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The Effect of Arsenic Doping on the Performance of $CdSe_xTe_{1-x}$/CdTe Solar Cells

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***Abstract*—The effect of Arsenic doping in the $CdSe_xTe_{1-x}$ (CST)/CdTe solar cells with different Se (x) compositions and processed under various $CdCl_2$ annealing temperatures has been investigated. The superstrate cell configuration was ITO/MZO/CST: As/CdTe/Back Contact. The CST was doped with Arsenic during the CSS deposition. The Se (x) composition of the CST was varied between_-6 and 27%. The V_{oc} decreased and J_{sc} increased at higher Se (x) compositions for both undoped and doped cells, due to a decrease in the bandgap of CST. For undoped cells, the maximum net p-doping was found to be around 3.20E+14 cm^{-3} for 22% Se composition, and for Arsenic doped cells 1.87E+15 cm^{-3} for 27% Se composition. The V_{oc} for the Arsenic doped cell was found to be 30-40 mV lower than the undoped cells presumably due to lower minority carrier lifetimes.**

Keywords—Arsenic, Se Composition, lifetime, Net p-doping, Bandgap

I. INTRODUCTION

The highest efficiency of CdTe thin-film solar cell demonstrated to-date is 22.1% which is still far below the theoretical limit [1]. The use of CST helped to bring the current density near the theoretical limit for CdTe (31.7 mA/cm^2). With J_{sc} and fill factor are near their theoretical limits, the gap between the experimental efficiency and theoretical limit is now because of the limitations in achieving V_{oc} higher than 900 mV. V_{oc} above 1000 mV has only been demonstrated in monocrystalline CdTe solar cells [2]. A significant effort in the research community is now dedicated to improving V_{oc} over 1000 mV for polycrystalline devices. Achieving this goal requires a higher net p-doping concentration ($>10^{16}$ cm^{-3}) and lifetimes of several-to-tens of ns [3]. For that reason, p-type doping of CdTe solar cells is of great interest.

The ex-situ copper introduced during the back contact fabrication can play an important role in enhancing the p-doping concentration [4]. Although a certain amount of copper is beneficial for enhancing the cell performance, higher Cu concentrations also lead to degradation the performance of the cell. The back contact annealing temperature controls the amount of copper in the absorber layer. For a certain optimum temperature, the optimum amount of copper can diffuse into the absorber. At lower and higher temperatures, the copper diffusion is detrimental for the lifetime, and it also affects the long-term stability of the cell by shunting [5]. For the optimum amount of copper, the p-doping concentration is found as 10^{14} cm^{-3}, which is not enough for achieving V_{oc} over 1000 mV.

P-type doping in CdTe is challenging [6]. Group V elements such as Arsenic (As), Phosphorous (P), or Antimony (Sb) can be used as a p-type dopant [7]. They can occupy the Te site by substituting for Te. Adding a CST layer in the CdTe cell structure is beneficial because it increases the current density and Se has been found to lead to higher lifetimes. So, doping the CST layer is an alternative way to increase the overall absorber doping concentration.

In this study, the effect of Arsenic doping of the CST absorber layer at different Se compositions under different $CdCl_2$ annealing temperatures is investigated. The device performance/properties, i.e open circuit voltage (V_{oc}), short circuit current density (J_{sc}), fill factor, bandgap, and net p-doping concentration has been studied.

II. EXPERIMENTAL

Our cell structure is superstrate configuration: ITO/MZO/CST: As/CdTe/Back Contact. The glass substrate is corning EagleXG glass. First, the glass was cleaned and the Indium Tin Oxide (ITO) and Magnesium Zinc Oxide (MZO) were rf sputter deposited. Arsenic doped CST alloys at different Se compositions were made by mixing CdTe (99.999%), CdSe (99.999%), and Cd_3As_2 powders, and co-subliming in H_2 ambient. CST was deposited by CSS process with source and substrate temperatures of 680^0C and 580^0C respectively. Then a CdTe layer was deposited at the same temperature as CST. Following the CST and CdTe depositions, the structures were $CdCl_2$ heat-treated at 410 and 430^0C temperature. Prior to applying the back contact, the samples were etched in a bromine methanol solution. Cu-doped graphite paste was used as the back contact. The devices were characterized by J-V, Spectral Response, and C-V measurements. A Hitachi SU800 was used to see the Scanning Electron Microscopy (SEM) image and Energy Dispersive Spectroscopy (EDS) to measure the Selenium composition. A panalytical X'Pert MRT was used for the X-ray diffraction measurements.

III. RESULT AND DISCUSSION

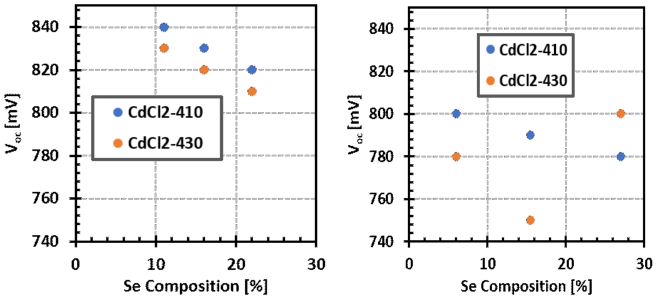

Fig. 1. V_{oc} Vs. Se composition for undoped (left) and As-doped (right) CST cells at 410 and 430^{0}C $CdCl_2$ annealing temperature.

