Ultrafast pump-probe reflectance spectroscopy: Why sodium makes Cu(In,Ga)Se₂ solar cells better

**Jessica Eid,[†] Anwar Usman,[†] Issam Gereige,[†] Jeroen Van Duren,[‡] Vadim Lyssenko,[§] Karl
Leo,^{†,§} and Omar F. Mohammed^{*,†}**

[†]Solar & Photovoltaics Engineering Research Center, Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology, Thuwal 23955-6900, Kingdom of Saudi Arabia

[‡]Intermolecular, Inc., San Jose, CA, U.S.A

[§]Institut für Angewandte Photophysik, Technische Universität Dresden, 01062 Dresden, Germany

Corresponding Author

*E-mail: omar.abdelsaboer@kaust.edu.sa (O.F.M.)

TOC graphic

CIGS thin-film samples were investigated for the first time using femtosecond pump-probe differential reflection spectroscopy with broadband capabilities and 120-fs temporal resolution. The pump-and-probe beams were focused on $\sim 1.6 \mu\text{m}$ -thick CIGS films. The reflected probe light from the samples was collected and focused on the broadband infrared detector (D) for recording the carrier dynamics of CIGS in real time.

ABSTRACT

Although Cu(In,Ga)Se₂ (CIGS) solar cells have the highest efficiency of any thin-film solar cell, especially when sodium is incorporated, the fundamental device properties of ultrafast carrier transport and recombination in such cells remain not fully understood. Here, we explore the dynamics of charge carriers in CIGS absorber layers with varying concentrations of Na by femtosecond (fs) broadband pump-probe reflectance spectroscopy with 120-fs time resolution. By analyzing the time-resolved transient spectra in a different time domain, we show that a small amount of Na integrated by NaF deposition on top of sputtered Cu(In,Ga) prior to selenization forms CIGS, which induces slower recombination of the excited carriers. Here, we provide direct evidence for the elongation of carrier lifetimes by incorporating Na into CIGS.

KEYWORDS

CIGS solar cells, ultrafast photophysics, pump-probe reflectance spectroscopy, carrier recombination, dielectric function model

1. Introduction

Improvements made over the years to increase CIGS solar cell efficiency include bandgap grading, which relies on liquid-assisted growth by the three-stage coevaporation method [1]: Na diffusion out of a soda-lime glass [2], postdeposition treatment (PDT) with NaF impacting grain boundary passivation [3], PDT with KF [4,5], and optimization of Ga/(In+Ga) composition [5-8]; however, improvements require substantially further study. In light of the important role that Na plays in CIGS layers, several groups have examined the growth and performance of CIGS layers by systematically varying Na content [9-12]. Typically, exposure to Na during growth of CIGS layers has been observed to change interdiffusion of Cu, In, and Ga [9,12] to modify grain size and orientation [9-11], which may result in a redistribution of oxygen [9,12]. Solar cells grown in optimal Na concentrations are typically more efficient because they have a higher open-circuit voltage (V_{OC}) and a higher fill factor (FF) [12,13]. This is predicted to result from increased net carrier concentration, which is typically one order of magnitude due to either an increased p-type doping concentration (potentially by a reduction of compensating donors) and/or reduced recombination. Several mechanisms have been proposed on the electronic impact of Na via both grain interior and grain boundaries [10-16].

Grain boundaries in CIGS are still a very active area of research and no agreement exists yet on the electronic activity of grain boundaries [17]. So far, polycrystalline CIGS outperforms monocrystalline CIGS, yet whether grain boundaries are detrimental (recombination centers), benign (e.g., combination of inactive and fully passivated grain boundaries) [18], or required for high-power conversion efficiency (e.g., due to type inversion) [19] remains debatable. Observed changes in grain boundary activity with Ga/(In+Ga) [7,17,20,21] and an interplay of Ga/(In+Ga) with KF PDT have been made [5]. Historically, the optimum Ga/(In+Ga) composition has been around 0.30, though the exact reason is not fully understood. The widening of the α -phase existence range from added Ga and the related increase in tolerance to composition deviations might play a role [22]. Potentially, reduced crystal lattice distortion leads to a minimum in defect concentration [23]. Furthermore, grain size and subsequently grain boundary area are sensitive to Ga/(In+Ga) [7,8,24]. Therefore, concomitant changes and interdependencies between Na, O incorporation, Ga/(In+Ga), and grain boundary area and activity present a challenge to unraveling the source of improvements made to the CIGS absorber and solar cell.

