

Alloy Loss Mitigation Through Use of Barrier Layers During CdCl₂ Processing of Cd_{0.60}Zn_{0.4}Te and Cd_{0.87}Mg_{0.13}Te

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Abstract — The main obstacle to realizing the use of polycrystalline wide bandgap alloys of CdTe with Mg and Zn in PV is the CdCl₂ processing step. This step, essential to CdTe device performance, removes Zn and Mg from the alloy films while producing less of the benefits seen from the process with CdTe. In this study, the use of Al₂O₃, CdS, and MgZnO films at the free surface of the alloys to prevent loss of Mg or Zn is investigated. It is found that Al₂O₃ is the most effective at reducing loss of Mg and Zn, followed by CdS and then MgZnO. A new method of evaluating the transition to CdTe from the as deposited alloy is proposed to account for differences in transition behaviors.

Index Terms – II-VI alloys, tandem photovoltaics, passivation, thin films

I. INTRODUCTION

Single junction (SJ) photovoltaic (PV) technologies are starting to mature and approach the theoretical limits for their respective bandgaps [1,2]. This has resulted in costs of PV using technologies with established or simple manufacturing techniques being reduced to the point of competing with conventional production methods [3]. However, it leaves little room for improvement in costs from increases in efficiency.

In order to break the SJ efficiency limits, multi junction (MJ) PV will have to be realized, and furthermore, for it to be practical, it will have to be cost effective. These two stipulations require a transition in MJPV production techniques and technologies, which have traditionally been costly production of III-V PV, to those that can provide high efficiencies while remaining low cost [2].

This leaves the obvious choice for a bottom cell when considering a 2 junction device: silicon PV. Si has a near ideal bandgap for a bottom cell of such a device at 1.12 eV. Furthermore, cost effective production is already proven to be possible on the large scale [4].

However, with an ideal bandgap for partnering with silicon at 1.72 eV, there are few options currently being mass produced with high efficiency and low costs [4]. The PV technology with the second highest share in the industry, CdTe, is just shy of the ideal bandgap with 1.5 eV [1,2,5]. Furthermore, it is possible to tune the bandgap with the addition of Zn or Mg to that of ideal [6,7]. This provides a tempting path towards affordable MJPV by pairing the low manufacturing costs and high production volume of these two common PV technologies.

Currently, however, wide bandgap alloys of CdTe have been plagued with a set of issues when processed in a similar manner to high efficiency CdTe devices. First, the post-deposition activation process, or CdCl₂ passivation, is ineffective and reduces the bandgap by the reduction of the ternary elements in the film [8,9]. Furthermore, current devices made of these materials use contacts optimized for CdTe, leaving potential for re-optimization with the wider bandgap materials for better band alignment and carrier selectivity. Finally, to the knowledge of the authors little to no investigation of doping in polycrystalline wide bandgap alloys of CdTe has been carried out and may pose additional problems.

This work investigates the first of these issues, and the most important to tackle. The first issue is activating the absorber at the correct bandgap. In order to achieve this, it is required that the Zn or Mg in the absorber will remain after a high temperature process in the presence of a source of chlorine, with a common choice in industry and research groups alike being CdCl₂ for CdTe [10]-[12]. The methodology used in an attempt to prevent loss of Mg or Zn during the chlorination process was to deposit thin films of un-like materials, Al₂O₃, CdS, and MgZnO, on the free surface of the absorber prior to a CdCl₂ passivation process to act as an out-diffusion barrier to the Mg, Zn, or species with those elements as a component.

II. MATERIALS AND METHODS

CdMgTe and CdZnTe absorbers were deposited on a superstrate of commercially available TEC10 glass from Pilkington, consisting of soda-lime glass and a SnO₂:F TCO. Prior to deposition of the absorbers, a layer of MgZnO (MZO) was deposited. This was done using an RF planar magnetron sputtering method with a MZO target composed of 11% MgO and 89% ZnO by weight in an environment of 5 mTorr 97% Ar/3% O₂ and a RF power of 180 Watts over a 4 inch diameter target.

