Carrier Lifetime as a Function of Se Content for CdSexTe1-x Films Grown on Al2O3 and MgZnO

Preprint

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NOTICE

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Abstract—**Time-resolved photoluminescence (TRPL) with two excitation wavelengths – 670 (standard) and 405 nm – was used to examine the effect on carrier lifetime of two significant recent advances in CdTe: the incorporation of Se to form graded CdSe$_x$Te$_{1-x}$ and the use of Mg$_y$Zn$_{1-y}$O buffers. The two excitation wavelengths probe depths of approximately 130 and 35 nm, respectively, and their comparison helps differentiate interface and bulk contributions to carrier lifetime. It was found that x = 0.2 Se was required to obtain lifetime improvements, primarily in the bulk. Additionally, TRPL traces for Mg$_y$Zn$_{1-y}$O/CdSe$_x$Te$_{1-x}$ samples showed fast initial decay followed by a long-lived tail, which may be indicative of trap-dominated recombination. This behavior was not present for CdSe$_x$Te$_{1-x}$ films grown on Al$_2$O$_3$, which is currently state-of-the-art for surface passivation in CdTe. This indicates that further work is required to sufficiently passivate the front interface.**

Keywords—cadmium telluride; MZO; CdSeTe; TRPL; front interface

I. INTRODUCTION

Cadmium telluride (CdTe) is one of the leading photovoltaic (PV) technologies, supplying 40% of the U.S. utility scale market and >5% of the global PV market [1]. One of the primary benefits of CdTe is its near-ideal bandgap of ~1.4 eV, which should allow for open-circuit voltage (V_{OC}) of >1.1 eV in devices [2]. However, V_{OC} has stagnated at ~850 mV, despite impressive gains in carrier lifetime for test structures (~1 µs) [3] as well as devices (~200 ns) [4]. Two of the most significant improvements that have led to these long carrier lifetimes are the incorporation of Se to create graded CdSe$_x$Te$_{1-x}$ absorbers and the replacement of CdS with transparent buffer materials like Mg$_y$Zn$_{1-y}$O (MZO). Among the many benefits that accompany these two improvements, it appears that Se passivates (i.e., reduces recombination in) the absorber bulk [5]-[8] while MZO passivates the front interface [3], [9], [10], both of which should improve V_{OC}.

As bulk properties continue to improve, modeling suggests that the front interface becomes a bottleneck for performance [11]-[13]. Therefore, it is important to understand passivation quality at the front interface, particularly since such promising results have been shown using MZO [3], [4], [6], [7], [9], [10]. Here, we use a custom-built time-resolved photoluminescence (TRPL) spectrometer with two excitation wavelength options – 670 and 405 nm – which probe different depths and can thus begin to differentiate surface from bulk effects.

The dual-wavelength TRPL system was used to study the effect on carrier lifetime of incorporating different levels of Se into the CdSe$_x$Te$_{1-x}$ bulk (x = 0, 0.1, 0.2, 0.3) compared with graded CdSe$_x$Te$_{1-x}$ that would typically be used in devices. It was found that the higher lifetimes associated with CdSe$_x$Te$_{1-x}$ devices [5]-[8] were not observed until x $\geqslant$ 0.2, where the improvement was primarily a bulk effect. The passivation quality of the MZO/CdSe$_x$Te$_{1-x}$ interface was examined using "mirror" structures (i.e., only the interface of interest is passivated and the other is left as a free surface; all other processing conditions remain the same) and comparing to CdSe$_x$Te$_{1-x}$ grown on Al$_2$O$_3$. A fast initial decay in lifetime was observed for MZO/CdSe$_x$Te$_{1-x}$ samples followed by a long-lived tail, which can be indicative of trap-dominated recombination. This signature of trapping was absent for Al$_2$O$_3$/CdSe$_x$Te$_{1-x}$ samples, possibly due to improved field effect passivation. Because structures were processed using baseline conditions for NREL devices (e.g., Mg$_{0.04}$Zn$_{0.96}$O, graded CdSe$_x$Te$_{1-x}$, CdCl$_2$ treated), this suggests that further optimization is required to fully passivate the front interface.

