Advanced Co-sublimation of Low Bandgap $CdSe_xTe_{1-x}$ Alloy to Achieve Higher Short-Circuit Current

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Abstract — **Over 19% device efficiency with over 28 mA/cm^2 short-circuit current density has been achieved with thin-film using CdSeTe/CdTe graded absorber. A deep pocket sublimation source was used to deposit CdSeTe alloy. However, cross-section line scan using energy dispersive X-ray spectroscope showed that actual Se incorporation in the absorber films was much lower than the feed stock composition. Further lowering the band-gap of deposited CdSeTe films will further improve absorption of higher wavelengths leading to higher short-circuit current density. To overcome the limitation preferential sublimation of CdSeTe, advanced co-sublimation of Se and CdTe to achieve higher Se incorporation and lower bandgap is presented.**

***Index Terms*-Cadmium compounds, photovoltaic cells, selenium, alloying, II-VI semiconductor materials, solar energy**

I. INTRODUCTION

Thin-film CdTe photovoltaic technology has demonstrated a steep progress in the past several years. It has also been recognized as an important technology for low cost utility scale electricity generation [1]. With advances in research and commercial product development, research scale devices have recorded efficiencies as high as 22.1% [2] while commercial modules have achieved 18.6% [3] efficiency. The average production modules efficiency has increased from 13.5% to 16.2% between 2014 and 2016 [4], [5]. In addition, with recent developments in module technology for CdTe photovoltaics the cost of utility scale solar is projected to get as low as ¢1/kWh in the near future while the average cost of electricity in the U.S. is ¢11/kWh [6]. Further improving device efficiency without substantial increase in manufacturing cost is desirable to establish CdTe photovoltaics as a sustainable energy solution globally.

Authors have demonstrated 18.7% CdTe device efficiency using an optimized fabrication process using a scalable process on a commercial soda lime glass. These devices had short-circuit current density over 27 mA/cm^2 with antireflection coating [7], [8]. When a similar CdTe thin-film device was graded with selenium to form a lower bandgap CdSeTe allow at the front interface, a short-circuit current density of 28.4 mA/cm^2 was measured without the use of antireflection coating [9]. This clearly shows the advantage of using a lower band-gap CdSeTe alloy to grade CdTe. The alloy feedstock used for deposition of this CdSeTe alloy had 20% CdSe content. However, film composition had lower incorporation of Se than the feedstock composition. This is substantially lower than the anticipated amount.

According to Brill *et al*, the lowest bandgap of CdSeTe can be achieved with 40% Se incorporation in the film that would give a bandgap of ~1.35 eV [10]. Such a low band-gap absorber with optimized grading optimized grading the absorber layer would lead to much higher short-circuit current and thus improve device efficiency. But utilizing a higher Se composition is not conveniently viable for this purpose. To overcome this limitation authors have identified a co-sublimation of Se and CdTe to form CdSeTe alloy on a glass substrate to achieve higher Se incorporation in the absorber film. A similar effort has been reported by Swanson *et al* where Se and CdTe were co-sublimated [11]. This experiment is more controlled deposition of CdSeTe since more advanced co-sublimation hardware is utilized for this study. The advanced co-sublimation hardware has an inbuilt shutter mechanism that can precisely control the ratio of Se and CdTe. Using this method, it is possible to vary the deposition rates of Se and CdTe while keeping the source temperature constant.

II. EXPERIMENTAL

The cells fabricated for this study were deposited on NSG TEC 10 soda lime glass coated with fluorine-doped tin oxide (FTO), a transparent conducting oxide (TCO). An $Mg_xZn_{1-x}O$ (MZO) buffer layer instead of the more common CdS was deposited using RF sputter deposition. CdSeTe films were sublimated using an optimized deposition process followed by sublimation of the CdTe layer. The $CdSe_xTe_{1-x}$ (CdSeTe) layer was deposited using advanced co-sublimation hardware (figure 2). This was followed by CdTe deposition and $CdCl_2$ passivation treatment. All depositions were performed in-line without breaking vacuum using the advanced research deposition system (ARDS) at Colorado State University [12]. The substrate was heated to 520ºC before starting the sublimation of CdSeTe. The temperature of the substrate was measured in-situ using a pyrometer located outside the preheating station.