The deposition of the absorbers was done by a modified close space sublimation (CSS) technique described in greater detail in ref [7]. The CSS source consisted of two crucibles mechanically stacked on top of each other, with through holes spanning from the bottom of the upper source into the source's deposition pocket, allowing for the vapors of the two

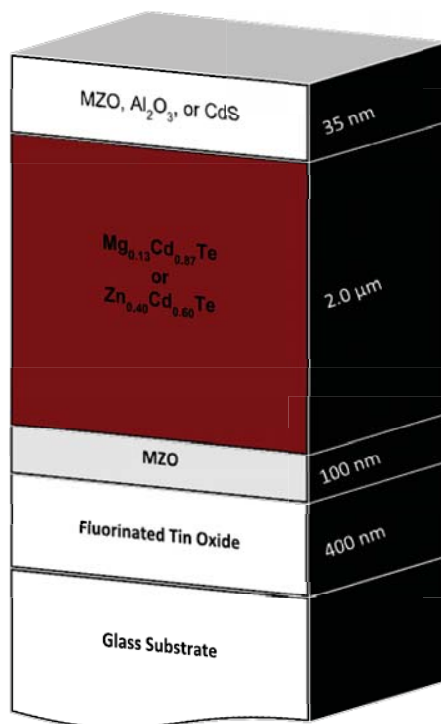


Fig. 1. Structure of film stack used in this study.

materials to mix prior to film deposition. These crucibles are heated independently, allowing for individual control of the temperature, and therefore the vapor pressure of the materials in the different crucibles. This allows for compositional control of the film deposited. In the case of both alloys, the top crucible was filled with CdTe and held at $\sim 560^\circ\text{C}$. In the case of CdMgTe, the bottom source was filled with 99.95% pure $\frac{1}{4}$ inch Mg pellets from Kurt J. Lesker and held at a constant temperature in the range of $440\text{--}460^\circ\text{C}$. In the case of CdZnTe, the bottom source was filled with 99.99% pure $\frac{1}{4}$ inch Zn pellets from Kurt J. Lesker and held at a constant temperature in the range of $320\text{--}340^\circ\text{C}$. For both alloys, the temperature of the bottom source was used to control the film composition, and therefore the bandgap. Transmission measurements and the Tauc Plot method were used to verify the bandgap of the as deposited films, which was chosen to be ~ 1.72 eV for this study due to its ideality for two-terminal tandems paired with Si.

Barriers were deposited using various techniques. Al_2O_3 was deposited using planar magnetron sputtering from a 99.999% pure target using a RF power of 240 Watts over a 4 in diameter target in an environment of 5 mTorr 92% Ar/8% O_2 . MgZnO deposition was done using an identical process to the MZO layer deposited on the TEC 10 prior to the absorber deposition. CdS was deposited using a CSS process similar to that described in ref [13], differing in that the source was held at 605°C and the film stack was heated to 460°C prior to exposure to the CdS vapor.

The final film stack can be found in Fig 1. It is seen that the $\text{SnO}_2\text{:F}$ was 400 nm thick, the MZO was 100 nm thick, the absorbers were $2\text{ }\mu\text{m}$ thick, and the barrier layers used were 35–40 nm thick.

After the film stack was deposited, the films were subjected to a CSS CdCl_2 process. In this process, the CdCl_2 source and top heater were maintained at the same temperature to yield a vapor process with no visible deposition of CdCl_2 . The temperature of these were changed in order to investigate the effectiveness of the caps as the intensity of the process was increased. The temperatures used were 400 , 420 , and 440°C . The film stack was exposed to the CdCl_2 vapor after being preheated in a 620°C heater for 100 seconds, yielding temperatures from 460 to 470°C as measured by a pyrometer. The films then cooled from this temperature to approach that of the CdCl_2 source temperature while in the CdCl_2 source. As the CdCl_2 source temperature increased the intensity of the process therefore increased both from the increased CdCl_2 vapor pressure and the increased average film temperature during the process.

