

Arsenic Doping of Polycrystalline CdSeTe Devices for Microsecond Life-times with High Carrier Concentrations

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Abstract— We report seminal advances in fabrication and understanding of group V (As) doped thin-film polycrystalline CdTe-based solar cells. The devices are fabricated using a novel approach, by sublimating layers of CdSeTe and CdSeTe:As. This new method allowed us to achieve minority carrier lifetime of over 1 μ s, carrier concentration of more than 5×10^{15} cm $^{-3}$ and external radiative efficiency of over 2% in a device configuration. We find an increase in open-circuit voltage when comparing As-doped, Cu-doped and undoped devices. The choice of CdSeTe instead of a CdTe-only absorber has been explained using first-principle density functional theory model. A SCAPS device model is used to analyze the potential causes for lower open-circuit voltage.

Keywords—II-VI semiconductor materials, thin film devices, photovoltaic cells, voltage, CdTe, selenium

I. INTRODUCTION

Thin-film CdTe-based photovoltaics is an important technology for large scale power generation. It is recognized as a prominent energy technology and owing to its low material cost and ease of manufacturing, CdTe-based photovoltaics have demonstrated some of the lowest cost of electricity [1]. With advances in fabrication methods and understanding of its properties and behavior, small area device with efficiency of 22.1%[2] and production modules up to 18.6% [3] have been fabricated. At Colorado State University (CSU) we have

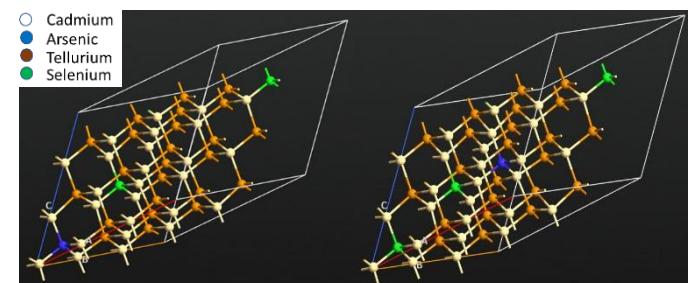


Fig. 1. Computational model of $\text{CdSe}_x\text{Te}_{1-x}$ with Se occupying Se site and As occupying Te site. The 54 atom model was developed and computational analysis was performed using Synopsys QuantumATK.

All of these improvements have been achieved by enhancing short-circuit current density (J_{SC}) and fill-factor while the open-circuit voltage (V_{OC}) has not increased. Achieving V_{OC} for polycrystalline devices over 900 mV has continued to be a challenge and further improvements in device efficiency are predominantly limited by lower V_{OC} than what is possible for a material with a bandgap of 1.4-1.5 eV. Shockley-Queisser calculations for the thermodynamic efficiency limit predict V_{OC} of 1.2V with the bandgap of ~1.45 eV.

A. Background

Modeling by Kanevce *et al* suggests devices with $V_{OC} > 1V$ and efficiency $> 24\%$ can be fabricated if surface recombination velocity $S \leq 100 \text{ cm/s}$, bulk recombination lifetime $\tau \geq 10 \text{ ns}$ and doping density $\rho \geq 10^{16} \text{ cm}^{-3}$ can be achieved. For polycrystalline CdTe-based films, recombination lifetime $\tau > 400 \text{ ns}$ and surface recombination velocity $S < 100 \text{ cm/s}$ have been demonstrated using a double heterojunction structures [6]. Copper is dopant for typical CdTe-based devices. However, in addition to Cu_{Cd} substitutional acceptor, Cu can also exist in interstitial sites as a donor which, being a trap, is not desirable. Perrenoud *et al* also show that Cu doping in CdTe devices may have a fundamental limitation [7]. Group V doped CdTe single-crystals achieved $> 1V$ V_{OC} and $\rho > 10^{16} \text{ cm}^{-3}$ [8]. In this study, arsenic doping is investigated to achieve high p-type doping density while maintaining other desirable properties, which should allow fabrication of polycrystalline CdTe devices with $V_{OC} > 1V$ and efficiency over 22%.

