The Effect of Cu-Zn Disorder on Charge Carrier Mobility and Lifetime in Cu$_2$ZnSnSe$_4$

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Abstract

Cu-Zn disorder is one possible origin for the limited efficiencies of kesterite solar cells and its impact on the band gap and band tails have been intensively studied. However, the effect on charge transport and recombination, which are key properties for solar cells, has not been investigated so far. Therefore, we probe the impact of the Cu-Zn order on charge carrier mobility and lifetime. To this end, we change the Cu-Zn order of a co-evaporated Cu$_2$ZnSnSe$_4$ thin film by sequential annealing and probe the impact by time-resolved terahertz spectroscopy. Aside from of the well-known band gap shift, we find no significant change in mobility and lifetime with Cu-Zn order. This finding indicates that Cu-Zn disorder is not limiting efficiencies of kesterite solar cells at their current status by means of charge carrier recombination and transport.

Keywords kesterite; disorder; mobility, lifetime; terahertz spectroscopy; solar cell

1 Introduction

Cu$_2$ZnSn(Se$_x$,S$_{x-1}$)$_4$ semiconductors in kesterite structure are promising candidates for thin film solar cells due to their beneficial properties such as: a high absorption coefficient, the abundance of the constituting elements, the stable solar cell performance and the cheap ink based deposition techniques [1]. However, their record cell efficiency of 10.0 %, has not reached the level of competing thin film technologies such as 22.9 % for Cu(In,Ga)(Se,S)$_2$ or 21.0 % for CdTe photovoltaics and also lags behind the emerging halide perovskites with 20.9 % [2]. Still, kesterites may be the "dark horse" winning the race of thin film solar cell [3] as it took decades for CdTe and Cu(In,Ga)(Se,S)$_2$ to reach their current efficiencies and perovskites face stability and toxicity issues. The limitation of kesterite solar cells is primarily

the low open circuit voltage (V_{OC}) that partially originates from low charge carrier lifetimes [4,5] and partially from an additional loss by charge carrier trapping [4] in a large density of band gap states as band tails, band gap fluctuations or defects [6,7].

A possible origin of both, short lifetimes and the band tails, is a sub-lattice disorder of the Cu and Zn sites which distinguish kesterites from other thin film photovoltaic materials [15].

It was shown that the degree of Cu-Zn disorder can change the band gap by up to 110 meV [8]. Hence, initially it was believed that fluctuations in the degree of Cu-Zn disorder may cause band gap fluctuations which then could explain the voltage deficit of kesterite solar cell [6] and the observed absorption tails [9].

However, this suspicion was partially contradicted by recent studies. It was shown that open circuit voltage of $Cu_2ZnSnSe_4$ solar cells increases with the band gap but the voltage deficit is unaffected by the Cu-Zn disorder [10]. Also no significant impact on the absorption tails was measured [5,11]. Only the carrier collection increased with the degree of Cu-Zn order which was attributed to a decrease in doping concentration and the corresponding increase in the space charge region width [10].

However, the influence of Cu-Zn order on other fundamental properties as charge carrier lifetime and mobility has not been studied so far. Such an influence could also cause an increasing charge carrier collection and would affect the internal quasi Fermi level splitting in a solar cell, both of which together govern its current and voltage output.

Here, we probe the charge carrier mobility and recombination after partial ordering and disordering of $Cu_2ZnSnSe_4$ thin films yielding up to 9.8 % efficient solar cells [12].

We observe the well-known widening of the band gap for the more ordered state by 70 meV. Simultaneously, the sub-band gap photoluminescence shifts by 90 meV to higher energies, indicating that the band gap states follow the shift of the band states. However, the sum of electron and hole mobility as well as their lifetime do not significantly change within the studied range of Cu-Zn order.

This behavior supports the model of a Cu-Zn order induced shift of the valence band with a relatively small mobility and a large Shockley-Read Hall capture rate for holes. The conduction band which does not consist of Cu or Zn orbitals is unaffected by their order and the relatively

large electron mobility and small Shockley-Read Hall capture rate for electrons dominate the measured sum mobility of electrons and holes and limit the charge carrier lifetime.