Photoluminescence measurements were taken with an excitation of 520 nm. Current through the excitation laser diode was maintained at 70 mA, giving ~ 40 sun excitation. A 575 nm longpass filter was used to remove reflection of the excitation from the output spectrum.

III. RESULTS AND DISCUSSION

Transmission data was used to screen for change in composition of the films. The telling effect was a shift in the onset of transmission from the as deposited bandgap to the longer wavelengths. This is because as the ternary elements are lost from the film, the bandgap is reduced towards that of CdTe. In some circumstances it has even been observed in the past that the bandgap can return to that of CdTe as enough Mg or Zn is removed. The transmission data can be found in Fig 2. Low sub-gap transmission is attributed primarily to measurement on a system with no integrating sphere, causing minimal measurement of scattered light.

It is clear from the transmission data that for both alloys, none of the barrier layers completely stopped loss from the film. Additionally, the trend for all of the cases is with increasing intensity of the CdCl_2 process, the greater the loss is. As previously noted in ref [8], the manner in which the transmission changes with loss differs between the CdZnTe and CdMgTe material, with CdZnTe showing a more horizontal shift in the transmission edge, and CdMgTe showing a more vertical shift as the material appears to transition nearly directly from the as deposited composition to CdTe.

In order to better compare the losses as quantified by transmission, a new quantitative metric was created. This metric, deemed optical transition is the percent difference in the integral of normalized transmission curves, otherwise

