensity ratio of $Q' = I_{339}/(I_{367} + I_{376})$ have a strong correlation with Cu-Zn disorder by comparing with solid state NMR[5]. As PDA temperature increases, Q' decreases and Cu-Zn disorder increases. At 300°C the Q' reaches the lowest value of 0.68. When re-annealing time at 150°C increases Cu-Zn disorder decreases. However, to reach initial ordered state with high Q' the CZTS cell needs more time.

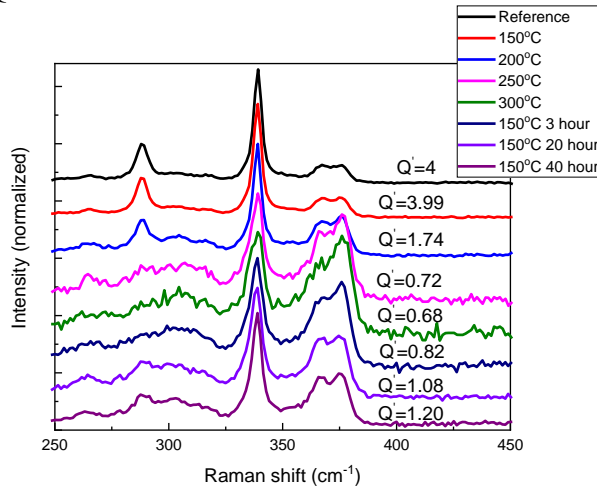


Fig. 1. Normalized Raman spectra of a CZTS solar cell after each PDA. The excitation wavelength is 785 nm.

PL spectra of the CZTS solar cell after each PDA treatment are shown in Fig. 2. In the high energy side, the Raman peaks of CZTS are visible, due to the near resonant condition using 785 nm laser. All PL spectra have been fitted using single Gaussian function to extract its center and FWHM (Table 1). Although there might be several peaks overlapping in a single

PL spectra the fitted Gaussian curve can be used to estimate the Cu-Zn disorder, which also connects to potential fluctuation at the bandgap structure[3]. PL peak position changes from 1.40 eV to 1.31 eV with increasing temperature from room temperature to 300°C, resulting in a redshift. However, the FWHM decreases as temperature increases. In principle, if the CZTS absorber was fully ordered, PL peak should reach the bandgap value of 1.5 eV.

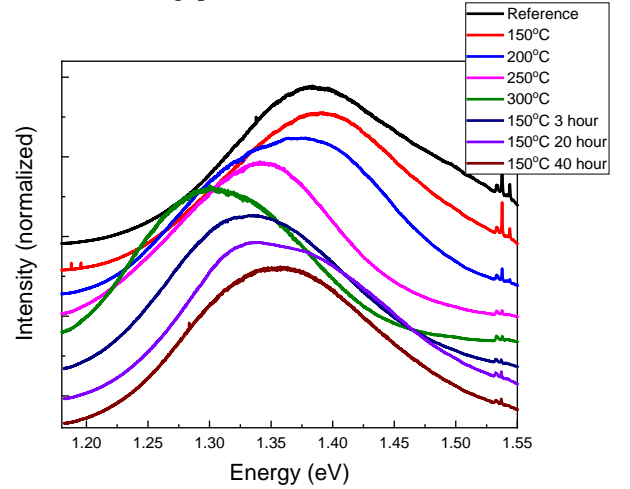


Fig. 2. Normalized PL spectra after each PDA on a CZTS solar cell

Temperature (°C)	Time (min)	PL peak (eV)	FWHM (eV)
Ref.	0	1.40	0.195
150	15	1.39	0.187
200	15	1.37	0.183
250	15	1.34	0.155
300	15	1.31	0.152
150	180	1.34	0.164
150	1200	1.36	0.188
150	2400	1.36	0.176

Table 1. Post deposition annealing (PDA) conditions and photoluminescence peak position and FWHM from single Gaussian fitting.

Fig. 3 shows the J-V parameters of different post annealing conditions of the same CZTS solar cell. The short-circuit current, J_{SC} is nearly constant in the low-temperature annealing 150 to 225°C range and shows a rapid increase from 250°C. The V_{OC} decreases with increasing annealing temperature, except for the dip around 200°C. The decrease in the V_{OC} can be associated with the Cu-Zn disorder, as indicated by the Raman and PL data. The subsequent increase around 250°C could be attributed to the Cd and Cu-Zn interdiffusion between CdS/CZTS interface which reduces disorder and promotes better band alignment [2].

The efficiency change as a function of annealing temperature shows two distinct regimes. Post annealing at a relatively low temperature of around 150°C results in a significant improvement of the efficiency as compared to the reference cell. This enhancement could be mostly attributed to an increase in the V_{OC} due to Cu-Zn ordering. However, no

significant change in the Raman spectra (Fig.1) between the reference and after 150°C PDA can be observed. In the case of PL, a slight 0.01 eV shift and FWHM decrease from 0.195 to 0.187 eV can be observed. The reason for this significant efficiency increase is not yet completely understood and needs to be further studied.

