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Effects of $Cd_{1-x}Zn_xS$ alloy composition and post-deposition air anneal on ultra-thin CdTe solar cells produced by MOCVD

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HIGHLIGHTS

- $CdCl_2$ anneal treatment resulted in S diffusing to the back contact.
- High Zn levels created mixed cubic/hexagonal structure at the p-n junction.
- Increased Zn in $Cd_{1-x}Zn_xS$ supressed S diffusion into CdTe.
- Device V_{oc} was enhanced overall with an additional back surface air anneal.

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ABSTRACT

Ultra-thin CdTe:As/$Cd_{1-x}Zn_xS$ photovoltaic solar cells with an absorber thickness of 0.5 μm were deposited by metal-organic chemical vapour deposition on indium tin oxide coated boro-aluminosilicate substrates. The Zn precursor concentration was varied to compensate for Zn leaching effects after $CdCl_2$ activation treatment. Analysis of the solar cell composition and structure by X-ray photoelectron spectroscopy depth profiling and X-ray diffraction showed that higher concentrations of Zn in the $Cd_{1-x}Zn_xS$ window layer resulted in suppression of S diffusion across the CdTe/$Cd_{1-x}Zn_xS$ interface after $CdCl_2$ activation treatment. Excessive Zn content in the $Cd_{1-x}Zn_xS$ alloy preserved the spectral response in the blue region of the solar spectrum, but increased series resistance for the solar cells. A modest increase in the Zn content of the $Cd_{1-x}Zn_xS$ alloy together with a post-deposition air anneal resulted in an improved blue response and an enhanced open circuit voltage and fill factor. This device yielded a mean efficiency of 8.3% over 8 cells (0.25 cm^2 cell area) and best cell efficiency of 8.8%.

1. Introduction

Thin film cadmium telluride (CdTe) has been an established technology for photovoltaic (PV) solar energy for a number of years [1]. Its commercial interest stems from the ease in material synthesis and ideal material properties coupled with high solar cell conversion efficiencies achievable (currently 22.1% for a cell [2] and 18.6% for a module with aperture area of 7038.8 cm^2 [3]). However, the rate at which Te can be supplied is largely dependent on the mining of Cu and its availability may become limited if the demand of global Te increased significantly [4]. In addition, a decline in the rate of Cu extraction [5] could also impact the Te supply. Reduction of CdTe absorber thickness becomes an important consideration for continued large scale production of CdTe solar modules [6–8]. The use of less material will also have a positive impact for reducing manufacturing costs and carbon footprint providing that the PV conversion efficiency does not deteriorate significantly. However, ultra-thin (≤1 μm) CdTe solar cells are more susceptible to lateral inhomogeneity across the device [9,10] which is a limiting factor for industrial production.

There have been several studies on ultra-thin CdTe PV cells [6,11–13], reporting a best cell efficiency of 11.2% for close spaced sublimated (CSS) CdTe cells with an absorber thickness of 0.6 μm [11] and an 11% best and 10% mean efficiency over 25 dot cells

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(0.06 cm^2 cell area) for 0.5 μm thick CdTe produced by sputtering [13]. These PV cell performances are very respectable when compared to standard CdTe solar devices and absorber thicknesses of 2–5 μm [14,15]. The power output per mass of material (or tellurium) used (W/g_{Te}), which will be referred to as *material power yield*, increases as the CdTe thickness is reduced. This relates directly to the fact that the majority of carriers are generated close to the junction [9]. The enhanced material power yield with reduced CdTe thickness can be demonstrated considering the reported world record 22.1% efficiency for a CdTe cell [2]. Assuming a CdTe thickness of 4 μm for this 22.1% efficient cell, gives a W/g_{Te} of 0.19. For an equivalent 2 μm and 0.5 μm CdTe solar cell using the world record efficiency [2], the W/g_{Te} would be 0.38 and 1.51 respectively. For the reported [13] 11% cell with 0.5 μm CdTe the material power yield is 0.75 W/g_{Te}, which is a significant improvement compared to solar cells with (≥2 μm) CdTe thicknesses, even with the current world record efficiency for 2 μm CdTe thickness. This shows the incentive for reducing the CdTe thickness in future commercial production of CdTe modules. This becomes more desirable if there is a sufficient drop in the manufacturing cost from using less material and the deterioration in solar cell/module performances for ultra-thin devices is minimised.

An improved spectral response in the blue region of the solar spectrum has been achieved for ultra-thin CdTe solar cells upon addition of Zn to the CdS layer giving a $Cd_{1-x}Zn_xS$ alloy window layer with a larger band gap [10,16]. Previous work [17] has shown that metal-organic chemical vapour deposition (MOCVD) can introduce Zn into the CdS window layer in a controlled manner with determination of the optimised levels to give enhanced solar cell performance before the series resistance increases and a change in the lattice structure deteriorates collection at the junction. However, $CdCl_2$ activation treatment was found to reduce the Zn content in the $Cd_{1-x}Zn_xS$ alloy window layer due to Zn leaching [10]. This is significant when the CdTe absorber thickness is reduced. Although the Zn composition in the $Cd_{1-x}Zn_xS$ alloy window layer reduced as the $CdCl_2$ deposition increased, an improvement in open circuit voltage (V_{oc}) was also observed [18]. This work considers the approach of using higher concentrations of Zn in the $Cd_{1-x}Zn_xS$ alloy window layer to compensate for Zn leaching resulting from $CdCl_2$ activation.