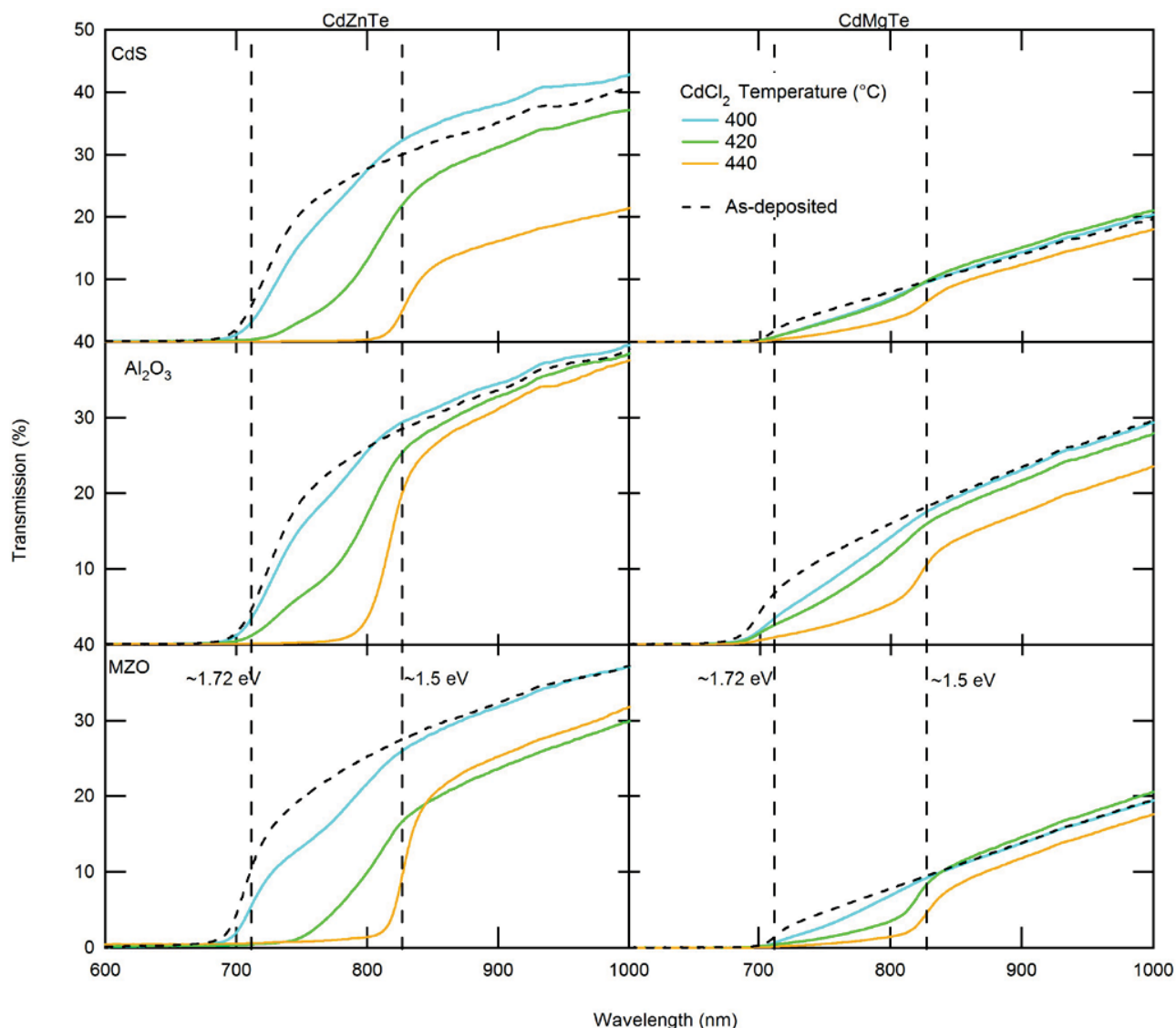


Fig. 2. Transmission of as deposited and CdCl₂ processed CdZnTe (left) and CdMgTe (right) films which used CdS (top), Al₂O₃ (middle), and MgZnO (bottom) films as a barrier to Zn or Mg out – diffusion.

known as the difference in area under the transmission curve between the as deposited film and a CdTe film. As loss occurs, the transmission in this region decreases as material with a lower bandgap forms, which effectively reduces the value of this integral. It is noted that 0% loss indicates that the transmission curve did not change after CdCl₂ and therefore little to no loss of the ternary elements occurred. On the flip side, 100% loss indicates that at least in some portion of the film, all of the ternary elements are lost and the transmission then is then similar to that of a pure CdTe film. The equation can be found in Eq. 1. In Eq. 1, NT is the transmission

spectrum normalized at 900 nm to account for differences in sub-gap transmission.

This metric allows for comparison of loss for which the shift in transmission differs, as is the case when comparing CdZnTe and CdMgTe. This is enabled by using an integral rather than the location of the transmission onset. As the transmission curves show multiple slopes and decreased sharpness in the transmission edge, the integral method simply sees this all as a similar decrease in area under the curve between the bandgap of the as deposited film and that of CdTe.

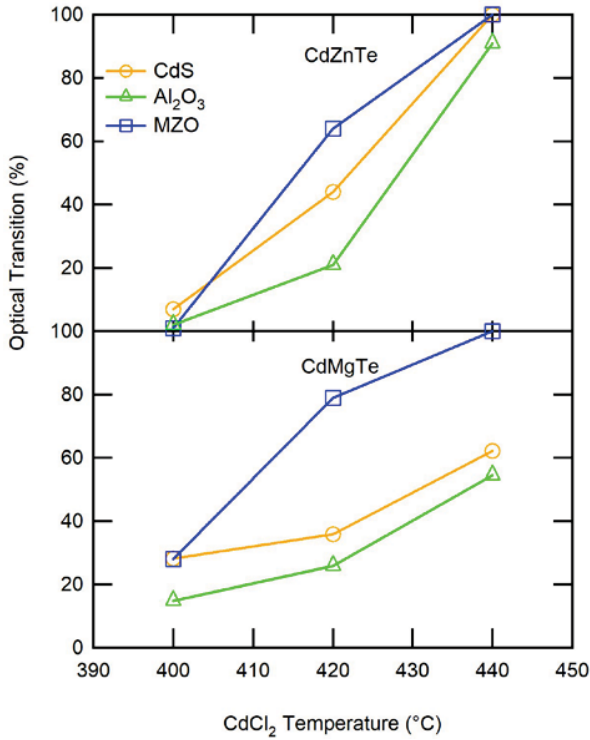


Fig. 3. Optical Transition vs CdCl₂ Temperature for CdZnTe (top) and CdMgTe (bottom) with CdS, Al₂O₃, and MgZnO as barriers.