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CdSeTe alloy was deposited using the advanced co-sublimation hardware that was designed and developed at Colorado State University. This hardware comprises a primary CdTe sublimation source that is assembled on top of a co-sublimation source [13]. The two sources are separated by a ceramic sheet and heating of these sources are independently controlled. The co-sublimation source has an advanced shutter mechanism that is controlled externally using a visual user interface with a resolution of ~1 µm. This shutter has very fine slots machined in a graphite plate to precisely control the ratio of CdTe and CdSe vapors. In addition to the two heaters for sublimation, an additional substrate heater is placed on top of the CdTe source to control the temperature of the substrate during deposition.

The Se source was heated to 280ºC and 320ºC for two different experiments. ~300 nm films with varying shutter position were deposited on TEC10 glass to measure the band-gap using transmission and Tauc plot.

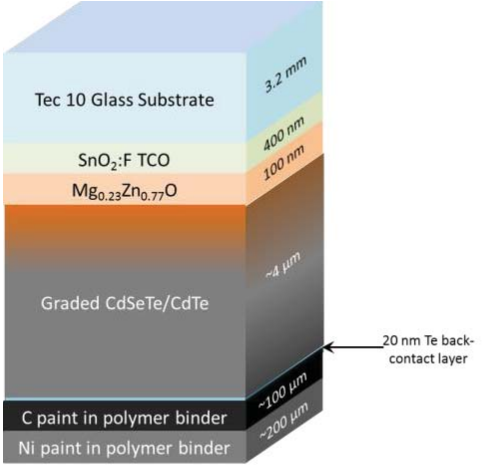

Fig. 1. Schematic of the CdSeTe/CdTe graded absorber device. (not to scale).

For device fabrication, CdTe source was maintained at 555ºC for fabrication of CdSeTe/CdTe devices. ~1.5µm film of CdSeTe with varying Se compositions was deposited by controlling the Se source shutter. After deposition of CdSeTe, the sample was moved to the CdTe sublimation vapor source and a film ~3.3 µm thick was deposited. The CdTe sublimation source temperature was maintained at 555ºC. The CdSeTe/CdTe interface in the cells was formed after an aggressive $CdCl_2$ treatment, which is known to promote recrystallization and grain growth. The passivation treatment was performed for 600 seconds. This temperature gradient was maintained to ensure a thin film of $CdCl_2$ was deposited on the substrate. The CdSeTe/CdTe film stack was exposed to $CdCl_2$ vapor in vacuum to promote the inter-diffusion of the CdSeTe and CdTe layers.

The films were cooled in air and excess $CdCl_2$ deposited on the substrate was rinsed using deionized water and dried using pressurized flow of ultrahigh purity nitrogen gas on the surface.