II. METHODS

Mirror structure architectures are shown in Figure 1. 100 nm of either MZO or Al$_2$O$_3$ was deposited on Eagle XG glass. MZO was deposited via RF magnetron sputtering using a hot pressed mixed powder (MgO and ZnO) sputter target of 4 wt% Mg in an ambient of 1% O$_2$ in Ar and no intentional heating. Al$_2$O$_3$ was deposited via electron beam evaporation at a pressure of ~mid 10^{-6} T, 2 Å/sec deposition rate, and 9 kV accelerating voltage. CdSe$_x$Te$_{1-x}$ films were deposited on top of the Al$_2$O$_3$- or MZO-coated glass via thermal evaporation using powder sources. On each type of substrate, a series of CdSe$_x$Te$_{1-x}$ films of uniform Se content (x = 0, 0.1, 0.2, 0.3) were grown along with a film of graded Se content. The uniform films were deposited from a single source to 3.5 µm thick. For the graded films, 150 nm of CdSe was deposited followed by 3.5 µm of CdTe from two separate sources. All films were deposited at a substrate temperature of 450°C. Film stacks then underwent a CdCl$_2$ anneal in a close-spaced sublimation configuration with the substrate temperature held at 435°C for 10 min under 400 T of He. These processing conditions reflect what is commonly used as NREL's baseline process that generally produces 16% to 17% efficient devices, but can achieve as high as 19%. However, test structures used here were not intentionally Cu doped, possibly leading to worse passivation at the front interface due to reduced Te oxidation [14].

TRPL measurements were taken and an additional 100 nm of Al$_2$O$_3$ was deposited at the back surface to make a complete double heterostructure. However, no change in TRPL was
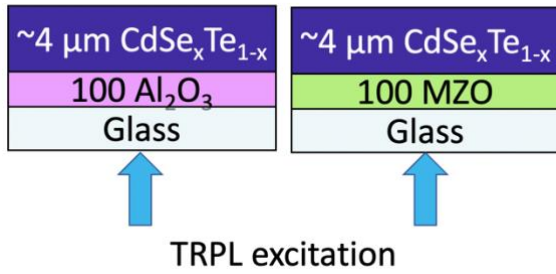
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Figure 1. Architecture of mirror structures used, where the $CdSe_xTe_{1-x}$ layer either had uniform composition (x = 0, 0.1, 0.2, or 0.3) or was graded with 150 nm CdSe and 3.5 µm of CdTe interdiffused. Films were deposited on either Al_2O_3- or MZO-coated glass. TRPL excitation was through the glass.

observed and the results were not included here. This agrees with previous studies which have found a second $CdCl_2$ anneal to be required after Al_2O_3 deposition to see passivation benefits [3], [9], [10]. The second $CdCl_2$ treatment was omitted here in order to maintain standard device processing conditions for the front interface.

TRPL spectrometer set-up is described in Ref. [19]. Data was taken using 125 kHz repetition rate and 50 µm beam diameter; power was varied to obtain a consistent $2x10^{16}$ cm^{-3} injection level for all films. While a more typical repetition rate used for CdTe is ~1 MHz, 125 kHz was used here to capture particularly long-lived τ_2 values for films grown on MZO under 405 nm excitation (see Figure 2d). TRPL data were fit with the minimum number of exponential fit terms required to fully capture each curve (peak to average background noise level). Fits were taken over the entire decay rather than the slow portion only since there is no junction in the structures studied here (i.e., no charge separation effects that dominate the initial fast decay). Data taken using 670 nm excitation typically required two exponential fit terms, while 405-nm-excitation data typically required three. This may be due to the stronger influence of interface recombination (e.g., trapping) for data taken using 405 nm excitation.

III. Results and Discussion

While it is clear that Se incorporation into CdTe improves carrier lifetime, it is not clear how lifetime changes with the amount of Se incorporated. A recent study by Ablekim et al. examined the effect of varying Se content on lifetime in $CdSe_xTe_{1-x}$/CdTe devices [4], but those samples had the added complications of compositional grading and junction field. Here, we isolate the effect of varying Se content on bulk and interface passivation by growing uniform-composition $CdSe_xTe_{1-x}$ (CST) films (x = 0, 0.1, 0.2, 0.3) on passivated substrates and comparing to graded CST. Figure 2 shows TRPL traces for such films grown on (a-b) Al_2O_3- and (c-d) MZO-coated glass using (a, c) 670 nm and (b, d) 405 nm excitation. Extracted lifetime values are provided in Table 1.

Interestingly, films grown on Al_2O_3 consistently demonstrated longer carrier lifetimes using 405 nm excitation, despite the generation volume being constricted closer to the interface than for 670 nm excitation. This indicates that the Al_2O_3/CST interface is better passivated than the bulk, which is most likely limited by grain boundary recombination. Al_2O_3 is commonly thought to passivate CdTe surfaces through field-
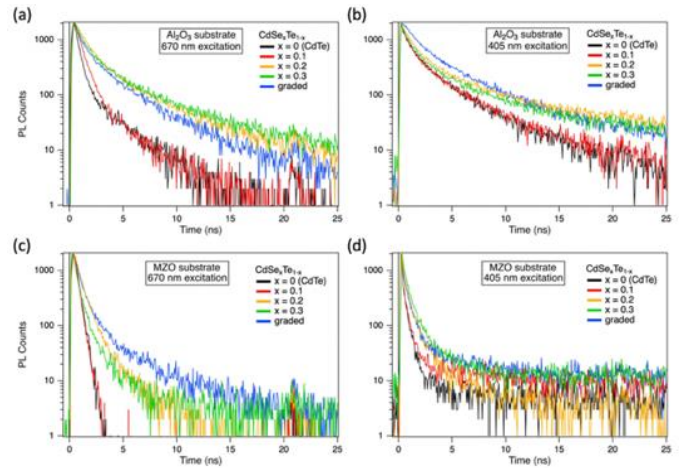