This is an appropriate metric for the top cell application as well. A tandem device requires high transmission of photons with less energy than the desired top cell bandgap to the bottom cells. CdTe and alloys thereof have similarly strong absorption of light. Because of this, a thin layer of CdTe forming from loss of any alloying component will severely reduce the transmission of these photons, as the lowest bandgap material in the device will dominate the transmission. It then stands that while the absorber may still contain Zn or Mg in some regions of the film, the effective transmission approaches that of CdTe, which is not ideal for current matching with Si in a 2 terminal tandem device.

Optical transition vs CdCl₂ temperature can be found in fig. 3. It becomes clear that Al₂O₃ is the most effective at reducing loss for both materials. CdS is then the next best and MgZnO is the worst.

Additionally, it becomes increasingly clear that CdZnTe is more prone to the transition occurring, in that the slope with increasing CdCl₂ intensity is steeper. The one exception is seen in CdMgTe and a MZO barrier during CdCl₂ which shows similar or greater loss at each temperature compared to the CdZnTe with an MZO barrier. This is likely due to the diffusion of Mg into and Zn out of the MgZnO layer at the interface of MZO and CdMgTe. This has been seen previously and follows a favorable reaction wherein ZnTe and MgO form

[8]. A likely reason for the reduced stability of CdZnTe with respect to CdMgTe is related to loss mechanisms discussed previously [8]. In the case of CdMgTe, the loss is localized and where there is not yet loss, a composition similar to that of the as deposited film is still present. On the other hand, Zn diffuses to create a gradient of Zn from the glass side to the free surface. These behaviors indicate a slower diffusion of Mg in the alloy, compared to Zn diffusion, which would explain the observation of less loss under the same conditions for CdMgTe.

Yet, with a lower CdCl₂ process intensity, the CdZnTe is more stable. This is observed in the 400°C CdCl₂ process: no matter the capping layer, CdZnTe remains closest to 0% optical transition where as CdMgTe shows ~20% average transition. This suggests that the onset of the CdMgTe loss mechanism is faster than that of CdZnTe. In keeping with the previously observed loss mechanisms, CdMgTe's localized loss may explain this effect. As Cl travels down the grain boundaries, it likely immediately can react with local Mg. However, additional loss after this is difficult due to the apparent slower diffusion of Mg in the CdMgTe alloy bulk. CdZnTe loses Zn from the free surface, and relies on the diffusion of Zn through the bulk to for further loss to occur. This then makes sense as to why the onset is immediate for CdMgTe, despite the apparent faster diffusion of Zn in CdZnTe, as grain boundary diffusion is generally much faster than bulk diffusion, and so Cl diffusion along the grain boundaries governs initial loss in CdMgTe but bulk diffusion governs the loss rate for CdZnTe.

Another appropriate metric for identifying loss is the location of the steady state photo-luminescence (SSPL) peak. The peak location of a SSPL measurement taken at room temperature is indicative of the bandgap of the material [14]. Therefore, any change in peak location for CdZnTe or CdMgTe films is expected to be from a change in bandgap, and when CdCl₂ processed, we anticipate a redshift toward the bandgap of CdTe.

SSPL spectra can be found in Fig 4. The loss behavior between CdZnTe and CdMgTe is different as previously observed [8]. The transition in the peak generally follows with the optical transition in the case of CdZnTe, showing a shift in the peak location as Zn is lost. The PL spectra also seem to indicate in the case of CdZnTe that Al₂O₃ is the most effective at slowing the loss of Zn. This is seen in the peak corresponding to the highest temperature process. Despite this process being the most aggressive, the peak is found at ~795 nm, whereas the MZO and CdS peaks both have a strong or single component at ~820 nm for the same process, which is close to the bandgap of CdTe. This corroborates the transmission data.