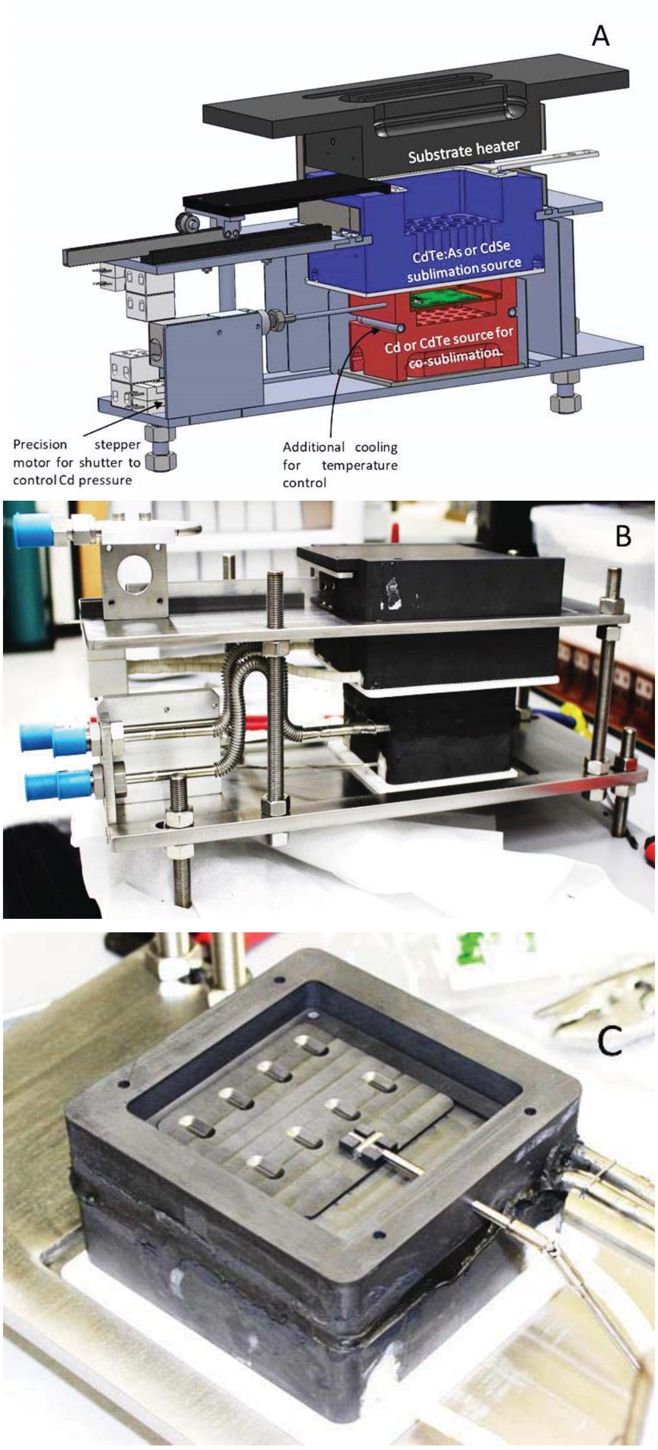

Fig 2. (A) CAD model of the advanced co-sublimation hardware (B) photograph of the co-sublimation hardware (C) photograph of the bottom source of co-sublimation hardware showing the shutter for compositional control

Thereafter, the films were heated to ~140ºC, and CuCl was deposited on the film surface for 100 seconds with the CuCl source temperature set at 200ºC and the substrate heater at 170ºC. This was followed by 220 seconds of annealing at 220ºC, both in vacuum to form a Cu back contact. A 20-nm Te film was evaporated to improve the back-contact. Carbon and nickel paint in a polymer binder where then sprayed on these films to form the back electrode.

Figure 1 shows a schematic of the full device structure. The individual cells were delineated using a mask and bead blasting to fabricate 25 small scale devices on the substrate. The devices each had an area of ~0.65 cm^2.

III. CHARACTERIZATION

Transmission measurements and tauc plot were used to measure the band-gap of the deposited CdSeTe films on TEC10 glass substrates. Various sublimation source temperatures were investigated out of which two most representative results are shown in figure 3. In the first case the CdTe deposition source was maintained at 555ºC while Se source temperature was maintained at 320ºC and films with various shutter bottom source positions were deposited. 70% to 100% open shutter did not show any substantial change in band-gap which was understood to be due to very high Se vapor pressure. Sweeping from 60% to 0% shutter position a change in band-gap of CdSeTe films that was similar to reported results was observed [10], [14], [15]. Using a lower Se source temperature of 280ºC and maintaining the CdTe temperature at 555ºC, a better control over the band-gap was observed as seen in figure 3 (bottom). It must be noted that the lowest band-gap of CdSeTe achieved using this method was ~1.40 eV which is comparable to reported value by Muthukumarasamy et al [14].

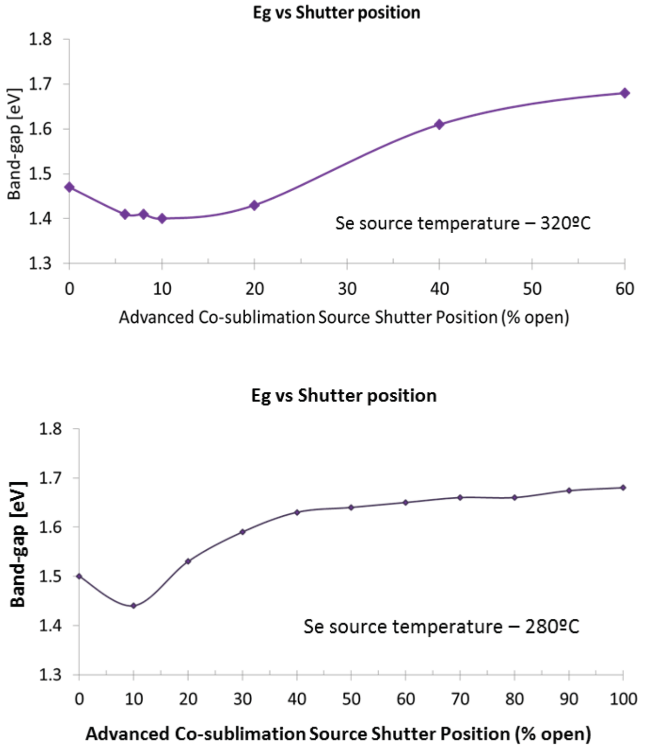

Fig 3. Sweep of CdSeTe band-gap using shutter positions in the advanced co-sublimation source (Top) Se sublimation source at 320ºC (Bottom) Se sublimation source at 280ºC

