

MOCVD Deposition of Group V Doped CdTe in Sublimated CdTe and CdSeTe Devices

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Abstract — Increasing doping density in CdTe absorbers remains one of the most promising avenues for increasing the open-circuit voltage (V_{oc}) of photovoltaic devices. This work aimed to develop methods for quickly incorporating group V as a p-type dopant using Metal-Organic Chemical Vapor Deposition (MOCVD) precursor injection. CdTe:N was deposited by MOCVD injection during sublimation of CdTe. CdTe:As was deposited via MOVCD onto an existing sublimated CdSeTe layer to produce doped CdSeTe/CdTe devices. Nitrogen doping resulted in increased external quantum efficiency and an improved diode curve as compared to a device exposed to cadmium overpressure without the presence of MOVCD nitrogen.

Index Terms- Cadmium compounds, photovoltaic cells, nitrogen, II-VI semiconductors materials, solar energy

I. INTRODUCTION

Thin film CdTe photovoltaic panels have demonstrated very low cost of photovoltaic electricity generation, particularly for utility scale applications [1]. With improvements in device fabrication processes, as well as module design, research scale small devices have recorded efficiencies as high as 22.1% [2] and commercial modules have achieved 18.6% [3]. The average production efficiency of such modules has steadily increased from 13.5% in 2014 [4] to 16.2% in 2016 [5]. Continued improvements in module design are expected to drive down the cost of CdTe-generated electricity to as low as $\phi 1/\text{kWh}$ in the near future, while the national average cost of electricity in the United States remains at $\phi 11/\text{kWh}$ [6].

CdTe remains one of the most important thin film photovoltaic technologies and is currently the only thin film technology with annual module production exceeding 3GW/yr [7]. Further increasing the efficiency of devices without substantially increasing the manufacturing cost is key to ensuring CdTe photovoltaics remains a viable electrical energy solution. One way of increasing the efficiency of thin-film photovoltaic devices is to improve the open-circuit voltage. The authors have previously demonstrated devices with an open-circuit voltage (V_{oc}) of 854 mV and 19.1% photovoltaic conversion efficiency for polycrystalline thin-film

CdSeTe/CdTe using high deposition temperatures, a graded CdSeTe/CdTe interface, and a Te layer in the back contact [8]. This study aimed to improve upon this device structure by incorporating high levels of group V doping in the CdTe layer using MOCVD injection.

Effective doping of the CdTe material is necessary in order to achieve device efficiencies in excess of 20%. Colorado State University's current highest efficiency device, which was copper-doped, had a hole concentration of $\sim 10^{14} \text{ cc}^{-1}$. Group V elements such as nitrogen and arsenic are ideal candidates for p-type doping experiments in CdTe. Colorado State University's (CSU) current dopant, copper has significant interstitial diffusion, which limits the amount of copper doping that is possible before it begins to have detrimental effect on the device performance. This work aimed to achieve hole densities that met or exceeded the doping levels currently shown by copper doping methods. The Centre for Solar Energy Research, using MOVCD methods, has previously shown hole densities as high as $4 \times 10^{15} \text{ cc}^{-1}$ in CdTe films using MOCVD injection of arsenic precursors [9,10].

II. EXPERIMENTAL DETAILS

The cells used in the study were deposited on NSG TEC 10 soda lime glass coated with fluorine-doped tin oxide (FTO), a transparent conducting oxide (TCO). An $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ (MZO) buffer layer was deposited using RF sputter deposition. CdSeTe films were sublimated using an optimized deposition process in a nitrogen ambient at 40 mTorr. The substrate was heated to 530°C before starting the sublimation of CdTe. The temperature of the substrate was measured in-situ using a pyrometer located outside the preheating station.

The CdTe films were sublimated using an optimized deposition process in an N_2 ambient at 40 mTorr using co-sublimation hardware at Colorado State University as shown in figure 1. The CdTe vapor source was heated to 560°C and CdTe films of $1.7 \mu\text{m}$ thickness were deposited. The cadmium source temperature was swept from 135°C to 260°C. Argon was bubbled through the nitrogen precursor, *tert*-Butylamine, and injected into the sublimation source just above the cadmium

source. The flow of argon bubbled through precursor was swept from 1 to 80 sccm.