Figure 2. TRPL curves of uniform $CdSe_xTe_{1-x}$ films with x= 0 (black), 0.1 (red), 0.2 (orange), 0.3 (green), and graded $CdSe_xTe_{1-x}$ (blue) grown on (a-b) Al_2O_3- and (c-d) MZO-coated glass using (a, c) 670 nm and (b, d) 405 nm excitation. A strong difference is seen between x = 0.1 and x = 0.2, primarily in the bulk (670 nm data).

effect (i.e., band bending that repels carriers of one type away from the defective interface) due to its wide bandgap [15] and ability to build up negative surface charge [6], [16]. However, it has also been found that a $CdCl_2$ anneal is required after the Al_2O_3/CST interface formation in order to obtain passivation benefits. This suggests that there is also a chemical component to Al_2O_3/CST passivation, likely due to Te oxidation [17] and/or monolayers of two-dimensional $CdCl_2$ at the interface [18].

For films grown on both Al_2O_3 and MZO, there appeared to be a critical Se level (0.1 < x < 0.2) that triggered a step function in carrier lifetime for $CdSe_xTe_{1-x}$ films, where x = 0.1 behaved much like CdTe and lifetimes essentially saturated for x ⩾ 0.2 (Figure 2). This may be a reason that certain studies have focused on x = 0.2 [3], [10], due to improved performance. It is noted that the true Se concentrations may have been slightly higher than expected, as a study by Kuciauskas et al. measured $CdSe_{0.29}Te_{0.71}$ when attempting to deposit $CdSe_{0.2}Te_{0.8}$ using the same source material and evaporator as the current study [10]. The difference in lifetime between x = 0.1 and 0.2 is more pronounced for 670 nm excitation, consistent with its probing the properties of the bulk absorber. This is supported by the 405-nm-excitation data for films grown on Al_2O_3 (Fig. 2b), as the difference becomes more pronounced at longer time scales.

The shape of the MZO curves, on the other hand (Fig.2d), may be due to trapping at the interface, where the initial fast decay is dominated by trap filling and the long-lived component is dominated by re-emission. The difference in interface passivation may also explain the change in lifetime for graded films grown on Al_2O_3 compared to MZO. The grading in Se concentration produces a bandgap grading in the film [8] and, therefore, a built-in field that sweeps carriers away from the interface. In the case of films deposited on Al_2O_3 (Fig. 2a), where the interface is better passivated than the bulk, this leads to a modest decrease in lifetime. Alternatively, sweeping carriers away from the MZO/CST interface (Fig. 2c), which is not well passivated, improves lifetime.

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TABLE I.   CARRIER LIFETIMES FOR FIGURE 2 TRPL DATA

CdSe$_x$Te$_{1-x}$	670 nm excitation		405 nm excitation		
	τ_1 (ns)	τ_2 (ns)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)
	Al$_2$O$_3$		Al$_2$O$_3$		
x=0	0.2	2.4	0.7	4.3	
x=0.1	0.4	2.3	0.7	5.2	
x=0.2	0.7	9.8	0.8	5.2	40
x=0.3	0.5	11	0.8	6.0	56
graded	0.5	4.6	0.9	4.5	25
	MZO		MZO		
x=0	0.2		0.08	9.5	
x=0.1	0.2		0.08	0.4	54
x=0.2	0.3	1.3	0.1	1.4	44
x=0.3	0.2	6.1	0.1	1.9	115
graded	0.3	9.8	0.1	3.8	147

IV. CONCLUSION

Recent developments for CdTe solar cells have occurred rapidly in recent years. Two of the most notable improvements have been the incorporation of Se into the absorber to form graded CdSe$_x$Te$_{1-x}$ and the replacement of CdS with transparent buffer materials like MZO. Both of these changes have resulted in major improvements to carrier lifetime. Using a custom dual-wavelength TRPL spectrometer, bulk and interface contributions to carrier recombination were examined as a function of Se incorporation. Lifetime improvements were not observed until x $\geqslant$ 0.2, which was primarily a bulk effect. Additionally, the MZO/CdSe$_x$Te$_{1-x}$ interface was inferior to Al$_2$O$_3$/CdSe$_x$Te$_{1-x}$, and possible evidence for trapping at the junction was observed. This indicates that further work is required to sufficiently passivate the front interface. This is consistent with recent modeling that shows front interface recombination becomes a bottleneck for performance as bulk properties continue to improve. Tunneling barriers, selective contacts, and/or improved carrier concentration in the buffer may all be paths toward passivating the front interface and improving open-circuit voltage.

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