Regarding kesterite solar cells, we concluded that Cu-Zn disorder does not limit their efficiencies at the current status.

2 Experimental Details

2.1 Sample characterization

The charge carrier mobility was measured by time-resolved terahertz spectroscopy (TRTS) in reflection geometry. This is a pump-probe technique that records the reflection of a terahertz probe pulse (1 THz $\triangleq$ 4.1 meV $\triangleq$ 300 µm). Upon carrier generation by an 800 nm pump pulse, the reflection of the terahertz probe pulse changes. This change was modelled by the transfer matrix method as described in [13] and, at terahertz frequencies, it is dominated by free carrier absorption of mobile charge carriers and the corresponding change in the refractive index of the sample. The modelling yields the sum of electron and hole mobility as both kinds of charge carriers are excited and both kinds absorb the terahertz probe pulse. The doping does not affect the measurement as only the pump-induced change is measured.

Further, this technique measures the mobility of the charge carriers in the oscillating field of the terahertz probe pulse. Therefore, the mobility is derived as function of the terahertz frequencies which are present in the terahertz probe pulse.

Additionally, the transient of induced photoconductivity can be measured by scanning the delay of the optical pump pulse with respect to the terahertz probe pulse. The pump pulse has a center wavelength of 800 nm and pulse length of 150 fs. It originated from an amplified titanium-sapphire laser with 150 kHz repetition rate and with a photon flux of 1.2×10^{13}/cm^2/pulse on the sample. The terahertz pulse was generated by optical rectification in a ZnTe crystal and was detected by electro-optical sampling, also in a ZnTe crystal.

The band gap was estimated from the infra-red reflection of the sample which was measured in an Ulbricht sphere of a commercial Perkin Elmer spectrometer.

The band gap states were probed by photoluminescence which was recorded in a confocal setup under 660 nm excitation with a 10 µW laser focused to a diameter of ca. 25 µm.

2.2 Sample preparation

The Cu₂ZnSnSe₄ thin film was deposited by coevaporation of the individual metals and selenium on a molybdenum coated soda lime glass as detailed in a previous publication [12]. During cooldown the Zn and Se sources were kept open which resulted in a few nanometer thick ZnSe capping layer. The final composition was $Cu/(Zn+Sn) = 0.73$ and $Zn/Sn = 1.6$ including some ZnSe grains at the back interface and the ZnSe capping layer as measured by X-ray fluorescence spectroscopy [14].

The partial ordering and disordering of the sample was achieved by annealing on a hot plate in N_2 atmosphere. The temperature was set by the hot plate and the sample was covered with a quartz lid to prevent significant temperature differences between hot plate and sample. The partial disordering was performed at 300°C for 10 minutes which is significantly above the critical temperature of 200°C, followed by thermal quenching to room temperature as illustrated in Fig.1. The partial ordering was performed by stepwise annealing below the critical temperature at 150°C for 6 hours, at 110°C for 12 hours, 90°C for 24 hours and finally at 70°C for 24 hours.
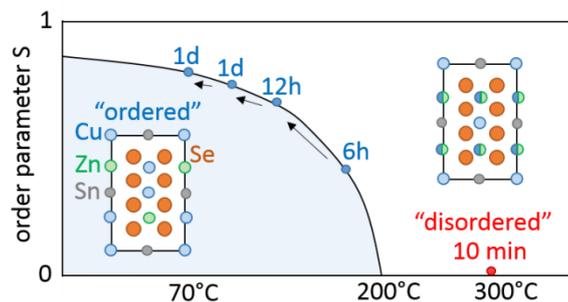
Fig.1: Illustration of the stepwise annealing of the Cu₂ZnSnSe₄ thin film which results in a relatively ordered kesterite structure with an order parameter S close to 0.8. Annealing at 300°C above the critical temperature of ca. 200°C induces Cu-Zn disorder close to S=0 on the sub-lattice which is conserved by rapid quenching to room temperature.

