Arsenic – doped p'-ZnTe back contact films for CdTe solar cells

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Introduction

Thin film CdTe is considered as one of the leading thin film photovoltaic (PV) technologies [1]. With absorption coefficient >10^4 cm⁻¹, bandgap energy of 1.45 eV, and low-cost manufacturing, CdTe is ideal for very high-performance PV applications. Although record efficiencies of up to 22.1% have been demonstrated [2], there is need for much more improvement to close the gap towards the theoretical maximum of ~30% [3]. The use of a wide bandgap back contact layer (BCL) to CdTe absorber has shown promise for improving device performance [4]. One such material is the zincblende (cubic) ZnTe, which has a bandgap of ~2.26 eV. It has a negligible valence band discontinuity to CdTe with the conduction band offset (CBO) being large enough to serve as an electron reflector. The CBO is expected to minimise carrier recombination at the back contact [4]. Moreover, ZnTe with higher p-type doping capacity than CdTe, can provide a low resistive Ohmic contact to the metal electrode.

Compared to the approach of Cu doping near the back surface of CdTe [5], p-type ZnTe BCL replacement would eliminate the problem with Cu diffusion towards the n-type window layer, which ultimately results in electrical shunts, instability and thus poor device performance [6]. In this study, we used metalorganic chemical vapour deposition (MOCVD) to grow As-doped polycrystalline (poly-)ZnTe layers and assess their performance as the BCL on Cl-activated CdTe solar cell structures for the first time.

Experimental

Reference films of ~500 nm ZnTe:As were first grown on uncoated borosilicate glass substrates using MOCVD. Transmittance and Hall-effect measurements were carried out to determine the optical and electronic properties of the ZnTe:As films. The p-type property of ZnTe thin film was controlled by varying the arsenic dopant flow between 0 – 10 sccm. The solar cells in this study were fabricated in superstrate configuration. The baseline device structure follows the schematic in Fig. 1, where the heavily-As doped CdTe BCL layer is followed by CdCl₂ heat treatment (CHT). Further experimental details can be found elsewhere [7]. Upon verification of p-type character (by Hall measurements) in heavily-doped ZnTe:As films, these were then incorporated to the baseline device structure as the BCL. The cell structure in Fig. 1 was grown by omitting the heavily-doped CdTe layer, and then finished with p'-ZnTe deposition (~335 nm). Prior to ZnTe:As deposition, samples were cooled to room temperature and excess CdCl₂ rinsed off with DI water. The As dopant flow for ZnTe film was chosen as 10 sccm. By varying the processing conditions, three different sets of devices with ZnTe:As BCL (A, B, and C) were fabricated as follows. In device A, ZnTe:As BCL was deposited following excess CdCl₂ rinse and annealing the samples in air at 170°C for 90 minutes. For device B and C, ZnTe:As was deposited after the CdCl₂ rinse only. Sample B was subjected to a ZnCl₂ wet treatment prior to annealing under flowing H₂ gas 420°C for 10 minutes to improve ZnTe crystallinity and its interface to bulk CdTe. For sample C, no treatment was performed prior to the H-anneal. ZnCl₂ has been suggested in the literature as an alternative to CdCl₂ heat treatment, to avoid Zn leaching from ZnTe [6]. For ZnCl₂ deposition, sample B was immersed in a 10% ZnCl₂/methanol solution for 2 minutes and then left to dry in air before transferring into the MOCVD reactor. A control device was also fabricated, which was similar to the baseline device, but without the heavy-doped CdTe BCL. Device structures were completed by evaporation of Au as a back contact.

AM 1.5 J-V measurements were performed using an Abet Technologies Ltd. solar simulator with the light power density calibrated using a GaAs reference cell. C-V characteristics were measured using a Solartron Impedance Analyzer. External quantum efficiency (EQE) measurements were carried out using a Bentham spectral response system. The system response was corrected by scanning the output of a c-Si reference detector. The energy dispersive X-ray spectroscopy (EDX) analysis was obtained using a Hitachi TM3000 table top scanning electron microscope (SEM).
Table 1: Summary of parameters from light J-V curves and C-V measurements.