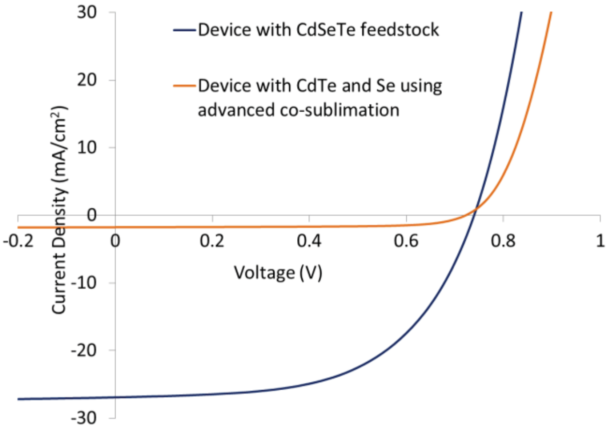

Fig 4. Current density vs voltage comparison of CdSeTe/CdTe devices with CdSeTe deposited using advanced co-sublimation vs CdSeTe feedstock with similar band-gap

As mentioned earlier, using the advanced co-sublimation hardware CdSeTe films with a band-gap of ~1.40 eV were deposited on MgZnO buffer layer to fabricate full devices. Similar devices were fabricated using CdSeTe with comparable band-gap using CdSeTe feedstock. A very large difference in performance of these devices was observed as can be seen in figure 4. Although CdSeTe using both methods had a comparable band-gap, device performance using co-sublimated CdSeTe was very poor with the low short-circuit current (J_{SC}) being the most distinct difference. The performance parameters of both of these devices are summarized in table 1.

TABLE I: SUMMARY OF J-V PARAMETERS OF DEVICES IN FIG 4

	J_{SC} (mA/cm^2)	V_{OC} (mV)	% Fill-Factor	% Efficiency
CdSeTe feedstock	26.9	740	56.8	11.31
CdSeTe cosublimated	1.8	722	69.7	0.89

IV. DISCUSSION

Practical application of advanced co-sublimation source for deposition of ternary alloy is demonstrated. Thin-films of CdSeTe ternary alloys with varying band-gap can be sublimated with good control using this hardware. The goal of such a co-sublimation was to achieve CdSeTe with a band-gap lower than 1.40 eV and improve J_{SC}. While the co-sublimation hardware was successfully able to vary the band-gap of the deposited films, a major limitation was encountered. Although lowest band-gap theoretically predicted for CdSeTe is ~1.36 eV, after multiple experimental iterations CdSeTe with such as low band-gap was not achieved. In a comparable study, Muthukumarasamy *et al* achieved the lowest band-gap of 1.39 eV [14].

The devices fabricated using the co-sublimated CdSeTe also gave a lower device performance than a similar device that had CdSeTe deposited straight from the feedstock. This is believed to be due to the difference in arrival ratios of the vapor species from the source material as the interface is formed and formation of undesired phases in the deposited films. Some evidence to justify this can be found in characterization presented by K.J. Hayes [16]. In this study it has been shown as-deposited CdSeTe films have large concentrations regions of zinc blende and wurtzite phases. While CdCl2 passivation treatment transforms all the deposited material into zinc blende structure, the presence of even a very small wurtzite phase is understood to be highly detrimental to CdSeTe photovoltaic device performance. It has also been reported that beyond ~45 At% of Se in the film, even after $CdCl_2$ passivation treatment, there can be a sharp increase in presence of wurtzite phase in the deposited film. This may explain the reason for lower device performance using co-sublimated CdSeTe when compared against a similar device fabricated using CdSeTe feedstock.

V. CONCLUSIONS

$CdSe_xTe_{1-x}$ films with varying composition and thus varying band-gap can be efficiently fabricated using the advanced co-sublimation hardware. Films with varying band-gap have been demonstrated while keeping the deposition source temperatures constant and only varying the so-sublimation shutter position to change deposition ratio of CdTe and Se. The intended goal of fabricating theoretically predicted 1.36 eV was not successful and the lowest band-gap of 1.40 eV was demonstrated. CdSeTe/CdTe graded absorber band-gap devices with similar 1.40 eV band-gap using two different sublimation methods, co-sublimation and sublimation from straight feedstock, were tested. Results show that similar devices fabricated using different sublimation methods have a large difference in performance and based on literary evidence such a difference in performance can be due to difference in arrival ratio of species being deposited and formation of undesired phases such as wurtzite. Further characterization of these films is required to reinforce reasoning indicated by literary evidence.

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