In addition to the improvements in using a $Cd_{1-x}Zn_xS$ alloy window layer, a post-$CdCl_2$ treatment air anneal at low temperature has been found [19,20] to be beneficial to MOCVD-produced CdTe solar cells. X-ray photoelectron spectroscopy (XPS) has shown [19] that there is oxidation of the CdTe after the air anneal and capacitance-voltage (*C-V*) measurements have confirmed [20] an increase in acceptor carrier concentration, as well as a reduction in the back contact barrier. These observations were for solar cells with a CdTe absorber thickness of 2.25 μm, but the impact of this treatment on devices with reduced CdTe absorber thickness has not been reported. Other literature report [21,22] an improved CdTe solar cell performance carrying out the $CdCl_2$ anneal treatment with oxygen present in the chamber.

Changes to the solar cell composition and structure after the same $CdCl_2$ activation treatment are investigated using XPS depth profiling and X-ray diffraction (XRD). Comparison between as-grown and air annealed devices is also made. These results are correlated with the corresponding PV solar cell performance.

2. Experimental

Ultra-thin $Cd_{1-x}Zn_xS$/CdTe solar cells were produced using MOCVD in a single growth chamber. Boro-aluminosilicate glass coated with indium tin oxide was used as the substrate, with a thickness of 1.1 mm and sheet resistance of 4–8 Ω/□. A wide band gap $Cd_{1-x}Zn_xS$ alloy window layer with a thickness of 0.24 μm was employed to enhance the spectral response in the blue region [16–18,24]. The 0.24 μm window layer thickness included a 0.05 μm CdS nucleation layer, the first layer to be deposited (at 315 °C) in the MOCVD growth chamber on to the ITO, which improved surface coverage of the $Cd_{1-x}Zn_xS$ alloy window layer grown at the higher temperature of 360 °C. Interdiffusion of the CdS layer into the $Cd_{1-x}Zn_xS$ alloy occurred during CdTe growth and Cl activation treatment. Different Zn concentrations in the alloy were achieved through varying the Zn precursor partial pressure, P_{Zn}. Arsenic was used as the CdTe acceptor dopant with a mean concentration of ~5 × 10^{18} atoms/cm^3, and was introduced into the MOCVD growth chamber during CdTe deposition at 390 °C. All devices were treated in the same MOCVD chamber after CdTe growth, with the same $CdCl_2$ activation process; a $CdCl_2$ deposition time of 179 s at 200 °C and a thermal anneal at 420 °C for 10 min. The devices being subjected to a post-growth air anneal were placed in an oven at 170 °C for 30 min. Details of the processing parameters employed for the different samples are given in Table 1. In this Table, a comparison has been made to an equivalent MOCVD-grown ultra-thin CdTe device receiving no $CdCl_2$ anneal treatment (reference) and a CdTe device with absorber thickness of 2.25 μm (baseline). A previous study [18] determined that a greater $CdCl_2$:CdTe thickness ratio was necessary compare to baseline devices produced using the same method. The approximate $CdCl_2$ thickness has been given, assuming a 1.2 nm/s growth rate determined in previous work [25]. Device PZN07 had a modest increase in the Zn precursor partial pressure (P_{Zn}) than that typically employed (i.e. for the baseline, reference and PZN06 devices) during window layer deposition. For device PZN14, P_{Zn} was raised further, to double that used for device PZN07.

An anneal treatment without $CdCl_2$ was not carried out in this study as the aim of the work was to study the efficiency enhancement associated with Cl^- diffusion in the activation process. After rinsing excess $CdCl_2$ from the surface with deionised water, a further low temperature anneal was carried out for 30 min in air using an extracted oven set at 170 °C for devices PZN07 and PZN14 prior to back contact formation. Each ultra-thin CdTe solar cell device consisted of 8 × 0.25 cm^2 cells defined by evaporating Au through a shadow mask. These cells are four times larger in size than other reported [13] high efficiency CdTe solar cells with reduced absorber thickness making them more susceptible to lateral inhomogeneities. The reason for this was to enable comparison to equivalent MOCVD-grown devices with the baseline CdTe absorber thickness. No Cu was added to the Au contacts and

Table 1
Ultra-thin $Cd_{1-x}Zn_xS$/CdTe solar cells with variable window layer Zn content controlled using different Zn precursor partial pressures (P_{Zn}) during deposition.

Device	CdTe (μm)	P_{Zn} (atm.)	$CdCl_2$ (s)	$CdCl_2$ (~μm)	Anneal (s)	Air anneal (s)
Baseline	2.25	6.0×10^{-5}	359	431	600	0
Reference	0.5	6.0×10^{-5}	0	0	0	0
PZN06	0.5	6.0×10^{-5}	179	215	600	0
PZN07	0.5	6.9×10^{-5}	179	215	600	30
PZN14	0.5	1.4×10^{-4}	179	215	600	30