3 Theory of disorder transition

Disorder in the Cu-Zn sub-lattice of the kesterite structure on the 2c and 2d positions in the Wyckoff notation is illustrated in the inset in Fig.1 and was confirmed by neutron scattering [15]. It can be described by an order parameter S in the Vineyard model [16] which is 1 for the ordered kesterite structure and 0 for random distribution of Cu-Zn on the 2c and 2d sites. The degree of ordering depends on the thermal history of the sample. Above the critical temperature T_C of ca. 200 °C the order parameter approaches zero in the long time limit and

the Cu and Zn atoms will distribute randomly on the 2c and 2d sites [8]. Below that critical temperature the Cu and Zn atoms will start to order until they reach an equilibrium with an order parameter S given by $S = tanh(S\ T/T_C)$. Full order with $S=1$ is only reached at zero Kelvin and accounting to reference [8] the maximum order parameter at the lowest annealing temperature of 70°C for our sample is ca. 0.8. However, the actual degree of order approaches the maximum values for a certain temperature over time and if the sample is quenched to room temperature, a certain degree of order can be frozen. Hence, the "ordered" and "disordered" state of the $Cu_2ZnSnSe_4$ thin films have a significantly different order parameter of approximately 0.8 and 0 but are not completely ordered or disordered.

4 Results

4.1 Optical properties

To validate the thermal treatments to have resulted in a significant change in Cu-Zn order, we probed the band gap, which is expected to increase approximately linearly with the order parameter S [8]. However, the band gap could not be estimated from transmission measurements as the sample was deposited on non-transparent molybdenum coated glass in order to reflect the properties of usual kesterite solar cells. Instead, we used the infrared reflection R shown in Fig. 2a as a pseudo absorption measurement. For photon energies above the band gap, the measured reflection exclusively originates from the interface of kesterite and air. The light that enters the kesterite layer will be absorbed under this condition. In contrast, sub-band gap light can transmit trough the kesterite layer, is reflected at the molybdenum and contributes to the measured reflection. This additional reflection can be seen in Fig.2a at the lower phonon energies and the band gap is estimated by the maximum of the reflection increase dR/dE. The thermal treatments result in a band gap shift of 70 meV which proves a significant change in the Cu-Zn order of the sample to have taken place.

The absolute values of the band gaps are 0.89 eV for the disordered state and 0.96 eV for the more ordered state. This compares to a band gap of 0.97 eV derived from the maximum increase of the quantum efficiency of a completed solar cell from the same deposition process. Therefore, the reflection measurement may underestimate the band gap by several tens of meV but the relative change between the more ordered and disordered states will be accurate for a constant offset.
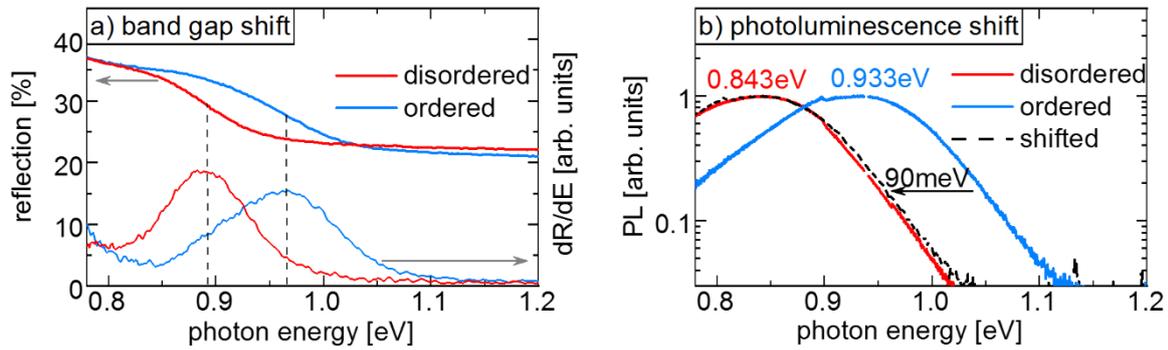
Fig.2: a) The infrared reflection of the sample in the relatively disordered state exhibits the band edge feature at 70 meV lower photon energies. b) The photoluminescence shifts by 90 meV to lower photon energies too.