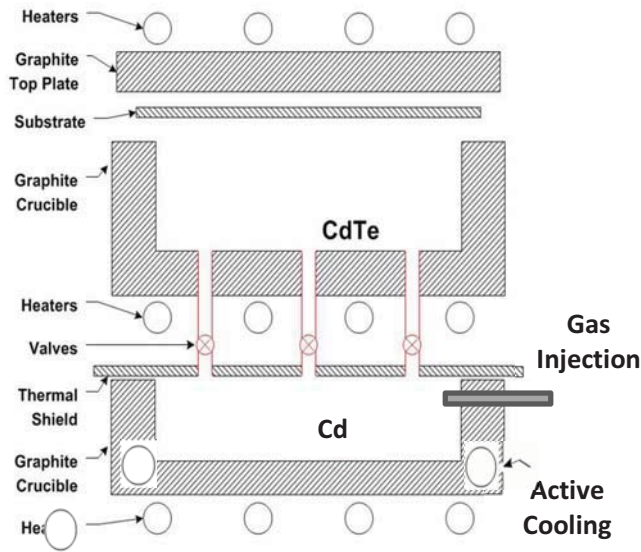


Figure 1: Co-sublimation hardware configuration used in the MOCVD experiments

Figure 2 shows a schematic of the full device structure. The small area devices were delineated using a mask and bead blasting to fabricate 25 devices on the substrate. The devices each had an area of $\sim 0.60 \text{ cm}^2$.

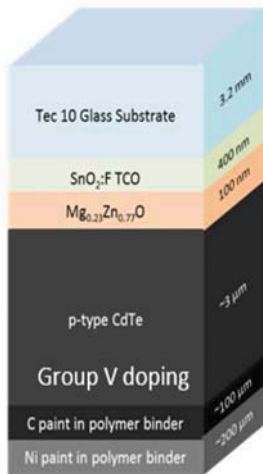


Fig. 2. Schematic of the doped CdTe absorber device. (not to scale).

III. RESULTS

Figure 3 shows the Current Density vs Voltage (J-V) curves for the CdTe devices under various cadmium overpressures

with no nitrogen injection. As the cadmium source is heated to greater temperatures, the cadmium partial pressure increases and all J-V parameters (V_{oc} , J_{sc} , fill-factor) progressively degrade. Further increasing the cadmium source temperature causes the cadmium vapor pressure to climb so high that virtually all CdTe deposition eventually halted.

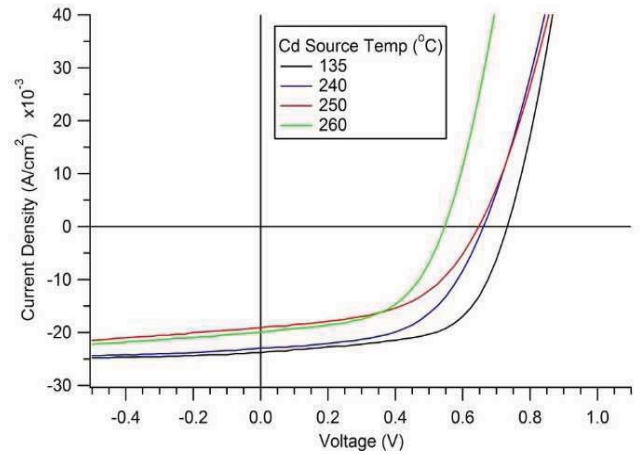


Figure 3: J-V curves showing the effects of increasing Cd overpressure

The nitrogen precursor was then injected into the co-sublimation source using argon as the carrier gas. As the flow-rate increased, the electrical performance that was lost due to the cadmium overpressure was recovered, as seen in figure 4. Note that the 260°C Cd source temperature curve is the same in figures 3 and 4, and is useful for observing the degradation of performance as the Cd temperature is increased and the subsequent performance recovery as the precursor gas flow is increased. The V_{oc} , J_{sc} , and fill-factor improved when just 1 sccm of nitrogen is injected and further improved as the flow rate was increased to 40 sccm. After 40 sccm, no further improvement in device performance was observed.

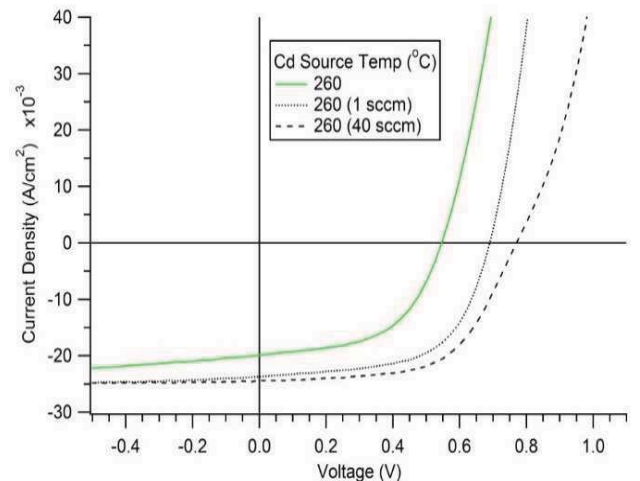


Figure 4: J-V curves showing the effects of increasing N injection in the presence of Cd overpressure

