Advanced co-sublimation hardware for deposition of graded ternary alloys in thin-film applications

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***Abstract* — CdTe photovoltaic devices with efficiency over 22% have been demonstrated. Sublimated CdTe photovoltaics with efficiency over 19% have been reported using graded alloying of Se in CdTe absorber films. Grading of alloy films has been identified as an important characteristic to achieve higher device performance using more complex device structures. An advanced co-sublimation source has been designed and developed to deposit highly controlled CdTe based ternary alloys. An advanced shutter mechanism enables changing the composition of the deposited films during sublimation. The hardware used for advanced co-sublimation and initial materials characterization is presented in this study.**

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

I. Introduction

Thin-film CdTe photovoltaics is an important technology for utility scale electricity generation. It has been recognized as one of the most realistic technologies for large scale, affordable and sustainable energy solution [1]. Research scale single junction devices with efficiency up to 22.1%[2] have been demonstrated while commercial modules with efficiency up to18.6% have been fabricated [3]. A very competitive module cost of ¢40/watt was realized in 2013 for large scale manufacturing by First Solar Inc. [4]. Current lowest cost of electricity using CdTe photovoltaics has been reported to be ¢3.8/kWh [5]. Further improvements in efficiency without substantial increase in manufacturing cost would lead to further reduction in the cost of electricity.

One of the methods to achieve higher efficiency photovoltaic devices is to create a multijunction or a tandem device. In such a device structure, more than one set of p-n junctions are stacked together. In such a structure, each junction is optimized to operate in a different wavelength of light, thus increasing the overall output. Using this concept, 5 junction cell with efficiency over 38% has been demonstrated by National Renewable Energy Laboratory (NREL) [2].

Sublimated CdTe devices with graded band-gap [6] have shown higher device performance than comparable CdTe-only single band-gap devices [7]. For fabrication of CdTe-based affordable and scalable photovoltaic devices with tandem or multijunction structure CdMgTe or CdZnTe alloys for high

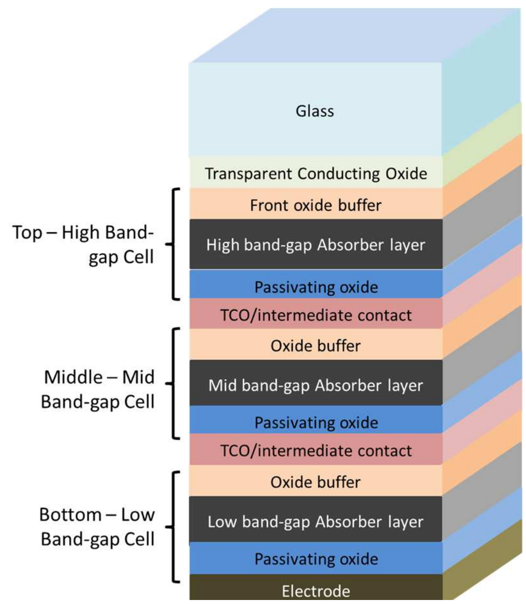

Fig. 1. Conceptual layout of a CdTe-based multijunction photovoltaic device

band-gap top cell are considered to be critical. A conceptual layout of such a multijunction structure is shown in figure 1. These alloys would form a high band-gap top cell in a

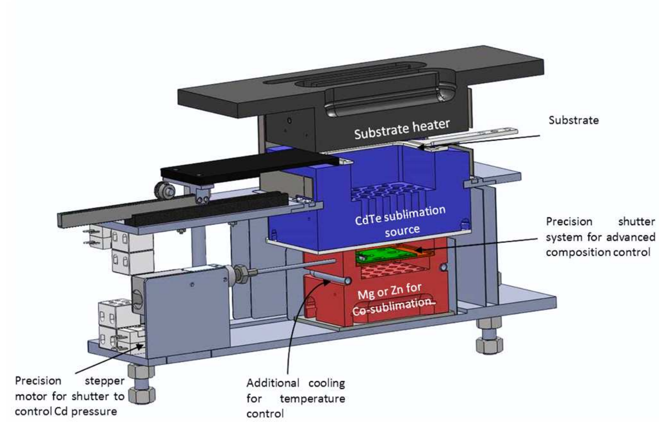

Fig. 2. Computer Aided Design (CAD) model of the advanced co-sublimation source for CdMgTe or CdZnTe ternary alloy deposition.

multijunction device structure with a band-gap >1.7 eV. However, fast rate sublimation of CdMgTe or CdZnTe is difficult due to preferential sublimation of Mg and Zn. To overcome this limitation, a co-sublimation hardware has been developed at Colorado State University [8]. While this hardware effectively co-sublimated CdMgTe and CdZnTe ternary alloys, there was a further necessity identified to precisely control the deposition ratio of CdTe and Mg/Zn deposition. This control can be achieved by altering the temperature of the Mg/Zn sublimation source. However, the change in deposition rates is very slow with such a process and control is very limited.