Measuring the minority carrier lifetime provides the most direct measurement of CIGS absorber quality. The most common method to measure minority carrier lifetime in CIGS has been time-resolved photoluminescence, with lifetimes varying from a few ns to 250 ns, depending on absorber quality and air exposure [25,26]. However, carrier lifetime measurements by varying Na concentration have not been reported. For this reason, we investigate the ultrafast carrier dynamics in polycrystalline CIGS by varying Na concentrations and measuring the impact of Na on minority carrier lifetime.

We show that the fundamental photophysical properties of these semiconductor films can be directly resolved by applying broadband pump-probe spectroscopy to excite and detect the wavelengths around the exciton absorption peak, located in the near-infrared region. Powerful pump-probe spectroscopy [27-29] allows for the direct determination of the dynamics of the electron-hole pairs, charge separation, intraband relaxation, multiple excitations, multi-exciton generation, and Auger recombination—all of which govern the photophysical processes in semiconductor CIGS thin films [26,30] or in other semiconductors such as PbS quantum dots for solar cell applications [31].

Here, we report the first femtosecond transient reflectance data on CIGS absorber layers grown with and without added NaF prior to selenization of Cu(In,Ga). By analyzing the dynamics of the transient signal, we show that Na in CIGS significantly increases the lifetimes of the excited carriers. More specifically, our results clearly demonstrate significantly slower carrier recombination when Na is added, up to a certain level, which enhances the performance of solar cell devices.

2. Experimental Methods

1.1. CIGS thin-film preparation.

CIGS layers were prepared on soda-lime glass substrates and coated with an Na-diffusion barrier by sputtering Cu(In,Ga) followed by H₂Se batch selenization with active added Na using different NaF thicknesses (0–30 nm). Selenisation was performed at 250 °C for 60 min followed by 1-5 min at 500 °C, giving the composition range of Cu/(In+Ga)=0.8–1 and Ga/(In+Ga)=0.30–0.45. All detailed preparations and characterizations of CIGS layers have been previously reported [11]. Eid et al. [11] demonstrated that the thickness of added NaF to the CIGS layers changes the efficiency of solar cells: increasing NaF thickness from 0 to 15 nm increased solar

cell efficiencies from <10% to 16.0% (without antireflective coatings), but increasing NaF thickness from 15 to 30 nm decreased solar cell efficiencies. Here, CIGS layers grown with 0-, 10-, 15-, 20-, or 30-nm NaF (CIGS-0NaF, CIGS-10nmNaF, CIGS-15nmNaF, CIGS-20nmNaF, CIGS-30nmNaF, respectively) were chosen in our time-resolved spectroscopic study.

1.2. Time-resolved broadband differential reflection spectroscopy.

The CIGS thin-film samples were investigated using time-resolved pump-probe differential reflection spectroscopy with broadband capabilities. In this method, the pump-pulse action successfully promoted electrons to the conduction band (CB). Subsequently, the decay process from the latter band to various defect levels or/and valence bands could be directly probed in real time. The experimental setup employed a white-light continuum probe pulse, generated in a 2-mm-thick sapphire plate in an Ultrafast System LLC spectrometer, using a few μJ pulse energy of the fundamental output of a Ti:Sapphire femtosecond regenerative amplifier, operating at 800 nm with 35-fs pulses and a repetition rate of 1 kHz [32]. The pump pulses at 1080 and 1500 nm (related to the excitation at the blue and red sides of the energy gap, respectively) were created from spectrally tunable (240-2600 nm) femtosecond pulses generated in the optical parametric amplifier (Newport Spectra-Physics). The pump-and-probe beams with a diameter of 700 and 500 μm , respectively, were focused on $\sim 1.6\text{-}\mu\text{m}$ CIGS thin films. The beams were nearly perpendicular to the CIGS surface with an angle of less than 5° to the normal. In this study, the pump pulse excites carriers in the CIGS layer, which induces changes in the optical properties of the sample that lead to changes in reflectivity (ΔR). The reflecting metallic layer below the CIGS layers are also largely influenced by absorptive changes. The reflected probe light from the samples was collected and focused on the broadband infrared detector for recording the time-resolved transient reflectance spectra.