Table 1 summarizes the device performance for the CdTe devices under the varying cadmium overpressure and nitrogen injection conditions. With 40 sccm of nitrogen injection, the device V_{OC} increased by more than 220mV, the fill-factor increased by nearly 6% and the J_{SC} increased by 4.5 mA/cm². The best performing device in this experiment had a photovoltaic conversion efficiency of 11.3%

TABLE 1
DEVICE PERFORMANCE FOR CdTe DEVICES UNDER
VARYING CADMIUM OVERPRESSURE AND NITROGEN
INJECTION CONDITIONS

Cd Source Temp	V_{oc} [mV]:	Fill Factor [%]:	J_{sc} [mA/cm ²]:	Efficiency [%]:
135	733	60.6	23.8	10.5
240	662	55.2	22.9	8.4
250	648	51.2	19.1	6.3
260	547	54.3	19.9	5.9
260 + 1 sccm N	691	60.2	23.7	9.8
260 + 40 sccm N	771	60.0	24.4	11.3

When comparing the Capacitance-Voltage (C-V) plots for the CdTe devices under varying nitrogen MOCVD injection rates, a sizable increase in the doping density is noted when even a small amount of nitrogen is injected as compared to the undoped (0 sccm N) case (figure 5.)

The marginal benefit of adding additional nitrogen decreases as only a small increase in the belly of the C-V curve is seen as nitrogen precursor flow increases from 5 to 40sccm. There is also an accompanying decrease in the depletion width, as the nitrogen flow increases, which may serve as another indicator of doping.

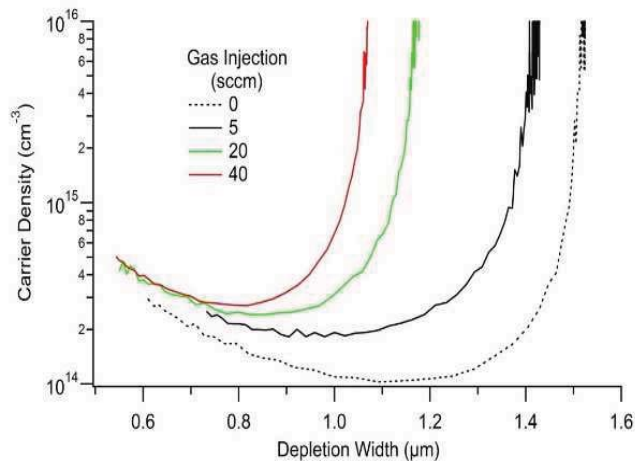


Figure 5: C-V profile for CdTe devices with varying nitrogen MOCVD injection rates

Similarly, figure 6 shows a considerable increase in the spectral response as nitrogen dopant injection is increased. Once again, the marginal benefit of adding additional nitrogen quickly decreases as after the large QE gains when going from undoped to 10 sccm of gas flow, there is very little increase in quantum efficiency as the flow rate increases. This increase in

QE aligns with the increase in J_{SC} noted in the J-V curves seen earlier.

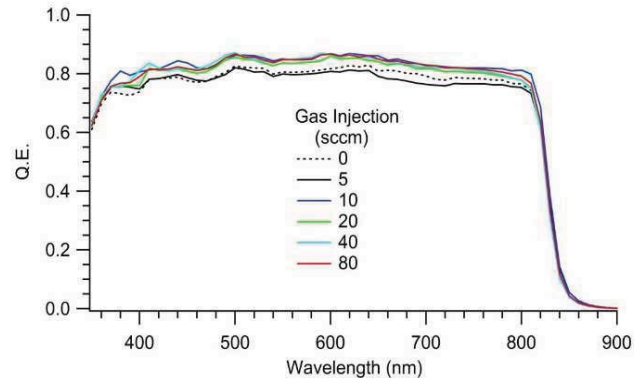


Figure 6: External Quantum Efficiency profile for CdTe devices with varying nitrogen MOCVD injection rates

IV. DISCUSSION

The introduction of cadmium overpressure without the addition of the MOCVD gas injection is detrimental to device performance. This can be explained by the fact that CdTe deposited by sublimation is naturally p-type due to cadmium vacancies [11]. As the cadmium overpressure increases, the number of cadmium vacancies decrease, as does the p-type doping in the bulk CdTe. For the group V doping strategy to be effective, the cadmium overpressure must produce enough Te vacancies, which are then substitutionally replaced by a nitrogen atom to overcome the loss of the inherent p-type doping. As the flow rate of nitrogen is increased, the J-V parameters universally improve when compared to the 260°C cadmium overpressure only case, providing strong evidence that nitrogen doping is occurring.

The C-V plots show a continual trend towards higher doping densities as the MOCVD gas flow rate is increased. The belly of the C-V curve shows a small increase from 1E+14 to 4E+14 carriers/cc⁻¹. It can also be seen that when no nitrogen gas is flowed, the films are nearly fully depleted; the films were 1.7μm and the depletion width was 1.5μm. As the gas flow rate increases, the depletion width shrinks to ~1μm, indicative of greater doping.