II. EXPERIMENTAL

A. Material Selection

Doping $\text{CdSe}_x\text{Te}_{1-x}$ (CST) with As, can allow As to occupy either Selenium site (As_{Se}) or Tellurium site (As_{Te}). We therefore used first principles approach to study the behavior of As_{Se} and As_{Te} in $\text{CdSe}_{0.11}\text{Te}_{0.89}$ bulk. Density Functional Theory (DFT) with Linear Combination of Atomic Orbitals (LCAO) basis sets have been used to simulate the As doped $\text{CdSe}_{0.11}\text{Te}_{0.89}$ structure consisting of 54 atoms. The simulations have been performed using Synopsys QuantumATK software and this is one of the first uses of this approach for $\text{CdSe}_x\text{Te}_{1-x}$ material. The formation energies were calculated to understand the stability of As occupying Se and Te sites.

DFT calculations revealed that for As_{Te} , there was a release of 0.56 eV/atom, while for As_{Se} , the corresponding value was 1.36 eV/atom making Se preferred choice for As doping in CST compounds. A similar calculation was done for As_{Te} in CdTe, where the energy release was 0.77 eV/atom. Thus it was concluded that As_{Se} is most stable in $\text{CdSe}_x\text{Te}_{1-x}$ followed by As_{Te} in CdTe and As_{Te} in CST.

B. Device Fabrication

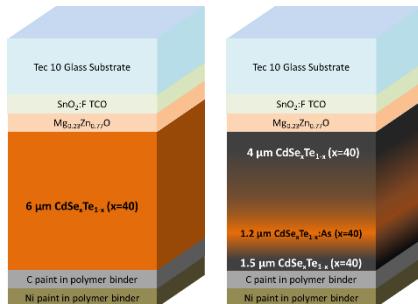


Fig. 2. Schematic of fabricated devices. (Left) device with no doping and copper doping, (right) device with arsenic doping. (not to scale)

Thin-film $\text{CdSe}_x\text{Te}_{1-x}$ devices were fabricated using sublimation. A reference device was fabricated that was not exposed to Cu or As. Another device was fabricated using $\text{CdSe}_x\text{Te}_{1-x}$ and was treated with CuCl for doping and forming the back-contact. Arsenic doped device was fabricated by

sublimating a 4 μm layer of $\text{CdSe}_x\text{Te}_{1-x}$ following which the substrate was moved to a different deposition system that had a co-sublimation system. The primary sublimation source had $\text{CdSe}_x\text{Te}_{1-x}:\text{As}$ source charge and the secondary source was filled with cadmium to allow sublimation under Cd-overpressure. The $\text{CdSe}_x\text{Te}_{1-x}$ source charge was fabricated using High-Pressure Bridgeman method at Washington State University. The goal here was to sublimate $\text{CdSe}_x\text{Te}_{1-x}:\text{As}$ under overpressure of Cd. Overpressure of Cd during sublimation of the film led to V_{Te} and V_{Se} that were understood to improve incorporation of As atoms within the film.

Following a deposition of 1.2 μm of $\text{CdSe}_x\text{Te}_{1-x}:\text{As}$ the substrate was moved to the earlier deposition system where a 1.5 μm layer of $\text{CdSe}_x\text{Te}_{1-x}$ was deposited followed by a CdCl_2 passivation treatment. A 20-30 nm layer of Te was deposited at the back of each substrate following CdCl_2 treatment. All 3 devices were contacted using a carbon and nickel conductive paint and delineated into 25 small area devices were fabricated on each substrate. Area of each cell was $\sim 0.65 \text{ cm}^2$. Performance of these devices were measured using current density vs voltage ($J-V$). Thereafter, selected devices were measured for carrier concentration vs distance from junction (N_A vs X). These selected devices were also used to characterization recombination lifetime and surface recombination velocity using time resolved photoluminescence (TRPL).