In Fig. 1, the V_{oc} for undoped and As-doped CST cells are shown for 410 and 430^{0}C $CdCl_2$ annealing temperatures. The V_{oc} decreases with the increasing of Se composition because of a decrease in the bandgap due to bowing effect. It is seen that the maximum V_{oc} for undoped and As-doped cells are 840 and 800 mV respectively. The As-doped devices consistently exhibited 30-40 mV lower V_{oc} than undoped devices presumably due to lower lifetime.

As shown in the same figure, for 430^{0}C $CdCl_2$ annealing temperature V_{oc} is lower than 410^{0}C. Higher $CdCl_2$ annealing temperature may create pinholes, and lead to excess chlorine in the CST and CdTe grain boundaries, which may work as the recombination center and decreases lifetime [8]. This can cause a lower V_{oc}. At the highest Se composition, V_{oc} increases possibly due to an increase in the bandgap and lifetime, and it is even higher at 430^{0}C.

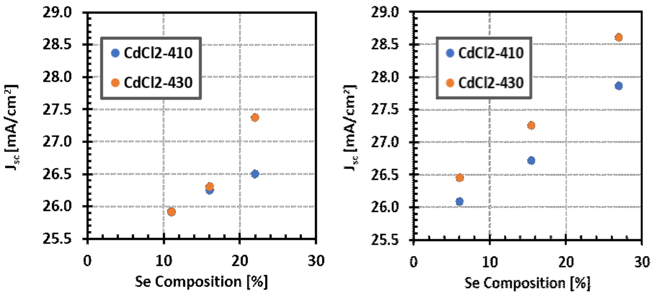

Fig. 2. J_{sc} Vs. Se composition for undoped (left) and As-doped (right) CST cells at 410 and 430^{0}C $CdCl_2$ annealing temperature.

From Fig. 2, it can be seen for both undoped and As-doped cells, J_{sc} increases with the increasing of Se composition. This is because of bandgap reduction at higher Se composition due to the bowing effect. Lower bandgap increases carrier collection at higher wavelength, which makes the J_{sc} higher. There is no significant difference found in J_{sc} for undoped and As-doped cells. However, As-doped cells have relatively higher J_{sc} because of lower bandgap compared to undoped cells at the same Se composition. Also, the J_{sc} is higher at 430^{0}C $CdCl_2$ annealing temperature than 410^{0}C for undoped cells because of the lower bandgap at higher annealing temperature due to intermixing of CST and CdTe may result a thicker CST layer. Same trend is found for the As-doped cells.

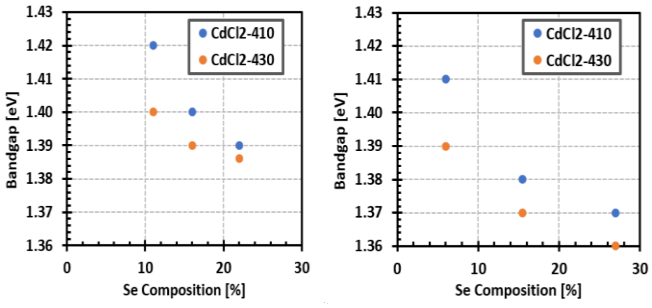

Fig. 3. Bandgap Vs. Se composition for undoped (left) and As-doped (right) CST cells at 410 and 430^{0}C $CdCl_2$ annealing temperature.

In Fig. 3, the bandgap for different Se compositions is shown for both undoped and As-doped cells. The bandgap is calculated from the absorption edge of the spectral response of our devices. For both types of cells, the bandgap decreases with increasing of Se composition as expected. This change in bandgap is responsible for the change in V_{oc} and J_{sc} described earlier. For the undoped cells, the bandgap is found to be 10-20 meV higher than the As-doped cells. Also, the 430^{0}C $CdCl_2$ annealing temperature leads to lower bandgap than 410^{0}C. This is believed to be due to the fact that higher $CdCl_2$ annealing temperature affects intermixing between the CST and CdTe, therefore changes the final composition of the CST layer. The same trend is found for As-doped cells.

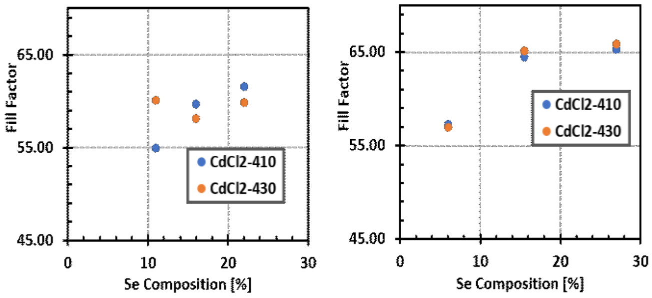

Fig. 4. Fill Factor Vs. Se composition for undoped (left) and As-doped (right) CST cells at 410 and 430^{0}C $CdCl_2$ annealing temperature.

