

# Investigation of $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$ Alloys for Tandem Solar Cell Applications

## Preprint

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# INVESTIGATION OF Cd<sub>1-x</sub>Mg<sub>x</sub>Te ALLOYS FOR TANDEM SOLAR CELL APPLICATIONS<sup>1</sup>

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## ABSTRACT

Theoretical modeling of two-junction tandem solar cells shows that for optimal device performance, the bandgap of the top cell should be in the range of 1.6 to 1.8 eV. Cd<sub>1-x</sub>Mg<sub>x</sub>Te (CMT) alloys have a lattice constant close to that of CdTe, and the addition of a small amount of Mg changes the bandgap considerably. In this paper, we present our work on developing CMT for solar cell applications. CMT films were prepared by vacuum deposition with co-evaporation of CdTe and Mg on substrates heated to 300°-400°C. Films with a composition in the range of x = 0 to 0.66 were fabricated, and optical analysis of the films showed that the bandgap of the samples ranged from 1.5 to 2.3 eV and varied linearly with composition. For the fabrication of devices using these alloy films, we also investigated the effect of post-deposition CdCl<sub>2</sub> heat treatment. We have investigated junctions between CdS and CMT alloys in the bandgap range of 1.5 to 1.8 eV for tandem cell applications. We have also worked on the ohmic contacts to the CMT alloy films using Cu/Au bilayers, and the preliminary data shows a significant effect of the contact processing on the device performance. We present the results on the materials properties of these alloys and the effect of post deposition treatments on the film properties and device performance for different alloy compositions and compare them to similar CdTe devices to determine their applicability in tandem solar cell applications.

## INTRODUCTION

Theoretical modeling of two-junction tandem solar cells shows that for optimal device performance, the bandgap of the top cell should be in the range of 1.6 to 1.8 eV [1]. Very few binary compound semiconductors are found within this bandgap range, so one needs to look at the multinary alloys to find suitable candidates. An obvious choice is to explore alloys based on CdTe to exploit the knowledge base developed for CdTe solar cells. In our previous work[1], we investigated Cd<sub>1-x</sub>Zn<sub>x</sub>Te (CZT) thin films prepared by interdiffusion of CdTe and

ZnTe thin films. Although it was possible to fabricate CZT alloy films in the desired composition range, we found that high reactivity of Zn with oxygen and chlorine results in the decomposition of CZT films. During post-deposition processing steps, such as CdCl<sub>2</sub> heat treatment in oxygen ambient, Zn from the alloy is leached out to form either volatile ZnCl<sub>2</sub> or ZnO. Cd<sub>1-x</sub>Mg<sub>x</sub>Te (CMT) alloys offer a wide bandgap range and have not been explored. CMT alloys have a lattice constant close to that of CdTe, and the addition of a small amount of Mg changes the bandgap considerably. A wide range of bandgaps can be obtained with CMT alloys with only a minimal perturbation to the lattice constant. In addition, this alloy system may be useful for understanding the mechanisms that limit the open-circuit voltage (V<sub>oc</sub>) of CdTe to 850 mV. At present, CdTe solar cells have achieved efficiencies of 16.5% [2], and one obvious avenue towards the efficiency improvement is through improved V<sub>oc</sub>. There is a very limited amount of published work available on CMT and most of it is related to bulk material and none for polycrystalline thin films.

A number of approaches were tried for the deposition of the polycrystalline CMT alloy thin films. Co-deposition using CdTe and MgCl<sub>2</sub> produced reasonable CMT films, but the films were irreproducible due to the inadequate control of the MgCl<sub>2</sub> source. Deposition from pre-alloyed Cd<sub>1-x</sub>Mg<sub>x</sub>Te source material produced CdTe films with negligible Mg due to fractionation of source material. Co-deposition of CdTe and MgF<sub>2</sub> was attempted, but was unsuccessful as MgF<sub>2</sub> did not decompose completely at the deposition temperatures used and resulted in two-phase films of CMT and MgF<sub>2</sub>. Co-evaporation of CdTe and Mg was found to be the most successful approach for deposition of CMT films. Due to the relative positioning of the substrate and CdTe and Mg sources, Mg concentration decreased as the distance from the Mg source increased. This facilitated deposition of a wide range of compositions in a single deposition. Here we report on the development of polycrystalline CMT for solar cell applications with an emphasis on alloys in the range of 1.5 to 1.8 eV.