The photoluminescence (PL) in Fig.2b is a broad peak with a maximum below the band gap as usually observed for $Cu_2ZnSnSe_4$. It has been attributed to processes like a tail to tail transition [10] or a free to bound transition [17], for example. With increasing Cu-Zn disorder, the PL maximum exhibits a shift to lower photon energies E by 90 meV. However, the spectral shape stays unaffected as shown in FIg.2b. Hence, the luminescing band gap states follow the shift of the band gap.

4.2 Electronic properties

The sum of the mobilities μ of the photo-excited electrons and holes in the $Cu_2ZnSnSe_4$ thin film as measured by TRTS is shown in Fig.3a. They are measured for AC-transport at terahertz frequencies f and their real part can be extrapolated to DC-mobilities of ca. 110 cm^2/Vs and 125 cm^2/Vs for the more disordered and ordered state, respectively. These values are in line with previous reports on mobilities in $Cu_2ZnSnSe_4$ ranging from 100 cm^2/Vs to 140 cm^2/Vs [14,18]. Also, the frequency dependence of an increasing real part and a negative imaginary is a common for kesterites and indicates charge carrier localization.

The slight difference between the more ordered and disordered states lies within the typical error for measurements performed on successive days and after sample realignment. Even if the observed increase in mobility by ~10 % was caused by the Cu-Zn ordering, the impact on charge carrier collection would be very limited and impose no fundamental limit on kesterite solar cells. Halide perovskites-based solar cells for example reach significantly higher power conversion efficiencies with lower TRST-derived mobilities of typically ca. 40 cm^2/Vs [19].
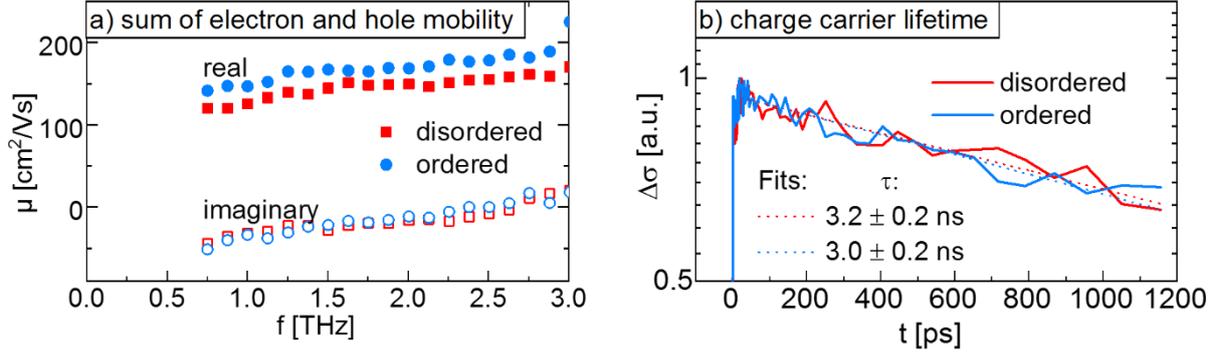
Fig.3: a) Charge carrier mobility μ of electrons and holes at terahertz frequencies f are similar for relatively ordered and disordered Cu₂ZnSnSe₄. b) Photoconductivity transients Δσ(t) are likewise unaffected by the induced change in Cu-Zn order.

The charge carrier recombination is monitored by the decay of the photoconductivity as shown in Fig.3b. Again, no significant difference is observed between the $Cu_2ZnSnSe_4$ thin film in the more disordered and ordered state. The transients are modeled with lifetimes of 3.0 ±0.2 ns and 3.2 ±0.2 ns which are similar within the uncertainty of the fitting procedure. Hence, the dominating recombination channel is unaffected by the Cu-Zn disorder, in the range of order parameters studied and in the range of uncertainty of the measurement.

5. Discussion

The lack of a change of recombination as well as transport properties with varying levels of Cu-Zn disorder is remarkable in light of the observed change of the band gap. It can be explained assuming a specific transport and recombination path model in kesterite as explained in the following. As a caveat it has to be said that this model cannot be proven here beyond all doubts. However, it explains our main results.

Simulations of the band structure show that the conduction band consists of Sn and Se orbitals, whereas the valence band consists of Cu and Se orbitals [20]. Hence, one can expect the Cu-Zn disorder to dominantly affect the valence band.

