The Effect of Nanocrystal Reaction Time on $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$

Solar Cells from Nanocrystal Inks

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Abstract

The sintering of nanocrystals to form a bulk film is a promising route for the production of low cost $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ solar cells. However, very little is known about how the synthesis of the nanocrystals impacts the properties of the sintered film or the performance of the resulting photovoltaic device. Here, we present a study in which devices were made from NC inks with different reaction times. Variation in reaction time produces inks with different average size, composition, and compositional heterogeneity. Accounting for the influence of composition, we find that longer NC reaction times result in improved current collection, larger quasi-Fermi level splitting, lower defect concentrations, and higher power conversion efficiency in the selenized devices. The improvements correlate well with the breadth of the x-ray diffraction peaks, suggesting that the longer reaction times result in larger crystalline domain sizes, and that grain boundaries may act as non-radiative recombination sites. Further, the crystalline domain size in the sintered film is proportional to the mean NC size in the ink, suggesting that some interparticle sintering occurs but that the ultimate grain size in the film is dependent on the starting NC size.

Keywords: CZTS; $\text{Cu}_2\text{Zn}(\text{S},\text{Se})_4$; solution processing; nanocrystal; earth abundant; kesterite

1. Introduction

Thin film solar cells based on the earth-abundant $\text{Cu}_2\text{ZnSnS}_4$ and $\text{Cu}_2\text{ZnSnSe}_4$ light absorbing layers, referred to as kesterites, have been the subject of intense research interest in recent years. Due to the high crustal abundance of the constituent elements, and the structural and electronic similarities to $\text{Cu}(\text{In},\text{Ga})\text{Se}_2$ (CIGSe), kesterites are a leading candidate for terawatt-scale production of photovoltaics. By simply substituting the kesterite absorber into a standard CIGSe device architecture, kesterite solar cells have reached 12.6% efficient [1] using a hydrazine solution process. Another promising route is the sintering of nanocrystal inks. Such devices have reached as high as 9.6% efficient [2] without the use of highly toxic materials. However, the use of colloidal nanocrystals as a precursor to a continuous thin film is still relatively new, and the sintering process in these PV materials has not been thoroughly studied. Strong criteria do not exist for predicting how ligands, particle size, and processing steps impact the resulting films and devices. For example, early attempts to make bulk materials from nanocrystals suggested that the carbonaceous ligands prevented effective sintering [3-5], but more recent work has shown large grained structures [6, 7]. Reports have even suggested that the carbonaceous layer commonly observed between the absorber and back contact [8-11] may

benefit devices by reducing back contact recombination [9]. To better understand how the properties of the nanocrystals impact the bulk film, we have performed a study in which photovoltaic devices were made from CZTS nanocrystal inks with varying reaction times. These inks vary in average particle size, compositional heterogeneity, and average composition.

Figure 1. The change in film composition as a function of time for the (1) “Standard” and (2) “All” particle fractions. Black lines indicate the composition of the doctorbladed film, red lines indicate the composition after selenization. The dashed blue line indicates the ratio of precursors added for NC synthesis.

2. Materials and Methods

2.1 Nanocrystal Synthesis

CZTSSe solar cells were made from nanocrystals characterized in detail in a previous publication [12]. Briefly, the nanocrystals are synthesized by injecting a 1M sulfur in oleylamine solution into a flask containing copper(II) acetylacetonate (Sigma 99.999%), zinc(II) acetylacetonate hydrate (Sigma 99.999%), and tin(IV) bis(acetylacetonate) dichloride (Sigma 98%) in oleylamine (Sigma, technical grade) at 225 °C and allowing the reaction to proceed for a set duration. Following NC synthesis, the reaction mixture is split equally between two centrifuge tubes. From one tube, we precipitate nearly all of the particles (the “All” fraction); from the other we only collect particles above a certain size threshold (the “Standard” fraction). The Standard procedure is the same as was used to produce a 7.2% efficient device [13]. The nanocrystals are washed multiple times to remove excess oleylamine then dispersed in hexanethiol to form a dense ink.

2.2 Device Fabrication

Device fabrication closely follows a previously published method [13]. To deposit films, the NC inks are doctorbladed onto molybdenum coated soda-lime glass then dried on a hot plate at 300 °C in air. Two layers are applied to produce a film that is approximately 1.2 μm thick. The films are then annealed in a graphite box with excess selenium at 500 °C for 20 minutes to form a polycrystalline CZTSSe film. Following selenization, complete devices are made using standard procedures, including chemical bath deposition of CdS, RF sputtering of i-ZnO then ITO, and thermal evaporation of a Ni/Al top contact. The samples are scribed into devices with a typical area of about 0.45 cm².