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## EXPERIMENTAL PROCEDURE

Two types of substrate were used in this study: Glass substrates were used for preparing the samples for the analysis of materials properties and glass/SnO<sub>2</sub>/CdS substrates were used for the device fabrication. CMT films were deposited by co-evaporation of CdTe and Mg using Radak II effusion cells in a vacuum system with a base pressure of  $2 \times 10^{-6}$  torr, at substrate temperature of 300°-400°C on 3"x3" substrates. CMT films with a thickness of 0.5-1  $\mu\text{m}$  were used for the materials analysis and films with a thickness of 3-4  $\mu\text{m}$  were used for the device fabrication. Post-deposition vapor CdCl<sub>2</sub> heat treatment was carried out in the He/O<sub>2</sub> ambient in the temperature range of 380°-420° C for 15 min. Prior to the application of the contacts, samples were etched in 0.25% bromine/methanol (BM) etch for 2 seconds or nitric-phosphoric (NP) etch for 10 seconds. For contacts, 10 nm of Cu and 180 nm of Au were deposited by evaporation in a vacuum system at pressure of  $2 \times 10^{-6}$  torr. Contacts were annealed in a tube furnace with He flow of 100 cc/min at 175°-250°C.

Reflectance (R) and transmittance (T) of the films were measured using a Cary 5 spectrophotometer equipped with an integrating sphere. Absorption coefficient ( $\alpha$ ) was calculated using R and T and the film thickness. Optical bandgap was calculated from the x-intercept of  $(\alpha h\nu)^2$  vs  $h\nu$  plots. Structural analysis was carried out by X-ray diffraction measurements using Scintag X-ray diffractometer model Xgen-4000. Composition of the films was determined by Electron Probe Micro Analysis (EPMA) using a JEOL model 8900L Superprobe at 10 and 20 kV. Beam size was 20  $\mu\text{m}$  and the beam current was maintained at  $2.5 \times 10^{-8}$  A. Solar cell performance was measured using an Oriel AM 1.5 solar simulator.

## RESULTS AND DISCUSSION

Transmission spectra of a number of as-deposited samples deposited on glass substrates are presented in Fig. 1. Due to the positioning of CdTe and Mg sources, the samples showed a range of compositions across a 3" width. A typical sample covered a range of approximately 30 nm, deduced from the shift in the absorption edge. Thus the data presented here are combined from a number of depositions. The absorption edge of the films ranged from a CdTe bandgap at 840 to 550 nm. Optical bandgaps vs Mg content of the alloy films determined from EPMA are presented in Fig. 2. It should be noted that when a sample contains a range of compositions, as in the case of the samples used in this study, the deduced optical bandgap corresponds to the lowest-bandgap alloy within measured area. On the other hand, the composition measured by EPMA is an average of compositions within the examined region. Thus the Mg content of the alloy corresponding to the bandgaps presented in the Fig. 2 is likely lower than indicated. The alloy films cover a wide range of bandgaps from 1.5 eV

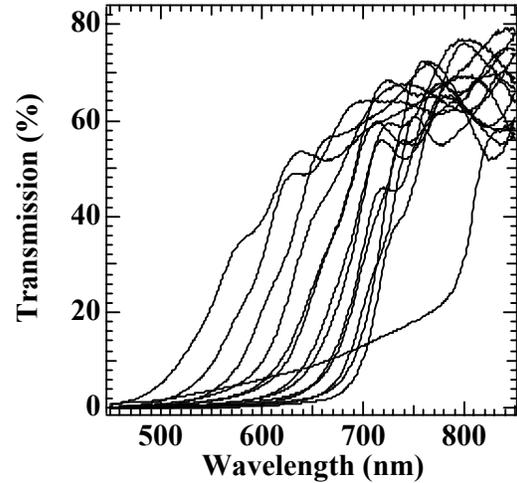


Fig. 1. Transmission spectra of as deposited Cd<sub>1-x</sub>Mg<sub>x</sub>Te alloy thin films.