Within this picture, the observed decrease of the band gap can be interpreted as an upward shift of the valence band with increased Cu-Zn disorder. The simultaneous red shift of the photoluminescence, attributed to transitions between band, tail and defect states, indicate that band gap states or band tails follow the shift of the respective band states.

The mobility of charge carriers is related to the nature of electronic states they occupy. For example, a charge carrier transports much slower in a localized defect state or in partially

overlapping band tail states than in an ideal Bloch state of the bands. Indeed, the observed frequency dependence of the mobility contradicts the usual transport in ideal band states and indicates some kind of charge carrier localization which may be connected to transport in band tails or potential fluctuations [14].

However, the measured sum of electron and hole mobilities in Fig.3a is not significantly affected by the Cu-Zn disorder. Therefore, this disorder cannot be the origin of the observed charge carrier localization.

The unaffected sum of electron and hole mobilities can be explained by our picture of a dominant impact of the Cu-Zn disorder on the valence states. We determined the individual mobilities for electrons of 128 cm^2/Vs and for holes of 7 cm^2/Vs on a similar $Cu_2SnZnSe_4$ thin film. A change in the valence states and a potential change in the relatively small hole mobility would affect the sum mobility little, as it would still be dominated by the larger electron mobility.

In general, the non-radiative (multiple-phonon) recombination is larger for a smaller energetically separation between initial and final state [21]. Hence, a shift of the valence band and its tail states by different Cu-Zn disorder should affect the recombination of holes. However, no effect of the Cu-Zn disorder on the effective lifetime of electrons and holes was found in figure 3b. Such behavior can be explained by dominant Shockley-Read-Hall recombination at mid-gap defects. According to this model, the effective lifetime is limited by the longer capture time of either holes or electrons into the deep defect. In the case of our kesterite sample, a change in hole capture time seems to have no impact. Therefore, the electron capture into the deep defects dominates the effective lifetime of electron and holes. This explanation indicates, that deep defects and not a valence band tail cause the non-radiative recombination in kesterite and limit the solar cell efficiency.

The demonstrated independence of recombination and transport properties from Cu-Zn disorder not only provides microscopic insights in charge carrier dynamics but is also encouraging for the further development of kesterite solar cells. A fundamental limit would be posed to kesterite solar cells if the lifetime was reduced by Cu-Zn disorder as the Cu-Zn disorder cannot be overcome entirely at room temperature. In contrast to this, we propose that the observed shift of the band edge may be used to improve the band alignment of the kesterite absorber with the contact layers.

References

[1] K. Ito, Copper zinc tin sulfide-based thin film solar cells, John Wiley & Sons, Chichester, 2014.

[2] M. A. Green, Y. Hishikawa, E. D. Dunlop, D. H. Levi, J. Hohl-Ebinger and A. W. Y. Ho-Baillie, Solar cell efficiency tables (version 52), Prog. Photovoltaics, 26 (2018) 427-436.

[3] S. K. Wallace, D. B. Mitzi and A. Walsh, The Steady Rise of Kesterite Solar Cells, ACS Energy Lett. 2 (2017) 776-779.

[4] C. J. Hages, A. Redinger, S. Levcenko, H. Hempel, M. J. Koeper, R. Agrawal, D. Greiner, C. A. Kaufmann and T. Unold, Identifying the Real Minority Carrier Lifetime in Nonideal Semiconductors: A Case Study of Kesterite Materials, Adv. Energy Mat. (2017) 1700167.

[5] S. Bourdais, C. Choné, B. Delatouche, A. Jacob, G. Larramona, C. Moisan, A. Lafond, F. Donatini, G. Rey, S. Siebentritt and others, Is the Cu/Zn disorder the main culprit for the voltage deficit in kesterite solar cells?, Adv. Energy Mat. 6 (2016) 1502276.

[6] J. J. S. Scragg, J. K. Larsen, M. Kumar, C. Persson, J. Sendler, S. Siebentritt and C. Platzer Björkman, Cu-Zn disorder and band gap fluctuations in Cu2ZnSn(S,Se)4: Theoretical and experimental investigations, Phys. Status Solidi B 253 (2015) 247-254.