The transition in CdMgTe is completely different, showing the development of a CdTe peak in addition to the CdMgTe peak which remains at the as deposited bandgap. This behavior is expected as it has been shown that formation of

$$\text{Optical Transition (\%)} = \frac{\int_{400}^{900} NT(\text{as deposited})d\lambda - \int_{400}^{900} NT(\text{CdCl}_2 \text{ Treated})d\lambda}{\int_{400}^{900} NT(\text{as deposited})d\lambda - \int_{400}^{900} NT(\text{CdTe})d\lambda} \quad (1)$$

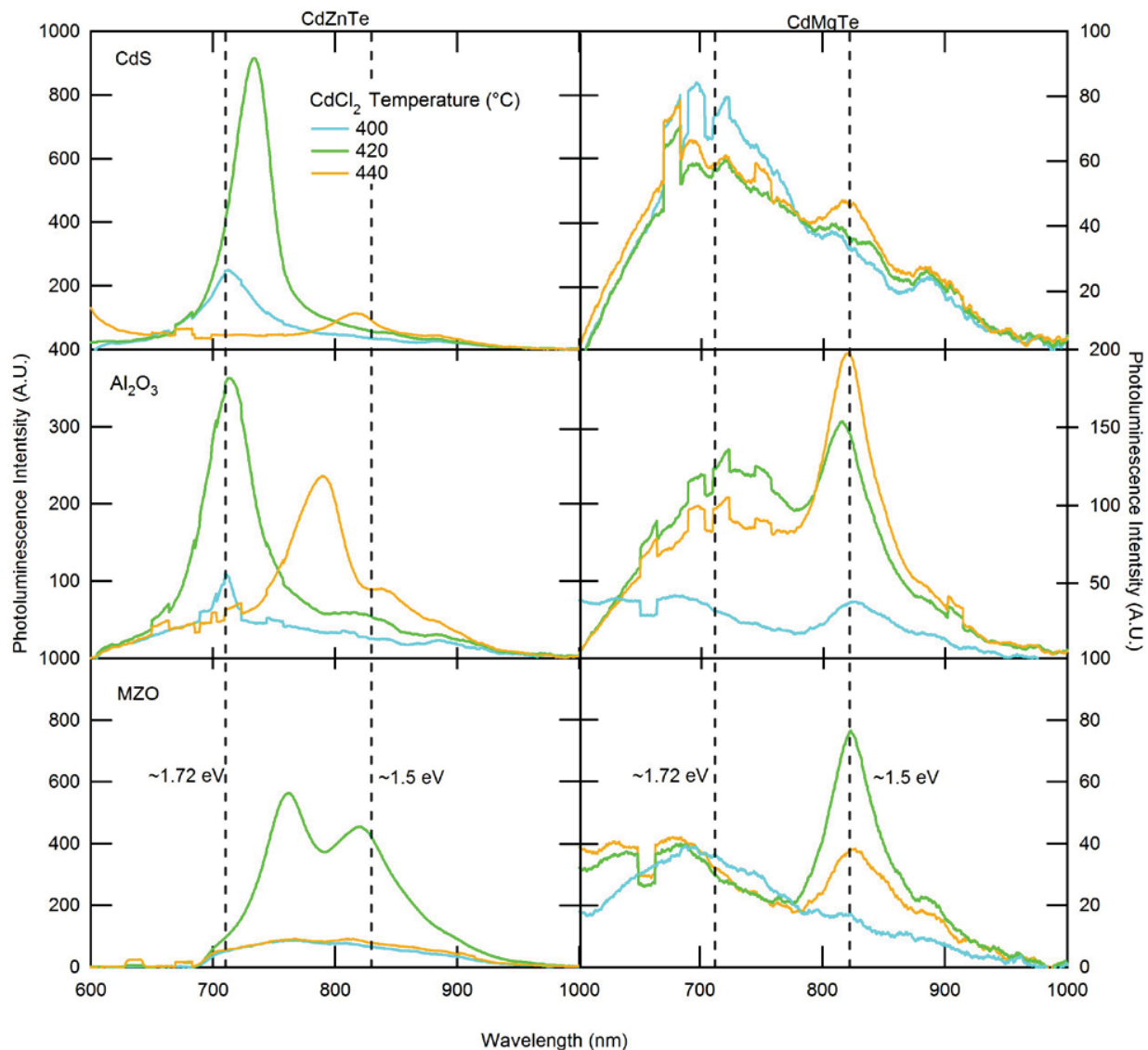


Fig. 4. Steady state photoluminescence spectra of CdZnTe (left) and CdMgTe (right) with CdS (top), Al₂O₃ (middle), and MZO (bottom) barrier layers used during CdCl₂

CdTe from Mg loss is localized. Additionally, the peak intensity at the CdTe bandgap which shows up with loss does not seem to trend with the increased loss, making the appearance of the peak indicative of loss, but not the extent. Interestingly, not all of the CdMgTe spectra show the CdTe peak as is observed with the CdS barrier, despite the transmission data for all of them showing a shift. As there is no trend in CdTe peak intensity with loss and the peak itself does not always show up with loss as observed in transmission, SSPL spectra are less effective for determining the loss extent for CdMgTe as they are for CdZnTe. The simplest explanations are that CdTe which has formed from the loss of ternary elements is prone to non-radiative forms of recombination, or that carriers produced by the excitation are not recombining in regions which have transitioned to CdTe.

Another interesting feature of the SSPL spectra is found in the spectrum of the CdZnTe absorber which has undergone CdCl₂ with a MZO barrier and a CdCl₂ source temperature of 420°C. One clearly sees two peaks in this spectrum, showing both behaviors expected of CdZnTe and CdMgTe. This is referring to the peak at shorter wavelengths being redshifted from the as deposited bandgap, as one would expect from CdZnTe. In addition to this is the peak corresponding to the CdTe bandgap, the development of which is uncommon in the pL spectrum of CdZnTe with loss, but common in that of CdMgTe with loss. A possible explanation for this is the MZO barrier layer forces localization of loss, similar to CdMgTe, but as Zn diffuses to these lower Zn concentration areas, the bandgap elsewhere decreases more slowly as we would typically anticipate from CdZnTe.