2.3 Characterization

The composition of the films was measured before and after selenization using energy dispersive spectroscopy (EDS) on a FEI Sirion scanning electron microscope at 20 keV. Completed solar cells are tested under simulated AM1.5G illumination produced using a 300W Xe arc lamp. The integrated light intensity is validated using a calibrated mono-crystalline Si reference cell. Current-voltage parameters are extracted using the method of Zhang et al [14]. The external quantum efficiency (EQE) is measured using a lock-in amplifier with monochromatic light, chopped at 153 Hz and the resulting spectrum is integrated over the AM1.5G spectrum and compared to the measured short circuit current. Drive-level capacitance profiling (DLCP) is performed at room temperature using a Solartron SI 1260. The DC peak voltage was varied from -0.5 to +0.5V with the AC signal ranging from 10-300 meV over the frequency range 0.1-46.4 kHz. For determining the defect density, the device was assumed to be a planar one-sided junction and the dielectric constant was assumed to be 8.6 [15]. Absolute intensity photoluminescence (AIPL) spectra are collected on a modified Horiba Labram steady-state PL instrument calibrated using a NIST-calibrated blackbody source. The AIPL spectra are collected over a 110x110 μm area using 785 nm laser excitation at approximately 10 suns. A minimum of 6 PL measurements are taken on each sample and the fitted parameters are averaged. The crystallographic structure of the films was analyzed by powder x-ray diffraction (PXRD) using a Bruker D8 Focus with a Cu K-alpha radiation source. The XRD instrumental broadening was measured using a single crystal silicon wafer which had a FWHM of 0.115 2θ, less than half of the narrowest FWHM observed in any of the CZTSSe films.

3. Results and Discussion

3.1 Temporal Changes to Composition

With increasing reaction time we see significant changes in the average composition of both the Standard and All NC inks. As detailed in a previous publication [12] and shown in Figure 1, the short reaction time inks are extremely Sn-poor, but over time the composition of the inks approaches that of the starting precursors. The NC reaction product contains at least two distinct particle populations: large Zn-rich particles and small Zn-poor particles. Fewer of the small particles are collected in the Standard fraction than in the All ink, causing the All fraction to have higher Cu/(Zn+Sn) ratios and lower Zn/Sn ratios than the Standard fraction. However, because the NC growth mechanism involves the ripening of the small particles into the larger

particles, the composition of the All fraction precedes that of the Standard fraction. For example, the Cu/(Zn+Sn) and Zn/Sn ratios for the Standard fraction reacted for 1 h are 0.83 and 1.18; values close to that of the All fraction after only 0.5 h of reaction at 0.83 and 1.22. After about 4 h of reaction nearly all of the particles are collected in the Standard fraction, so the two compositions converge. Comparing the film compositions before and after selenization, we observe that both the Standard and All fraction shift to higher Cu/(Zn+Sn) ratio as a result of both Zn and Sn loss. For reaction times less than 2 h, when the material is very Zn-rich, the shift primarily results from Zn loss, as indicated by a reduction in the Zn/Sn ratio, but for reactions longer than 2 h we also see evidence of Sn loss, as has been documented previously [16-20]. Because ZnS(e) has a very low vapor pressure, the loss of Zn suggests that there is likely unbound (metallic) zinc present during annealing. The elemental losses are significantly lower for the longer reaction times, when the average composition is closer to stoichiometric. Conveniently, for reaction times of 2-4 h, the elemental losses that occur during selenization shift the composition ratios very close to the composition targeted by the NC synthesis (dashed line). A summary of the cation ratios is provided in Table 1.

Reaction Time	<u>Standard</u>		<u>All</u>	
	Cu/(Zn+Sn)	Zn/Sn	Cu/(Zn+Sn)	Zn/Sn
0.125 hrs	0.79	3.94	0.87	1.81
0.25 hrs	0.74	2.02	0.82	1.31
0.50 hrs	0.74	1.52	0.83	1.23
1 hrs	0.84	1.17	0.84	1.14
2 hrs	0.84	1.16	0.86	1.15
4 hrs	0.88	1.10	0.86	1.09
12 hrs	0.81	0.88	0.77	0.87
24 hrs	0.78	0.89	--	--

Table 1. Summary of cation ratios for the selenized films.

Figure 2. Parameters extracted from the current voltage characteristic of the Standard NC devices (red) and All NC devices (blue) with different reaction times. Error bars indicate the minimum and maximum values observed from 12 devices.