[7] U. Rau and J. H. Werner, Radiative efficiency limits of solar cells with lateral band-gap fluctuations, Appl. Phys. Lett. vol. 84 (2004) 3735-3737.

[8] G. Rey, A. Redinger, J. Sendler, T. P. Weiss, M. Thevenin, M. Guennou, B. E. Adib and S. Siebentritt, The band gap of Cu2ZnSnSe4: Effect of order-disorder, Appl. Phys. Lett. 105 (2014) 112106.

[9] C. Stroth, M. H. Sayed, J. Neerken, U. Mikolajczak, G. Rey, J. Parisi and L. Gütay, In-situ investigation of the order-disorder transition in Cu2ZnSnSe4 by optical transmission spectroscopy, AIP Advances, 7 (2017) 025303.

[10] G. Rey, T. P. Weiss, J. Sendler, A. Finger, C. Spindler, F. Werner, M. Melchiorre, M. Hala, M. Guennou and S. Siebentritt, Ordering kesterite improves solar cells: A low temperature post-deposition annealing study, Sol. Energ. Mat. Sol. Cells. 151 (2016) 131-138

[11] G. Rey, G. Larramona, S. Bourdais, C. Choné, B. Delatouche, A. Jacob, G. Dennler and S. Siebentritt, On the origin of band-tails in kesterite, Sol. Energ. Mat. Sol. Cells. 179 (2017) 142-151.

[12] I. L. Repins, J. V. Li, A. Kanevce, C. L. Perkins, K. X. Steirer, J. Pankow, G. Teeter, D. Kuciauskas, C. Beall, C. Dehart, J. Carapella, B. Bobb, J. S. Park and S. H.Wei , Effects of deposition termination on $Cu_2ZnSnSe_4$ device characteristics, Thin Solid Films 582 (2015) 184-187.

[13] H. Hempel, T. Unold and R. Eichberger, Measurement of charge carrier mobilities in thin films on metal substrates by reflection time resolved terahertz spectroscopy, Opt. Express 25 (2017) 17227-17236.

[14] H. Hempel, A. Redinger, I. Repins, C. Moisan, G. Larramona, G. Dennler, M. Handwerg, S. F. Fischer, R. Eichberger and T. Unold, Intragrain charge transport in kesterite thin films - Limits arising from carrier localization, J. Appl. Phys. 120 (2016) 175302.

[15] S. Schorr, The crystal structure of kesterite type compounds: A neutron and X-ray diffraction study, Sol. Energ. Mat. Sol. Cells. 95 (2011) 1482-1488.

[16] G. H. Vineyard, Theory of Order-Disorder Kinetics, Phys. Rev. 102 (1956) 981-992.

[17] S. Levcenko, J. Just, A. Redinger, G. Larramona, S. Bourdais, G. Dennler, A. Jacob and T. Unold, Deep Defects in $Cu_2ZnSn(S,Se)_4$ Solar Cells with Varying Se Content, Phys. Rev. Appl. 5 (2016) 024004.

[18] G. W. Guglietta, K. R. Choudhury, J. V. Caspar and J. B. Baxter, Employing time-resolved terahertz spectroscopy to analyze carrier dynamics in thin-film $Cu_2ZnSn(S,Se)_4$ absorber layers, Appl. Phys. Lett. 104, (2014) 253901.

[19] F. Staub, H. Hempel, J.-C. Hebig, J. Mock, U. W. Paetzold, U. Rau, T. Unold and T. Kirchartz, Beyond bulk lifetimes: Insights into lead halide perovskite films from time-resolved photoluminescence, Phys. Rev. Appl. 6 (2016) 044017.

[20] S. Chen, A. Walsh, X.-G. Gong and S.-H. Wei, Classification of lattice defects in the kesterite Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ earth-abundant solar cell absorbers, Adv. Mater. 25 (2013) 1522-1539.

[21] T. Kirchartz, T. Markvart, U. Rau and D. A. Egger, Impact of Small Phonon Energies on the Charge-Carrier Lifetimes in Metal-Halide Perovskites, J. Phys. Chem. Lett. 9 (2018) 939-946.