To further advance the co-sublimation capabilities, advanced co-sublimation hardware was developed. This hardware was designed to have a highly controlled shutter mechanism to alter the deposition rate of Mg/Zn by only adjusting the shutter position while holding the temperature constant. Such control of deposition rate provided the subtle control of sublimation required for fabrication of graded thin-films. Controlled grading of thin-films is critical for efficient fabrication of the photovoltaic devices with suitable band alignment for respective applications.

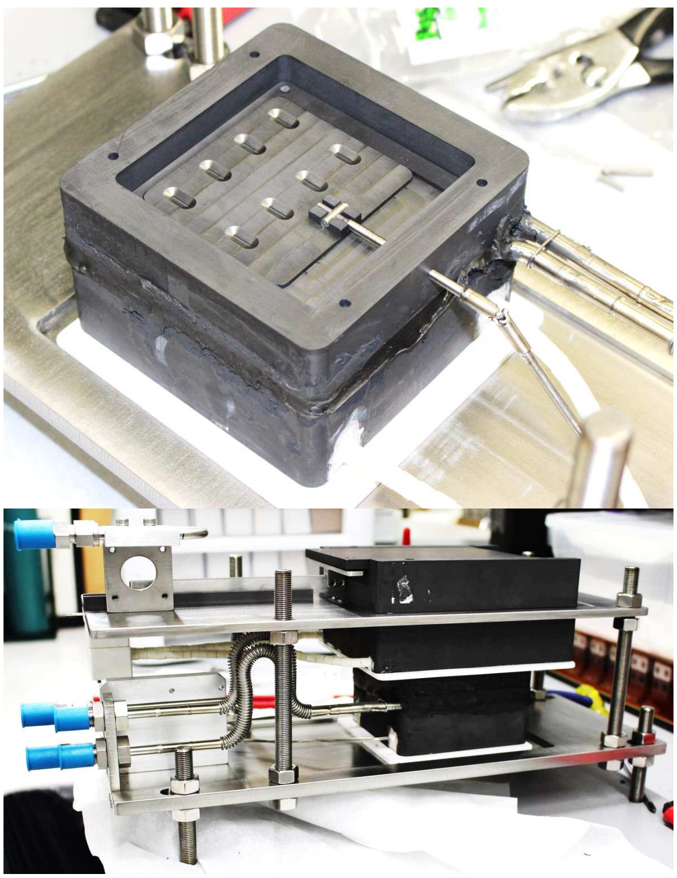

Fig. 3. Images showing the shutter mechanism in the bottom Mg/Zn source (top) and the assembly of top and bottom sublimation source (bottom). Active cooling elements and ceramic shields for better temperature control can be observed in both images.

II. Experimental

A computer aided design (CAD) model of the advanced co-sublimation source is shown in figure 2 and most important components of the assembly are labeled. The assembly consists of a bottom (secondary) source that is designed to hold the co-sublimation metal i.e. Mg or Zn. This source has a nichrome heating element. The top (primary) sublimation source for CdTe deposition is aligned on top of the Mg/Zn source and is shielded using a ceramic sheet with patterned holes to enable transfer of material and limit the conduction of heat. The top sublimation source usually operates at a substantially higher temperature than the bottom source. This often causes the bottom Mg/Zn source to operate at higher temperature than the desired set point. To get a better temperature control of the Mg/Zn sublimation source, an active cooling line is installed in the bottom source as can been seen in figure 2. Images of the bottom source and assembly of both these sources can be seen in figure 3.

The hardware described here is controlled electronically using a LabView program. The shutter mechanism is controlled using a high precision stepper motor with a resolution of ~1 μm. The LabView program allows gradually opening or closing the shutter to enable changing the proportion of CdTe to Mg/Zn. Completely shutting the Mg/Zn source shutter causes only CdTe film to deposit that had been verified using band-gap measurements and energy dispersive X-ray spectroscopy (EDS) measurements. Using the advanced co-sublimation hardware and associated LabView visual interface, graded films were deposited with varying proportions of Mg/Zn from front to the back of the film.