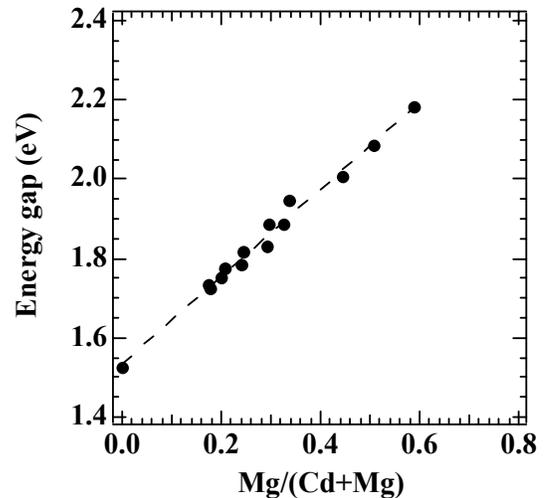


Fig. 2. Energy gap as a function of Mg content for Cd<sub>1-x</sub>Mg<sub>x</sub>Te alloy thin films.

2.3 eV. The optical properties of the CMT alloys are well behaved and can be fitted by a linear fit given by:

$$E_g = 1.1x + 1.54 \text{ eV} \quad (1)$$

In addition to the thin samples (0.5–1  $\mu\text{m}$ ), we have also deposited films with thickness in the 3–4  $\mu\text{m}$  range. These thicker films show high subgap transmission (>60%) indicating excellent material quality. High subgap transmission is essential for the use of these films in tandem solar cells. XRD data show that these films are single phase with systematic variation of lattice constant.

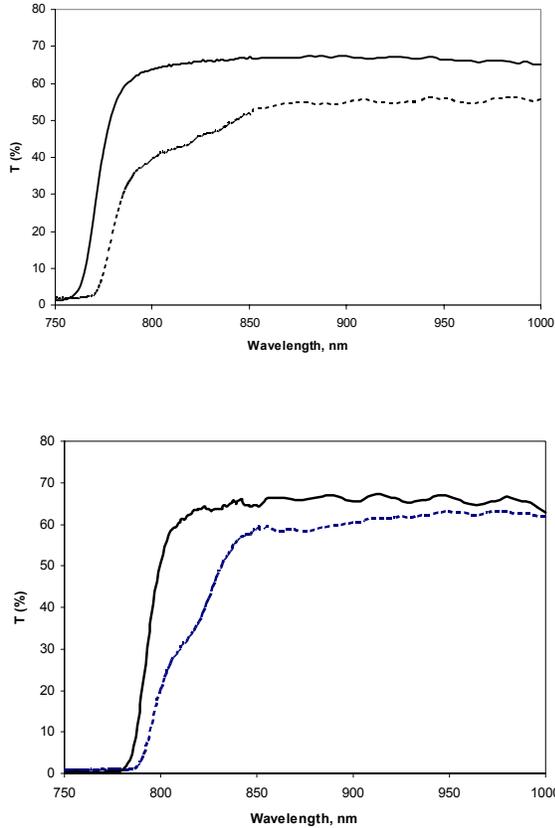


Fig. 3. Transmission spectra of a CMT device with NP (top) and BM (bottom) etch before (solid line) and after (dotted line) 420°C CdCl<sub>2</sub> HT.