III. RESULTS

A. Electrical Characterization

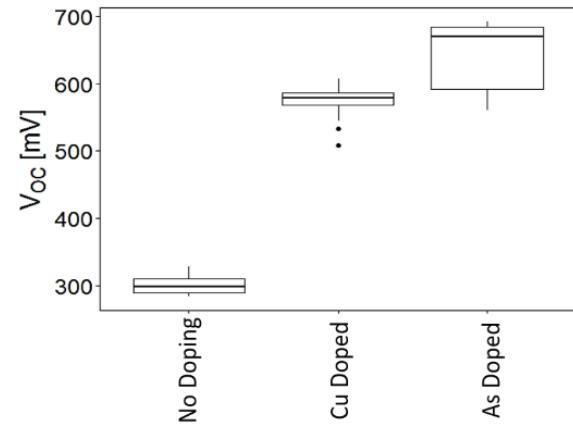


Fig. 3. Measured open-circuit voltage on device with no doping, copper doping and arsenic doping

Devices with arsenic doping showed improvement in open-circuit voltage (V_{OC}). As shown in figure 3, doping with copper improved the average V_{OC} from $\sim 300 \text{ mV}$ to nearly 600 mV . Arsenic doped devices showed a $V_{OC} > 650 \text{ mV}$. Two devices were examined using capacitance-voltage (CV) and showed carrier concentration of $1.28 \times 10^{15} \text{ cc}^{-1}$ and $4.2 \times 10^{15} \text{ cc}^{-1}$. This is substantially higher than $2.35 \times 10^{14} \text{ cc}^{-1}$ observed with the Cu doped device. Some devices were characterized using scanning capacitance microscopy (SCM) to measure the carrier concentration further away from the depletion region. The carrier concentration at about 3 μm from the junction was measured at about $1 \times 10^{18} \text{ cc}^{-1}$. When this was compared to secondary ion mass spectroscopy (SIMS) profile it showed a

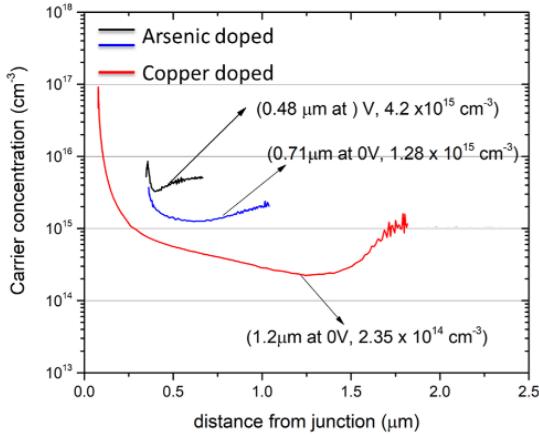


Fig. 4. Carrier concentration vs distance from junction (N_A vs X) for arsenic doped devices compared to copper doped devices.

very high arsenic dopant activation $\text{CdSe}_x\text{Te}_{1-x}$. This also indicates a graded doping profile that is highly favorable.

B. Spectroscopic Characterization

Low-injection time-resolved photoluminescence (TRPL) decays measured with excitation at 640nm are shown in Fig. 5. After pulsed laser excitation, electrons drift in the space charge field to the MZO interface and holes drift to the back contact. After quasi-equilibrium is established (drift/diffusion dynamics

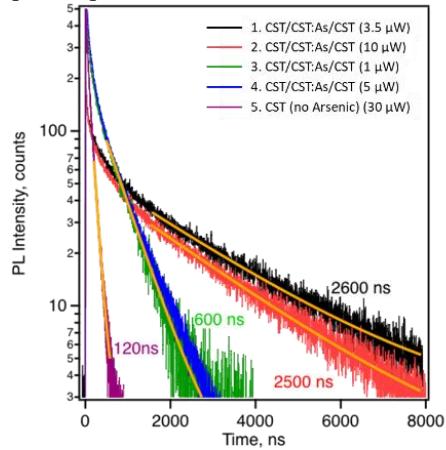


Fig. 5. Low-injection 1PE TRPL for device listed in the legend.

is over) we observe the slower component of the decay. Lifetime values for such “ τ_2 ” dynamics are indicated in the figure 5. Decays at two injections are shown for samples 1 and 2 (2.5-2.6 μ s) and samples 3 and 4 (600ns), where near-identical TRPL confirms low injection condition. For detailed analysis of TRPL data measured on solar cell devices, TCAD modeling need to be used [9]. Qualitatively, data in figure 5 indicates that bulk lifetime exceeds 200 ns for samples 1-4, and front interface recombination velocity was ~ 100 cm/s for samples 3 and 4 and < 100 cm/s for samples 1 and 2.