3.2 Current-Voltage Characteristics

To evaluate how the NC synthesis and particle collection procedure impact the resulting devices, CZTSSe solar cells were made from both the Standard and the All NC inks. Parameters extracted from the current-voltage characteristic are summarized in Figure 2, and SEM cross sections of the Standard devices are shown in Figure 3. We find that Jsc, fill factor, Voc, and power conversion efficiency (PCE) of both the Standard and All devices increase with reaction time up until 4 h. Short circuit current continues to increase after the 4 h mark, offsetting the losses to fill factor and Voc observed for the 12 and 24 h reaction times to yield devices with comparable efficiency. The changes in composition with time complicate the data interpretation, but by comparing samples with similar cation ratios, we are able to make clear conclusions about the effect of reaction time and the impact of different particle fractions. For example, the 1-4 h Standard and the 0.5-4 h All devices have similar cation ratios, yet the Standard ink, which on average has larger particles and is more homogeneous, tends to make slightly more efficient devices. The difference primarily results from enhanced Voc and fill factor. This contrasts with previous work, which reported that the small Zn-poor particles (such as those included in the All fraction but not the Standard fraction) had a beneficial effect on devices [21]. In that report, the addition of the small particles significantly changed the cation ratios of the similarly synthesized particles (the “R1” particles), but not the particles synthesized using an alternative method (the “R2” particles). The R1 particles are comparable to our 0.5 h particles, while the R2 particles were synthesized using a higher temperature reaction for a longer amount of time, and thus may be comparable to our 4 h particles. Comparing the Standard and All devices from these reactions, we see that the additional of the small particles benefits the 0.5 h

but not the 4 h. For the 0.5 h reaction, the changes in composition are so large it is difficult to determine what impact the small particles have. We also note, that the efficiency of the 0.5 h All sample is much worse than expected given the composition, which may be a result of poor film quality or processing error.

Figure 3. SEM cross-sectional images of the Standard devices with different NC reaction times. The samples are all approximately 1.2 μm thick and show varying degrees of grain growth. The scale bar is 1 μm in each image.

Among our samples with similar compositions, the clearest trend is an improvement in efficiency with reaction time. Between 1-4 h the composition of the Standard devices changes only slightly, yet the average efficiency increases by 3.0%. The effect is less pronounced in the All devices, but between 0.5-4 h we do see improvements. The performance of the longest reaction time devices provides additional evidence for the beneficial effect of reaction time. Reaction times up to 4 h produce films with a Cu-poor/Zn-rich composition. These conditions favor the formation of benign defects and defect clusters such as $[\text{V}_{\text{Cu}}+\text{Zn}_{\text{Cu}}]$ while suppressing the formation of more detrimental defects such as $[\text{2Cu}_{\text{Zn}}+\text{Sn}_{\text{Zn}}]$, Sn_{Zn} , and V_{Zn} [22-24]. For this reason, the most commonly reported optimum Cu/(Zn+Sn) and Zn/Sn ratios are 0.8 and 1.2, respectively [25]. However, the 12 and 24 h devices are Sn-rich, with Zn/Sn ratios near 0.9. At these compositions we anticipate much more unfavorable defect chemistry, and yet these devices perform as well or better than devices which have compositions close to the ideal. It should be noted that these devices were processed without any sort of post-growth etching to remove impurities. For Zn-rich films, we expect the precipitation of ZnSe, which is relatively benign, but the Sn-rich devices will likely have SnSe or SnSe₂, which are believed to be detrimental [26, 27]. In the SEM cross-sections (Figure 3) some brightly colored ZnSe precipitates are evident near the bottom of the film, but we do not see any obvious signs of Sn-based secondary phases.

Figure 4. External quantum efficiency of the Standard nanocrystal devices. We see improved carrier collection at almost all wavelengths with increasing reaction time.