Results and Discussion

Fig. 2 shows the transmission spectra of ZnTe:As thin films with varying arsenic doping concentration. As evident, the absorption increases with As doping. From Hall measurements, carrier concentrations up to $4.5 \times 10^{18}$ cm$^{-3}$ and low resistivity of 1.63 Ω cm were determined for As doping at 10 sccm flow.

Light J-V curves of the baseline device, control device without any BCL, and devices with $p^+$-ZnTe:As BCL are presented in Fig. 3. The device parameters obtained from the J-V curves and C-V measurements are also summarised in Table 1.

Except for device B, devices with ZnTe:As BCL showed a clear improvement in the short circuit current density ($J_{SC}$). Compared to the baseline device, an improvement in $J_{SC}$ by $\sim 2$ mA/cm$^2$ can also be observed, which correlates with the improved device red response, as is evident in Fig. 5. We suggest this could be attributed to the electron reflection property of the ZnTe layer [4]. In the case of device B for which the wet ZnCl$_2$ treatment (ZHT) was performed, the loss in $J_{SC}$ is also evidenced in the device red response. The red response for both device B and the control sample are similar, suggesting at first that the ZnTe:As BCL in B is removed. But EDX measurements confirmed the presence of Zn and Te on the sample surface, following ZHT (Fig. 6).
Therefore, we suggest that the origin of the observed loss in $J_{SC}$ is not related to the chemical composition but is electrical in nature. The low $FF$ for the devices A, B, and C is a clear indication of the presence of ZnTe:As. But $R_{SH}$ for B is poorer, so we suspect some selective etching along grain boundaries.

From C-V measurements (Fig. 4), we found that the acceptor concentration determined in the control device was comparable to the baseline device ($\sim 1.34 \times 10^{16}$ and $1.0 \times 10^{16}$ cm$^{-3}$, respectively), with corresponding narrow depletion widths. This correlates well with the high $V_{OC}$ values in comparison to the devices with ZnTe:As BCL, as it is generally accepted that the carrier concentration significantly affects $V_{OC}$ [10]. This can be seen clearly in devices A, B, and C, from which the measured acceptor concentrations were all up to one order of magnitude below the control device. Between devices A, B, and C, acceptor concentration in B and C shows some recovery towards $10^{16}$ cm$^{-3}$, following the annealing process after ZnTe:As BCL was deposited, where C showed the most recovery. There is also a corresponding narrowing of the depletion width after annealing (from 1.094 to 0.663 µm).

The reason for the lower values of acceptor concentration in devices with ZnTe:As BCL is rather unclear at this point. However, we suggest a number of factors that should be taken into consideration. One is interface contamination; after growing $p$-CdTe and performing CdCl$_2$ heat treatment, the device structure was taken out of the MOCVD reactor, and excess chlorine rinsed before reintroducing it back in the reactor for depositing the BCL. The contamination during this process may yield additional recombination centres, contributing to a reduction in some of the device parameters [11]. Another important factor is the lattice mismatch (5.8%) between ZnTe and CdTe, which according to Amin et al [4] could be responsible for the presence of interface states, which would probably have an adverse effect on device parameters via recombination losses.

These results show that understanding of the changes in carrier concentrations with different treatments in ZnTe:As BCL devices, and that addressing interface defects due to lattice mismatch and strain is critical to obtain high efficiencies in these devices.

**Conclusions**

We have investigated As-doped polycrystalline ZnTe back contact layers for CdTe thin film solar cells, grown by metalorganic chemical vapour deposition. The cells with ZnTe:As BCL showed improvement in $J_{SC}$, but $V_{OC}$ and $FF$ were reduced. The current improvement is attributed to the ZnTe:As BCL acting as an electron reflector. ZnCl$_2$ wet treatment and subsequent annealing further increased shunting and series resistance, thus limiting device performance. The recovery in acceptor concentration, after annealing confirms that the
activation of ZnTe:As is critical to device performance. Further annealing studies are therefore required to establish the optimum processing condition for ZnTe:As activation.

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