3. Results and Discussion

Fig. 1A represents the reflectivity spectra of CIGS-0NaF and CIGS-15nmNaF thin films, indicating that added NaF induces a clear red-shifted absorption spectrum or a decrease in the

CIGS bandgap. This is in agreement with previous secondary ion mass spectrometry (SIMS) data, where Na concentrations were found to be 3.3×10^{19} and 1×10^{20} atoms/cm³ for CIGS-0NaF and CIGS-15nmNaF, respectively [11]. Na concentration is highest at the CIGS surface and the back interface near the Mo electrode; the top layer of the CIGS grain-boundary area decreases with increasing NaF thickness [11], in accordance with the fact that Na is present at CIGS grain boundaries [33]. This further evidences that added Na changes the depth composition of Na, Ga/(Ga+In), and Mo [11], and subsequently the intrinsic carrier lifetime. This suggests that it is extremely difficult to keep Ga distributions in depth and hence the energy gaps to be similar upon NaF addition.

Fig. 1A also clearly shows that CIGS thin films show low reflectivity above the gap with a strong increase below the gap, indicating that most of the light is reflected by the Mo mirror for these wavelengths. In this sense, from an electrical viewpoint, the Mo electrode has two functions: it is a back contact electrode and it reflects the light back to the CIGS layer. Accordingly, some form of interference in the spectral portion below the gap is caused by the interaction of the light reflected at the CIGS surface with that reflected at the back contact of Mo.

As mentioned above, added Na reached only three factors higher than the background Na level. It is widely accepted that without an NaF layer, Na diffuses from the soda-lime glass substrate during the growth of the CIGS thin film and can enhance energy conversion efficiencies [2,34,35]. Thus, the Na concentration in the CIGS thin film can be varied by adding NaF prior to selenization of Cu(In,Ga). In our previous work, we found a distinct improvement in the performance of the device when the thickness of NaF was varied between 0 and 10 nm [11]. Several hypotheses attempt to define mechanisms by which Na (including small changes to Na levels) affects the performance of the device for CIGS thin films; however, most focus on the role of Na in the growing surface and improvement of the crystal structure, an increase in the Ga/(In+Ga) gradient, an increase in grain size, and improved morphology [13,36,37].

In Fig. 1B and C, we show the transient reflectance spectra of CIGS-0NaF and CIGS-15nmNaF at early time delays (from ~3 to 65 ps) upon optical excitation at 1500 nm. The photogenerated charge carriers induce several positive and negative bands which exhibit structured transient spectra typical of thin-film interference patterns, indicating significant reflection from the back

interface to the highly reflective Mo layer below the gap where the absorption is weak. The fringe pattern in the difference reflectance, including shifts in position and spacing, should be related to composition in depth of Na, Ga/(Ga+In), surface morphology, optical properties, and more importantly the change in the energy bandgap of the CIGS thin film. To understand these spectra, we simulated the transient spectra presented in Fig. 1B and C with a dielectric function model of the CIGS thin films using both Lorentzian and plasmonic contributions. (A detailed description of this modeling is beyond the scope of this paper and will be presented in a separate publication.) These simulations allow us to extract the progressive recovery of the refractive index after a 1080-nm pump pulse with a negligible recovery of the extinction coefficient, and vice versa, the dominant progressive recovery of the extinction coefficient can be extracted with negligible changes to the refractive indexes of CIGS-0NaF and CIGS-15NaF, respectively. We also note that in the spectral range of $\lambda > 1000$ nm for CIGS-0NaF, the excitation light modifies the Lorentzian bands, resulting in shifts of interference oscillations and symmetrical dynamics of electron-hole pairs with isosbestic crossings (Fig. 2A). In particular, the response of CIGS-15nmNaF is more asymmetric (no isosbestic crossing, Fig. 2B), which is caused by a transient change of the plasmonic behavior.