3.3 External Quantum Efficiency and Drive-Level Capacitance Profiling

Figure 4 shows the EQE of the highest efficiency Standard devices for each reaction time. We see that increasing reaction time enhances current collection across all wavelengths, suggesting a decrease in the defect concentration both in the quasi-neutral region and in the space charge region. The higher EQE between 400-500 nm for the 12 and 24 h devices could result from either a reduction in interfacial defects or a thinner CdS layer. However, given that the devices received identical CBD the latter seems less likely. To better quantify the changes in the defect density, the devices were characterized using drive-level capacitance profiling (DLCP). The DLCP derived defect densities are shown in Figure 5. In agreement with the current voltage data and the EQE, we find that the defect density decreases significantly with increasing reaction time, but is still quite high even for the best devices [1]. Again, some of the trend can be ascribed to changes in composition, but the 0.5-4 h All and 1-4 h Standard devices have similar compositions and yet we still see substantial reductions in the defect density with reaction time. The defect densities of the 4-24 h devices at 1 kHz are all approximately the same, but at 100 Hz, we see a significant reduction in the defect density of the 24 h device. At lower measurement frequencies, we expect to see deeper defects responding, thus the DLCP data indicates that the Sn-rich 24 h device has a lower density of deep defects than the Zn-rich 4 h device. This data conflicts with what is expected based on first principles calculations [27], but is consistent with the device performance and the photoluminescence data (discussed below).

Figure 5. Change in the defect concentration as a function of reaction time for both Standard and All devices. Values were determined using drive-level capacitance profiling

3.4 Absolute Intensity Photoluminescence (AIPL)

The performance of the long reaction time devices becomes even more intriguing when we look at the steady state absolute-intensity photoluminescence (AIPL). AIPL is a powerful technique for evaluating the overall quality of a material. A high quality material should not only absorb light efficiently, but it should also emit light efficiently. The high-energy tail of the PL peak contains information about the quasi-Fermi level splitting which is the maximum achievable open-circuit voltage. The low-energy tail of the peak contains information about local electrostatic potential fluctuations. Electrostatic potential fluctuations result from charged defects or defect clusters. They show-up in the absorption spectrum as a sub-bandgap absorption tail and in the PL spectrum as a redshifting of the PL peak maximum and a broadening of the peak full-width-at-half-maximum (FWHM). A good material should have a large quasi-Fermi level splitting ($\Delta\mu$), a narrow FWHM, and the peak position should be at energies close to or above bandgap. The values of these parameters are shown in Figure 6 and 7 for the different reaction time devices along with experimental PL spectra from the Standard devices.

As with the device parameters, we see improvement in the PL characteristics with reaction time. The 4 and 24 h Standard were the highest efficiency devices, and we can see that they have the highest energy peak positions. However, despite having similar efficiencies, the 24 h sample has a much narrower FWHM, indicating reduced potential fluctuations, and a larger quasi-Fermi level splitting. This is consistent with the DLCP data, and indicates that the 24 h sample has fewer SRH-active defects.

Figure 6. Typical absolute intensity photoluminescence spectra from the Standard devices (a) and comparison of the extracted quasi-Fermi level splitting to the measured open-circuit voltage (b).

As shown in Figure 6, we find a good correlation between $\Delta\mu$ and V_{oc} , with the largest deviations occurring at short and long reaction times. The short reaction times, such as the 0.5 h Standard, have V_{oc} 's lower than the $\Delta\mu$. The discrepancy likely results from the large quantities of ZnSe that undoubtedly exist in such a Zn-rich film. ZnSe has not been found to produce non-radiative recombination sites but it will interfere with current flow [28], and has been correlated with reduced V_{oc} in CZTS [29, 30]. The 12 and 24 h reaction devices have the largest quasi-Fermi level splitting ($\Delta\mu$), an observation which stands at odds with the current understanding of defect chemistry. However, we do not see this manifest as a higher V_{oc} in the devices. This could be due to the presence of SnSe or SnSe₂ at the CZTSSe/CdS interface. In chalcopyrites, much work has been devoted to figuring out why Cu-poor materials perform better despite the fact that Cu-rich materials have better optical and electronic properties [31, 32]. A leading explanation is that Cu-poor absorbers form a more favorable interface with CdS.¹⁰ A similar mechanism could be at play here, but further investigation is needed. Very little research has been published on Cu-poor/Sn-rich kesterites, and to the best of our knowledge this is the first report of large quasi-Fermi level splitting in devices with Zn/Sn < 1.

Figure 7. Photoluminescence peak position and peak full-width-at-half-max (FWHM) for the Standard and All devices.