The V_{OC} decrease with increasing temperature up to 200°C could be explained by the absorber layer becoming more disordered at higher temperatures. Afterwards, V_{OC} increases again above 225°C. In contrast with this observation, Pilvet et al. showed that PL position and V_{OC} correlate with each other without any dip at 200°C in the CZTS monograins without CdS [4]. However, in our study a full cell was investigated. Therefore, Cd from CdS and Zn from CZTS layers diffuse to each layers. Due to the different atomic size of Cd compared to Cu and Zn, Cd diffusion into CZTS absorbers increases order in the CZTS films. J_{SC} increases further as temperature keeps increasing. From 300°C, V_{OC} starts to significantly drop again, which might indicate that ordering effects induced by Cd diffusion into CZTS no longer dominate. It should be noted that 300°C is higher than the critical temperature $T_C=260^\circ\text{C}$ that induces fully disordered CZTS [3].

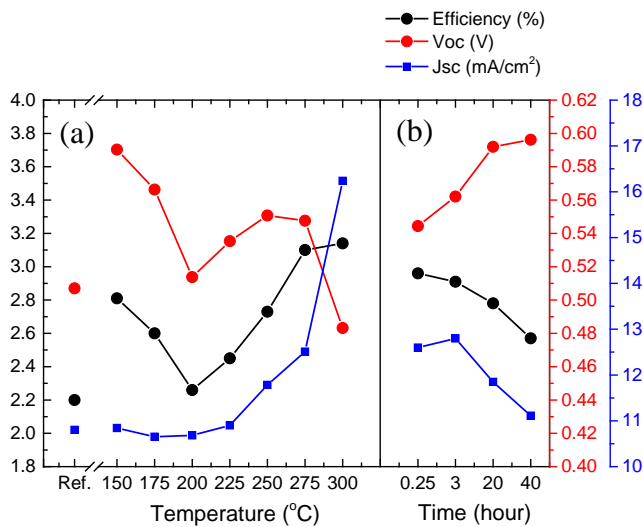


Fig. 3. JV parameters of CZTS solar cell with different PDA conditions: (a) temperature variations for 15 min and (b) 150°C for different times.

In the first 15 minutes re-annealing, it can be observed the ordering effect by V_{OC} increase and J_{SC} decrease. As time keeps increasing, this trend of V_{OC} increase and J_{SC} decrease remains for this re-annealing step. However, the solar cell efficiency was decreasing due to fill factor decrease (not shown here), evidencing that additional effects such as ZnO:Al layer degradation might play a relevant role. Nonetheless, an additional study to take into account the influence of PDA in every relevant layer, including ZnO:Al is discussed further on.

IV. DISCUSSION

In order to separate the effects of interdiffusion and Cu-Zn disorder on the performance of the cell at higher temperature, the cell was re-annealed at 150°C up to 2400 min. It is well known that full ordering will require longer time at lower temperature. Although V_{OC} increases in the low temperature regime, J_{SC} did not stabilize due to fill factor degradation. The V_{OC} improvement after re-annealing should be mostly coming from Cu-Zn reordering.

A future study of the PDA effects on bare absorbers, CdS coated absorbers and full cell both in air and inert atmosphere will be carried out. A comparison of these samples could allow to distinguish between interdiffusion phenomena, Cu-Zn disorder and other possible degradation effects.

By using a PDA in air at 150°C for 15 min, we recently obtained a 5.4% efficient solar cell. This is the highest efficiency reported by PLD.

IV. SUMMARY

We have performed a detailed study of PDA in air over a wide range of temperatures on CZTS full cells. It was confirmed that Cu-Zn disorder decreases V_{OC} and increases J_{SC} . Compared to the results of Timmo et al.[4], based on CZTS monograins annealing, a full cell in our study had a V_{OC} dip at 200°C and much higher V_{OC} drop at 300°C (above $T_C=260^\circ\text{C}$). We have concluded that Cd diffusion into the CZTS absorber might be the cause. The Cu-Zn disorder was partially reversed after PDA temperature reached 300°C by re-annealing at 150°C.

REFERENCES

- [1] M. A. Green *et al.*, "Solar cell efficiency tables (Version 53)," *Prog. Photovoltaics Res. Appl.*, vol. 27, no. 1, pp. 3–12, Jan. 2019.
- [2] C. Yan *et al.*, "Cu₂ZnSnS₄ solar cells with over 10% power conversion efficiency enabled by heterojunction heat treatment," *Nat. Energy*, vol. 3, no. 9, pp. 764–772, 2018.
- [3] J. J. S. Scragg *et al.*, "Cu-Zn disorder and band gap fluctuations in Cu₂ZnSn(S,Se)₄: Theoretical and experimental investigations," *Phys. Status Solidi Basic Res.*, vol. 253, no. 2, pp. 247–254, 2016.
- [4] K. Timmo *et al.*, "Influence of order-disorder in Cu₂ZnSnS₄ powders on the performance of monograin layer solar cells," *Thin Solid Films*, vol. 633, pp. 122–126, Jul. 2017.
- [5] M. Paris, L. Choubrac, A. Lafond, C. Guillot-Deudon, and S. Jobic, "Solid-State NMR and Raman Spectroscopy To Address the Local Structure of Defects and the Tricky Issue of the Cu/Zn Disorder in Cu-Poor, Zn-Rich CZTS Materials," *Inorg. Chem.*, vol. 53, no. 16, pp. 8646–8653, Aug. 2014.