C. Materials Characterization

The cross-section TEM image (figure 6) shows large distinct grains with low density of stacking faults. No distinct interfaces are observed for the deposited $\text{CdSe}_x\text{Te}_{1-x}/\text{CdSe}_x\text{Te}_{1-x}:\text{As}/\text{CdSe}_x\text{Te}_{1-x}$ layers after CdCl_2 passivation treatment. This

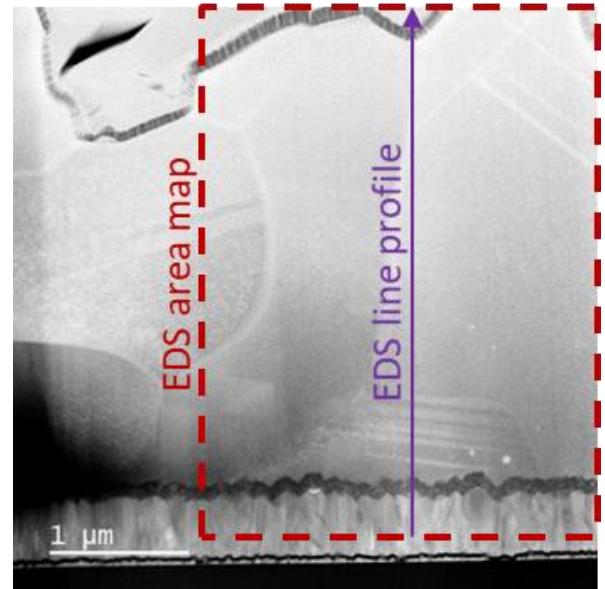


Fig. 6. TEM cross section for $\text{CdSe}_x\text{Te}_{1-x}/\text{CdSe}_x\text{Te}_{1-x}:\text{As}/\text{CdSe}_x\text{Te}_{1-x}$ device.

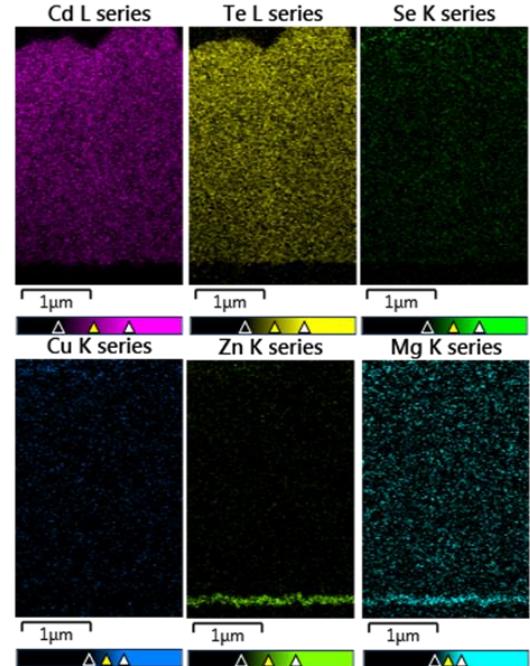


Fig. 7. Cross section EDS elemental maps for the area shown by dotted box in figure 6.

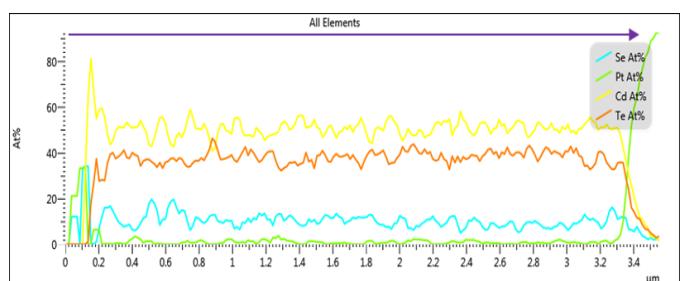


Fig. 8. EDS line scan for the scan direction shown by arrow in figure 6.

suggests epitaxial growth of films even with break in vacuum during deposition. This also suggests that CdCl_2 treatment