IV. CONCLUSIONS AND FUTURE WORK

In this work CdCl_2 processes on CdZnTe and CdMgTe film stacks were investigated, using a thin film of CdS , MZO , or Al_2O_3 as a barrier on the free surface of the absorber. It was found that the characteristic change in opto-electrical behavior varied with choice of barrier layer. Using a new metric for the change in optical behavior, it is shown that the Al_2O_3 layer is the most effective at reducing the change in transmission, and therefore change in film composition.

Changes in bandgap despite the presence of these barrier layers during CdCl_2 processing are confirmed with SSPL spectra. In CdZnTe , these changes in composition are marked by a shift in peak location, whereas with CdMgTe , the change in composition is marked by the development of a second peak with the bandgap of CdTe . This technique is most meaningful for the CdZnTe absorber as characteristic signs of loss in CdMgTe do not always appear, and do not seem to scale with the loss.

Despite the presence of the barrier layers of an unlike material, the loss mechanisms seem to be similar to that of films with a barrier of CdTe , a like material [8]. Reductions in loss therefore are likely the result of the barriers slowing the reaction/diffusion process necessary for loss. It is seen that the sensitivity of CdZnTe to CdCl_2 process temperatures is much greater than that of CdMgTe , with the increase in loss with temperature being much greater. At lower temperatures however, the CdZnTe is more robust, showing the least transition from any films in the study.

Additional work must be carried out to determine how effective the CdCl_2 process was for these films with the barriers present. A reduction in loss could be from the reduction of chlorine entering the absorber, which would result in the poor activation of the films. However, this reduction in loss can also be explained by the barrier layers acting as intended and reducing out-diffusion of Mg or Zn . This will determine if the lower temperature process on CdZnTe (where minimal loss was observed) is a feasible path forward for use of wide bandgap alloys of CdTe in PV.

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