All the Cd<sub>1-x</sub>Mg<sub>x</sub>Te alloy films deposited at substrate temperature of 300°C exhibit the sphalerite structure characteristic of CdTe, and only a small variation in lattice constant as expected for these alloys. Although we have been able to fabricate alloys in a much wider range, the present study is focused on the alloys between 1.5 and 1.8 eV to determine their usefulness in tandem solar cell applications.

The samples for the device fabrication were deposited on glass/SnO<sub>2</sub>/CdS substrates at a substrate temperature of 400°C. Devices fabricated from as-deposited CMT films showed poor device performance, so we used the same post-deposition CdCl<sub>2</sub> heat treatment (HT) used in the fabrication of CdTe-based solar cells.

CMT films treated with CdCl<sub>2</sub> HT up to a temperature of 400°C did not show any changes in their properties. Samples treated at higher temperatures showed recrystallization and grain growth. Transmission spectra of a sample before and after CdCl<sub>2</sub> HT at 420°C are shown in Fig. 3. Heat-treated sample were etched with NP etch (top) and BM etch (bottom) prior to the measurements. Wavelength-independent transmission

loss at higher wavelengths results from the absorption in the Te-rich layer formed during NP etch. A slight shoulder in the spectra seen at 850 nm indicates the loss of Mg from top film surface during CdCl<sub>2</sub> HT, resulting in a thin CdTe layer. Shift of the absorption edge may be the result of some Mg loss from the CMT alloy layer during HT. Partial decomposition of the CMT layer happens during the recrystallization process and is a function of HT parameters. Similar features are seen for the sample etched with BM etch, except that there is minimal transmission loss at higher wavelengths as the BM is a more stoichiometric etch and does not create a thick Te-rich layer. Optimization of HT process and pre-contact etching should mitigate these problems. CMT films are more resistant to these problems compared to CZT films, in which high reactivity of Zn results in a rapid loss of Zn during CdCl<sub>2</sub> HT [1].

Formation of ohmic contacts to p-type CdTe is problematic, and several processing schemes involving the use of Cu have been developed. For the CMT devices, we tried several approaches. Contacts using graphite paste doped with Hg and Cu resulted in poor device performance. Based on the preliminary work carried out so far, we have chosen a bilayer of 10-nm Cu and 180-nm Au. This worked satisfactorily, and we have employed it for the devices processed in this study. We processed devices with and without etching prior to contact application and found that the BM-etched devices performed better, so we have employed BM etch for the devices, unless specified otherwise.

Contact annealing temperature has a major influence on device performance. To illustrate this effect, J-V characteristics in dark and illumination of a device with Cu/Au contact, annealed at various temperatures, are presented in Fig. 4 and the device parameters are listed in Table 1. The device with no anneal was from the same substrate, and anneals were carried out on the same device.

Table 1. Device parameters of a CMT (E<sub>g</sub>= 1.55 eV) device after annealing at different temperatures

	No anneal	175° C 30 min	200° C 30 min	225° C 30 min
<b>V<sub>oc</sub>, mV</b>	224	440	597	629
<b>J<sub>sc</sub>, mA/cm<sup>2</sup></b>	19.2	17.7	17.9	17.5
<b>FF %</b>	28.6	36.2	44.2	49.7
<b>Eff [%]</b>	1.23	2.81	4.71	5.47

The diode characteristics of the device before contact anneal are poor. There is progressive improvement in both the diode characteristics and the device performance with successive contact anneals. Dark J-V characteristics show that the reverse diode saturation current for the device after 225° C anneal is the minimum, and the device performance is hampered by high series resistance. The performance of the CMT devices can be further improved by contact optimization.