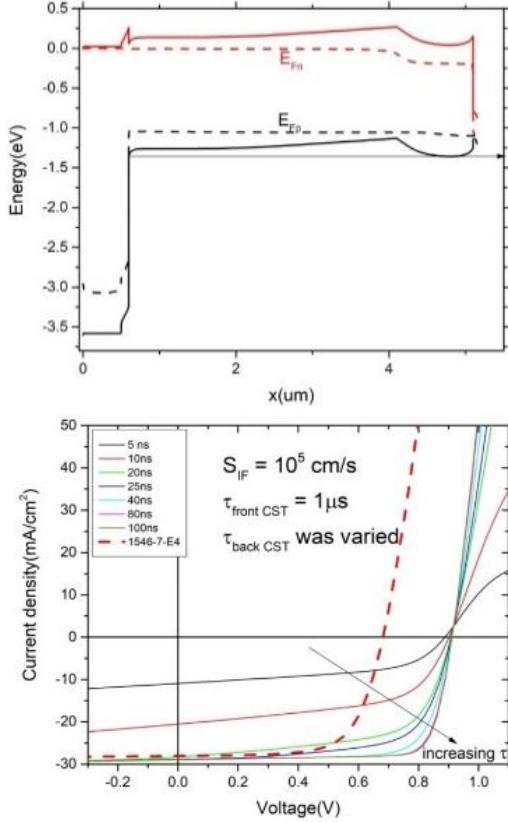


Fig. 9. SCAPS model of arsenic doped device and effect of increasing interface recombination velocity at the MZO/CdSe_xTe_{1-x} interface.

efficiently inter-diffuses the deposited layers as per initial assumptions. This would also lead to diffusion of interstitial arsenic from the doped layer into the undoped layer of CdSe_xTe_{1-x} leading to efficient doping and a graded doping profile which has been seen using scanning capacitance microscopy.

Energy Dispersive X-ray Spectroscopy (EDS) elemental maps showing in figure 7 for the part of the cross-section TEM image that is showing in figure 6 with the dotted box, does not show evidence of any arsenic clusters. More extensive measurements have been performed using high resolution STEM and EDS characterization on various deposited films and devices. No evidence of arsenic clusters in deposited films has been seen. This suggests that the arsenic is deposited in either monoatomic, dimer, tetramer, or AX center in the as deposited film. It is evident from free energy calculation; only monoatomic interstitial arsenic can diffuse during the CdCl_2 treatment diffusion. Presence of dimers, tetramers and AX centers cannot be easily identified using electron microscopy and therefore spectroscopy-based methods are being currently utilized to further this understanding.

The EDS line scan shown in figure 8 is for the line and direction shown in figure 6 with an arrow. There are no noticeable disruptions observed in the line scan and the proportion of selenium, cadmium and tellurium appear uniform

across the film. No evidence of significant amount of copper was observed in these films using EDS or SIMS.

IV. DISCUSSION

All the parameters predicted by published models that were deemed necessary to achieve device efficiency greater than 24% are met. In agreement with model predictions, device results show an increase in open-circuit voltage with arsenic doping. However, the improvement in efficiency and open-circuit voltage to the full potential of these device parameters have not been achieved. A SCAPS model based on the experimental values for the doping profile and recombination lifetimes was created. Low performance of the devices can be attributed to unfavorable band bending and a defective back CdSeTe with high interface recombination. It was observed that as the recombination lifetime at the back of the device was decreased, a reduction in J_{SC} was observed and a simultaneous increase in interface recombination at the back lowered the V_{OC} .

V. CONCLUSIONS

Devices were fabricated by sublimating CdSe_xTe_{1-x} films with three doping conditions *viz.* no dopant, Cu doping and As doping. CdSe_xTe_{1-x} was chosen as the absorber based on DFT model that showed it to be favorable for arsenic doping. Increase in average V_{OC} of about 350 mV from undoped sample and about 100 mV as compared to copper doped sample was observed for a set of 25 samples of each. A very high recombination lifetime of over 1 μ s and surface recombination velocity of <100 cm/s was measured. CV showed the highest carrier concentration of $4.2 \times 10^{15} \text{ cc}^{-1}$ while SCM showed that the carrier concentration exceeding $1 \times 10^{18} \text{ cc}^{-1}$, indicating very high dopant activation. We report the best material parameters for polycrystalline Cd(Se)Te. Full performance potential is not achieved for such device and based on the SCAPS model it can be attributed to poor quality of as-deposited arsenic doped CdSe_xTe_{1-x} film. Efforts are being made to remove this defect laden CdSe_xTe_{1-x}:As layer to further improve performance.

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