The EQE plot shows an increased spectral response for devices with nitrogen at all wavelengths below 840nm which corresponds with the CdTe bandgap of 1.49eV. After this initial increase, there are no discernable QE gains from further increasing the nitrogen flow, in fact there appear to be small losses at the very short and very long wavelengths as the gas injection rate exceeds 10sccm.

While the results presented in this paper have been for nitrogen-doped CdTe, additionally experiments were performed using MOCVD of an arsenic precursor with graded CdSeTe/CdTe films. The CdSeTe composition used for this

study had 40% Se in the source material and as-deposited films had a band-gap of 1.39-1.40 eV from transmission measurements. 1.5 μm of CdSeTe were deposited at Colorado State University (CSU) and then shipped to Swansea University (SU). At Swansea, the CdTe was deposited onto the CdSeTe layer in a conventional horizontal MOVCD reactor at atmospheric pressure of H_2 carrier gas. The CdTe was deposited at 390°C and incorporated $1\text{-}10 \times 10^{18} \text{cm}^{-3}$ Arsenic [10]. The films were grown to approximately 2 μm thick. The precursors for cadmium, arsenic, and tellurium were dimethylcadmium, *tris*-dimethylaminoarsenic and diisopropyltelluride. The samples were then sent back to CSU, where a back electrode was added, and the films were finished into devices. At present, no device improvement was noted. It is suspected that the lack of improvement is because the films were fabricated in two locations, in Fort Collins, Colorado, USA and St. Asaph, UK. During transit the samples may have been exposed to atmosphere and moisture which likely formed unknown interfaces and introduced possible contaminants. Further work to repeat and optimize these experiments are underway.

V. CONCLUSIONS

Improvement in doping of the CdTe absorber layer by using group V elements can lead to enhanced photovoltaic conversion efficiency. Doping remains one of the most promising methods for increasing the V_{OC} and conversion efficiency of CdTe devices. Using MOCVD methods, nitrogen was successfully incorporated into growing CdTe films. C-V measurements indicate that nitrogen successfully doped the CdTe p-type. The subsequent improvement of quantum efficiency and all J-V parameters with nitrogen injection resulted in a device with photovoltaic conversion efficiency of 11.3%

ACKNOWLEDGEMENTS

The CSU authors thank support from NSF's Accelerating Innovation Research, DOE's PVRD SIPS and NSF's Industry/University Cooperative Research Center programs. The SU authors wish to thank support from the European Regional Development Fund, through the Welsh

Government, for the 2nd Solar Photovoltaic Academic Research Consortium (SPARC II).

REFERENCES

- [1] N. M. Haegel *et al.*, "Terawatt-scale photovoltaics: Trajectories and challenges," *Science* (80-.), vol. 356, no. 6334, 2017.
- [2] M. A. Green *et al.*, "Solar cell efficiency tables (version 50)," *Prog. Photovoltaics Res. Appl.*, vol. 25, no. 7, pp. 668–676, 2017.
- [3] W. Eric, "Exclusive: First Solar's CTO Discusses Record 18.6% Efficient Thin-Film Module," *Greentech Media*, 2015. [Online]. Available: <http://www.greentechmedia.com/articles/read/Exclusive-First-Solars-CTO-Discusses-Record-18.6-Efficient-Thin-Film-Mod>.
- [4] S. K. David Brady, Steve Haymore, "First Solar, INC. Announces First Quarter 2014 Financial Results," Tempe, AZ, 2014.
- [5] S. K. Steve Haymore, "First Solar, Inc. 2016 First Quarter Financial Results," Tempe, AZ, 2016.
- [6] U. S. E. I. A. (EIA), "Electric Power Monthly with Data for November 2015," 2016.
- [7] I. Fraunhofer Institute for Solar Energy Systems, "Photovoltaics Report," 2018.
- [8] Munshi, Amit, J. Kephart *et al.*, "Polycrystalline CdSeTe / CdTe Absorber Cells With 28 mA/cm² Short-circuit Current," *IEEE*, vol. 8, no. 1, pp. 310–314, 2018.
- [9] G. Kartopu *et al.*, "Progression of metalorganic chemical vapour-deposited CdTe thin-film PV devices towards modules," *Prog. Photovolt Res. Appl.*, vol. 24, no. September 2015, pp. 283–291, 2015.
- [10] G. Kartopu, V. Barrioz, S. Monir, D. A. Lamb, and S. J. C. Irvine, "CdTe thin film solar cells produced using a chamberless inline process via metalorganic chemical vapour deposition," *Thin Solid Films*, vol. 578, pp. 93–97, 2015.
- [11] K. K. Chin, "p-Doping of CdTe Polycrystalline Thin Film Based on Cd Vacancy Theory," 61357058, 2012.