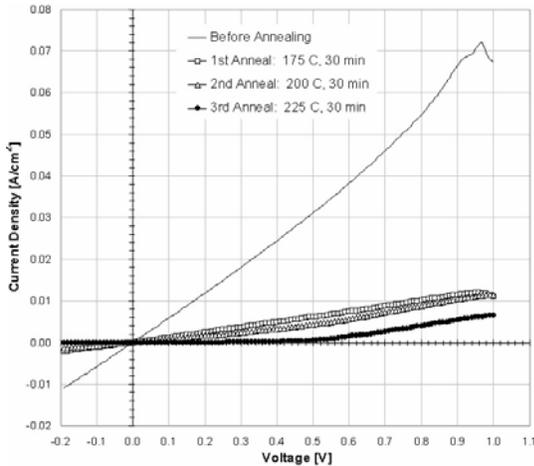
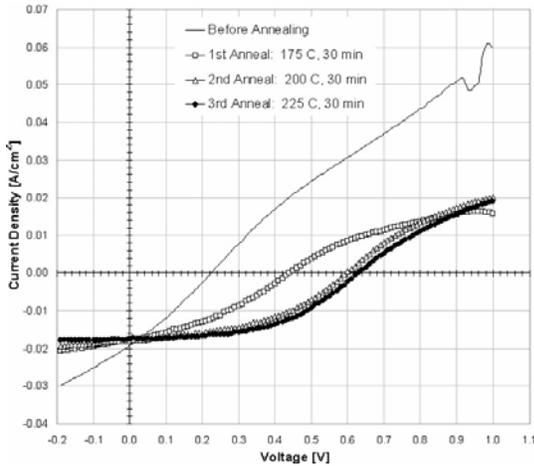


Fig. 4. Light (top) and dark (bottom) J-V plots of a CMT device after different contact anneals.

We have fabricated devices using CMT alloy films with bandgaps in 1.5 to 1.8 eV range. J-V characteristics of some of the devices with different Mg contents are shown in Fig. 5. We have also included a CdTe device deposited in the same system and processed under similar conditions for comparison. Device parameters of these devices are listed in Table 2.

**Table 2 . Device parameters of CMT cells with different compositions**

	CdTe	CMT 1.55 eV	CMT 1.57 eV	CMT 1.6 eV	CMT 1.7 eV
$V_{oc}$ , mV	726	629	636	649	800
$J_{sc}$ , mA/cm <sup>2</sup>	22.9	17.5	17.9	17.1	16.4
FF [%]	56.3	49.7	45.5	43.9	31.1
Eff [%]	9.35	5.47	5.17	4.87	4.08

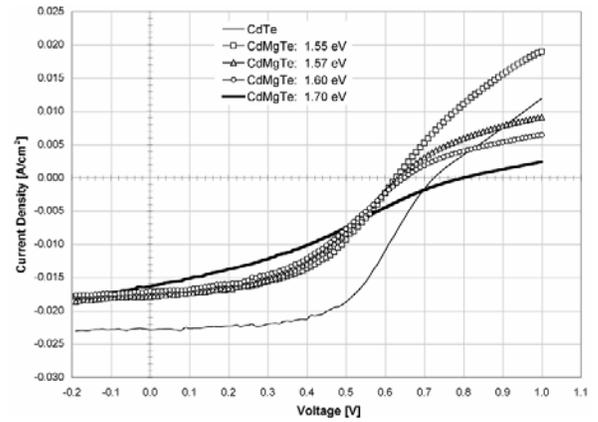


Fig. 5. Light J-V plots of CMT devices with different optical bandgaps.

We have been able to achieve device efficiencies over 5% for various alloy compositions. Although the performance of CdTe devices processed simultaneously is better, CMT devices have consistently given higher  $V_{oc}$ , with the highest  $V_{oc}$  of 800 mV resulting from a CMT device with a 1.7-eV bandgap. With further improvements in the post-deposition HT and improved back contact, we should be able to enhance the device performance of the CMT devices.

## CONCLUSIONS

We have demonstrated the fabrication of polycrystalline CMT thin films in a wide composition range. Optical and structural properties of these samples show that CMT alloy film are well behaved in the composition range covered in this study. Devices fabricated using these films show promising device performance and attest to the device quality of polycrystalline CMT thin films

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