3.5 X-ray Diffraction and Crystalline Domain Size

Thus far all data has indicated that longer reaction times lead to lower defect densities, larger quasi-Fermi level splitting, and thus better devices, but the question still remains: why? The answer is found by examining the XRD data, shown in Figure 8. In general, the peaks are all consistent with kesterite CZTSSe. We are able to see a number of minor peaks that are solely associated with the kesterite phase, and their relative intensities agree well with that of the diffraction standard (PDF #01-070-8930), indicating that the pattern primarily results from a kesterite phase. We only observe binary phases in the 0.125 h Standard, 0.25 h Standard, and 0.125 h All films. These films are all extremely Zn-rich, yet the only secondary phase that we can clearly discern corresponds to a CuSe phase. We are unable to distinguish a Zn(S,Se) phase in these samples due to the overlap of the most intense peaks with those of CZTS(e), an issue which is well documented in literature [33, 34]. However, from analyzing the relative intensity of the CZTSe peaks we can conclude that any Zn(S,Se) which may be present does not have a strong contribution to the diffraction pattern. Applying Vegards law, we calculate that the sulfur content is relatively consistent between samples at approximately 17%. Assuming an even distribution of the sulfur within the film, this should correspond to an optical band gap of 1.02eV [23]. Comparing this value with the position of the PL peak maximum (Figure 7), we see that the peak maximum is well below bandgap, as we would expect with significant potential fluctuations.

Figure 8. XRD from selenized Standard (left) and All (right) inks. Peaks corresponding to secondary phases are only observed in the 0.125 Std and All samples.

The most interesting result comes from looking at the changes in the FWHM of the primary CZTS diffraction peak. As shown in Figure 9, the crystalline domain size of the selenized film, determined using Scherrer's equation, increases with reaction time, and is consistently 2-2.5 times as large as the diameter of the starting sulfide NCs (assuming the particles are spherical). From exchange of sulfur with selenium, we would expect a volume change of about 15%, so some interparticle sintering must be occurring, but the extent is approximately similar in all of the films. In the SEM cross-sections (Figure 3) we see improvement in the apparent grain size and morphology with reaction time. The grains of the longest reaction times are larger and less faceted than those with shorter reaction times, but in all of the samples a significant un-sintered layer is present.

Figure 9. Plot of the crystalline domain size determined using Scherrer's equation showing the correlation with the size of the starting sulfide nanocrystals. We find that the size of the starting nanocrystal is proportional to the crystalline domain size in the film, indicating that limited interparticle sintering is occurring.

As shown in Figure 10, the crystalline domain size calculated from Scherrer's equations correlates very well with device efficiency. As the crystalline domain size increases, so does efficiency, suggesting that the grain boundaries act as a significant source of non-radiative recombination. This could also explain why longer reaction times exhibit comparable device performance, even when they have less favorable compositions. Longer NC reaction times lead to larger NCs; larger NCs lead to larger crystalline domains in the selenized film; and larger crystalline domains lead to fewer grain boundaries which are a source of deep defects. This conclusion would be consistent with previous theoretical calculations indicating that the grain boundaries of kesterites are not as passive as those of chalcopyrites [35, 36]. It could also suggest that a route to improving the efficiency of NC-derived solar cells is to simply synthesize larger NCs. However, we must emphasize that this is not the only interpretation of the XRD data. The narrowing of the FWHM could also result from a reduction in crystallographic defects or strain. Additionally, because of the possible co-existence of secondary phases with overlapping XRD peaks, the narrowing of the peak FWHM could simply indicate a reduction in the presence of weakly crystalline secondary phases. From looking at the minor diffraction peaks, we know that the contribution of secondary phases is minor, but they may still contribute to the breadth of the peak. Additionally, the narrowing of the FWHM could result from a reduction in crystallographic defects. Elimination of these phases would likely also have a beneficial effect on the devices, and may also explain the increase in efficiency with narrowing FWHM.

Figure 10. Plot of the crystalline domain size determined using Scherrer's equation showing the correlation with power conversion efficiency (PCE) for the Standard (left) and All (right) devices. The correlation is consistent with theoretical predictions that the native grain boundaries are not passive.

4.0 Conclusions

We have investigated how $\text{Cu}_2\text{ZnSnS}_4$ nanocrystal inks with different particle size, size distribution, average composition, and compositional heterogeneity impact the properties the selenized absorber layer. We find that longer NC synthesis produce larger NCs, and larger NCs lead to larger domain size after sintering, a lower concentration of deep defects, and more efficient solar cells. The strong correlation between crystalline domain size and the defect concentration (and resulting device efficiency) suggests that grain boundaries are a significant source of non-radiative recombination. Thus to make high efficiency devices, grain boundary passivation techniques or NC synthesis and sintering methods that allow better grain growth will need to be developed. We also find that the inclusion of small Sn-rich particles, leading to increased ink heterogeneity, has a slightly negative impact on device performance, but not on grain growth. Finally, we note for the first time large quasi-Fermi level splitting in devices with $\text{Zn/Sn} < 1$.

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