III. Results

The capability of the advanced co-sublimation hardware was used to fabricate graded CdZnTe absorber. The CdZnTe absorber is a suitable material for top cell in a two or three junction solar cell [9]. The band-gap of CdZnTe can be varied by controlling the zinc incorporation in CdTe [10], [11].

The Tec10 glass substrate was heated to ~500ºC and transferred over to the advanced co-sublimation source. At the start of the deposition, the bottom source shutter was in a closed position. A graded CdZnTe absorber was obtained by opening the shutter by 10% increments per 20 seconds. The total deposition time was 220 seconds. In the advanced co-sublimation source, the top source containing CdTe and the bottom source with zinc were maintained at 555ºC and 380ºC respectively.

A schematic of fabricated CdZnTe absorber with graded zinc is shown in the figure. 4.

To investigate the composition of the deposited film, Glancing Angle X-ray Diffraction (GAXRD) was carried out using a Bruker D8 system (λ = 1.5406 Å). The glancing angle was set to 3º and the detector was swept from 20º to 80º with an increment of 0.02ºper second. The diffraction pattern obtained from the graded CdZnTe absorber is shown in figure 4.

The position of the diffracted peaks from the graded absorber was between the CdTe and ZnTe peaks (ICDD #00-

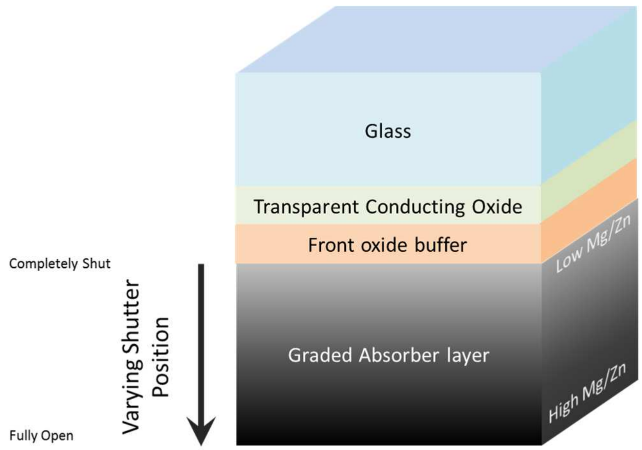

Fig. 4. Fabricated absorber structures with graded zinc/magnesium

015-0770 for CdTe and #00-015-0748 for ZnTe). The widths of all the peaks were broad suggesting variation of zinc in CdZnTe absorber. The preferred orientation of the deposited absorber was along the {111} plane. Based on the first peak (shown in figure 5), the estimated composition of the zinc varied from 5% to 60% by atomic percentage in the absorber.

Similar fabrication of CdMgTe film with varying Mg proportion during deposition using precision shutter position was also performed. These films were characterized using

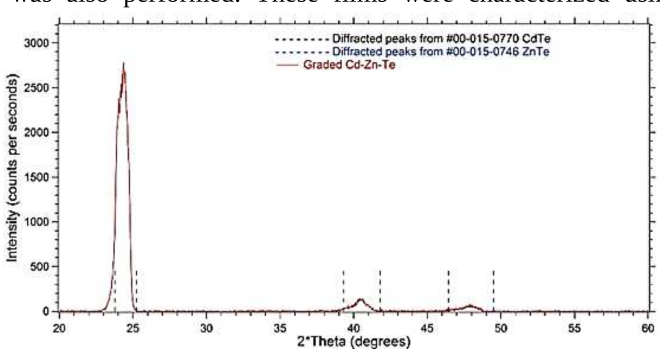

Fig. 5. Diffracted pattern obtained from GAXRD measurements

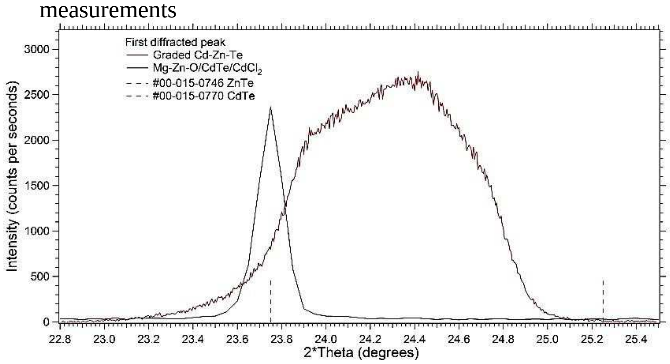

Fig. 6. First diffracted peak compared with the CdTe

cross-section TEM/EDS maps and line profile. Grading of Mg in these films can be distinctly observed. Figure 7a shows EDS map of CdMgTe graded film while figure 7b is an EDS line-scan of the same cross-section. It can be seen that there is