In Fig. 4, the variation of fill factor as a junction of Se composition is shown for both undoped and As-doped cells. For both cases, the fill factor is higher for higher Se composition, and comparatively it is higher for As-doped cell.

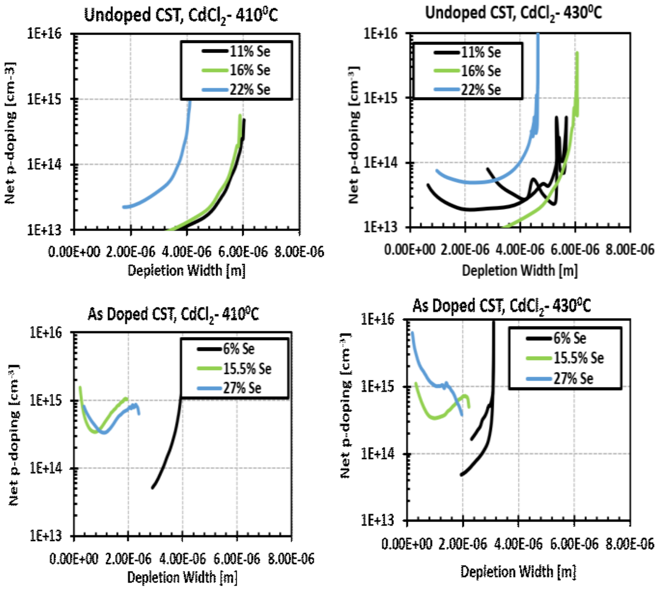

Fig. 5. C-V measurements for undoped and As-doped CST cells at 410 and 430⁰C $CdCl_2$ annealing temperature.

The C-V measurements at 410⁰C and 430⁰C for both undoped and As-doped cells are shown in Fig. 5. For both undoped and As-doped CST cell, the doping concentration increases with increasing of Se composition. It can be seen that the As-doped CST cells have a higher net p-doping suggesting that the As is acting as p-type doping substitutional impurity. than the undoped cells. The highest net p-doping is found at 22% Se for undoped cell and 27% Se for doped cell. The above results suggest that higher Se compositions may enhance the dupability of CST.

For undoped cells, the highest doping concentration measured is 3.20E+14 cm^{-3}, where for As-doped cell is 1.87E+15 cm^{-3}. It appears that doping higher than this value was not possible. It can be due to low activation or compensation. To-date these are the highest doping levels obtained for these devices regardless of the amount of As added to the CSS source material, suggesting that As activation is low due to compensation effects.

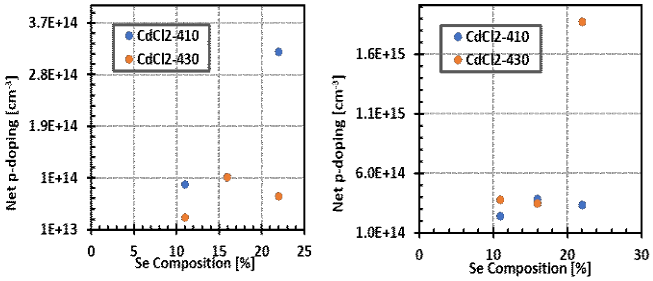

Fig. 6. Net p-doping Vs. Se composition for undoped (left) and As-doped (right) CST cells at 410 and 430⁰C $CdCl_2$ annealing temperature (NOTE: doping scale is not the same for two graphs).

The results in Fig. 5 are summarized in Fig. 6.

For the undoped cells, the doping concentration is found to be lower at 430⁰C $CdCl_2$ annealing temperature. The opposite trend is observed for As-doped CST cells.

IV. CONCLUSIONS

The effect of Arsenic doping of CST with different Se compositions (6 to 27%) and annealing temperatures (410 and 430⁰C) has been studied. The bandgap was found to decrease with increasing Se composition as expected; furthermore it appears that the bandgap for As-doped cells was lower than that for undoped cells; it is not clear at this time what causes the change in the bandgap for doped cells. For both cases, at low Se compositions (< 25%), V_{oc} decreases with Se compositions due to bandgap reduction. The maximum V_{oc} obtained for undoped, and As-doped cells was 840 mV and 800 mV respectively. The As-doped devices consistently exhibited 30-40 mV lower V_{oc} than undoped devices, presumably because of lower minority carrier lifetime. Also, at lower Se composition, V_{oc} decreases with increasing $CdCl_2$ annealing temperature for both types of cells. J_{sc} increases with the Se compositions due to the bandgap reduction. Higher $CdCl_2$ annealing temperatures lead to lower bandgap, estimated using SR data, which is the reason for the higher J_{sc}. The doping concentration was found to be higher at higher Se composition and for As-doped cells. The highest p-doping measured for As-doped cells was 1.87E+15 cm^{-3} for 27% Se composition, and for undoped cells 3.20E+14 cm^{-3} for 22% Se composition.

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