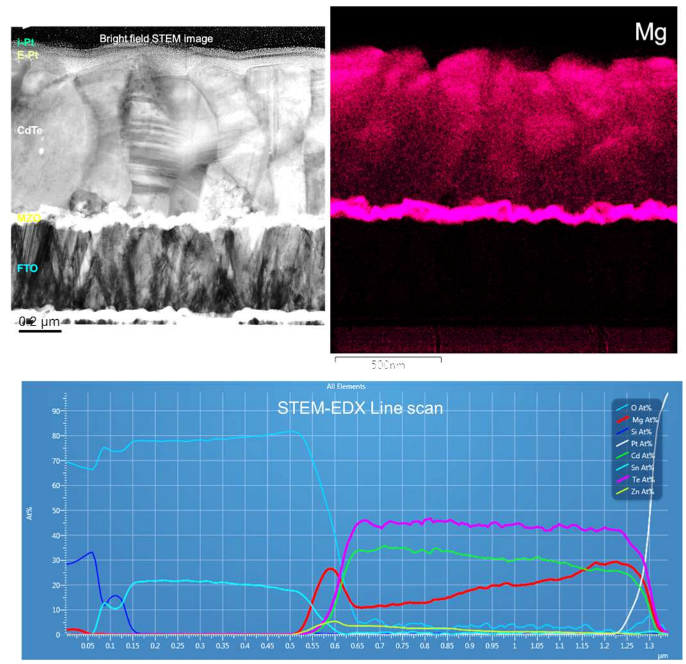

Fig. 7. (top) TEM/EDS cross-section elemental map of Mg showing effective grading in CdMgTe layer (bottom) TEM/EDS cross-section line scan showing Mg grading and corresponding change in Cd composition.

lower composition of Mg towards the front of the device near the MgZnO interface layer. As the film grows thicker, the Mg content is observed to increase. A corresponding change in Cd intensity can also be observed.

IV. Discussion

Open-circuit voltage and short-circuit current of a photovoltaic device are associated with the band-gap of the semi-conductor material used. Lower band-gap is advantageous for current generation while higher band-gap leads to greater voltage. The band-gap of ternary alloys can be altered by changing the composition and an optimum best suited for the respective application may be utilized. Ternary alloys can be graded by altering the composition of the alloying element. Such grading can lead to higher open-circuit voltage as well as short-circuit current than an alloy with a single band-gap. Such advantage has been demonstrated by grading of a CdTe device with Se [12]. Ternary alloys such as CdMgTe and CdZnTe cannot be easily deposited from a single feedstock. For this purpose a co-sublimation source was designed and developed. Using this source, the ternary alloy composition could be varied by changing the temperature of the secondary deposition source. However, controlling the band-gap of the material with temperature would be slow and therefore could not be used for fabrication of photovoltaic devices with graded ternary alloys. With further improvements and enhancements more dynamic in-situ control of absorber band-gap was achieved. Using this advanced co-sublimation hardware graded absorber films of CdZnTe and CdMgTe have been fabricated. Various characterization results show that the films had a graded composition which can further be used to fabricate photovoltaic devices.

V. Conclusions

Advanced co-sublimation source for the controlled grading of CdTe based ternary alloys has been described. This study has shown that changing the flux of ternary element using a shutter mechanism while maintaining a constant source temperature, grading of band-gap can be achieved. It is also shown that controlled shutter movement during deposition CdTe based semiconductor alloy absorber can be effectively graded. Such graded absorber device can be used to make photovoltaic devices that have a performance advantage over an absorber fabricated using alloy with only one band-gap. These higher band-gap photovoltaic devices can be used in multijunction photovoltaic device application and can have a fast throughput. Further investigation into defect and interface passivation as well as optimized contact formation is required to make efficient photovoltaic devices using these graded absorbers.

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