Fig. 3 shows the transient reflectance spectra of CIGS-0NaF at short- and long-time delays after optical excitation. Interestingly, the spectra in the early time delays show an increase in both the positive and negative bands with a time constant of ~ 1 ps. This increase is likely due to highly energetic free carriers, which are captured in the CIGS energy states and relax quickly into the lowest energy state. The capture of free carriers can occur via carrier-phonon or carrier-carrier interactions with a typical capture time of 0.6–4.5 ps, depending on the incident fluence [38]. Although the CIGS-15nmNaF carrier capture and recombination processes occur in the same manner as in CIGS-0NaF, as discussed below, carrier recombination of CIGS-15nmNaF is significantly slower.

By adding NaF, we observed an increase in CIGS grain size and an improvement in the roughness of the CIGS layer [11]. We believe that surface quality determines the reflectance of the CIGS layers but that the observed carrier dynamics will be unaffected. Meanwhile, thermalization of excited carriers can be excluded from our study for the following reasons: a) the carrier dynamics we observed are Na-concentration dependent (as shown in Figure 5) and b) the carrier recombination measured here is not sensitive to pump fluence. Importantly, the

ground-state bleach (negative signal) recovery took place within a couple of hundred picoseconds of the time constant, which can be attributed to electron-hole recombination. The 10-ps component in the presence of Na shown in Figure 4A, may reflect the excited charge carriers that are captured or localized in the CIGS energy states and that then quickly relax into the lowest energy state. This behavior has been observed for other semiconductor materials [31,39].

Fig. 4A compares the kinetic transients of carrier recombination in CIGS-0NaF and CIGS-15nmNaF; it shows that the rate of carrier recombination depends on incorporation of Na. The single-exponential fits of the ground-state bleach recovery show that added Na lengthens the recombination time from 310 ps in CIGS-0NaF to 477 ps in CIGS-15nmNaF. Moreover, the unrecovered negative band of CIGS-0NaF (within 1 ns) that reflects the unrecombined charge carriers is $\sim 3\%$, while that for CIGS-15nmNaF is $\sim 10\%$ (at a time delay of 1.3 ns). Fig. 4B shows the presence of a fast component on the positive band. The relatively longer-carrier lifetime in CIGS-15nmNaF keeps the charge carriers in a separated state after the photoexcitation, which provides more opportunity for charge carriers to be transferred and collected at the hetero-junction in the solar cell device, resulting in higher energy conversion efficiency. We continued to explore this phenomenon by examining the kinetics of CIGS with added NaF in the range of 0 to 30 nm prior to selenization of Cu(In,Ga) (see Fig. 5). The results show that CIGS-15nmNaF had the optimum recombination time and the largest concentration of remaining charge carriers. This observation is consistent with the dependence of solar cell efficiency on NaF thickness, where the maximum efficiency is given by CIGS-15nmNaF [11]. Although x-ray structural data, averaged over CIGS thickness (1.6 μm), show that the polycrystalline structure of the CIGS containing different Na concentrations remained intact [11], it is important to note that CIGS films with 0- and 30-nm NaF layers had considerably more Ga at the surface than did films with 10-, 15-, and 20-nm NaF layers. This indicates that Na concentration dictates the Ga/(In+Ga) depth profile (and bandgap grading) during development of CIGS-NaF thin films, in addition to grain size and power conversion efficiency [11]. Because the thicknesses of CIGS thin films are comparable, we can exclude film thickness-dependent short-circuit current densities [33]. On the other hand, the Ga/(In+Ga) depth profile results in a comparable graded bandgap profile [40], which determines the power conversion efficiency. In an earlier report [11], we demonstrated that the Ga/(In+Ga) depth profile is more graded with

increasing NaF thickness, indicating the influence of Na concentration on the optoelectronic parameters, defect densities, and power conversion efficiencies of CIGS thin films. Taken together, these results provide clear insight into the bandgap profile in the CIGS layer. Certainly, an increase in Na concentration impacted the Ga profile, which we explain in detail in our previous work [11].

Recombination time and remaining charge carriers are similar for CIGS-30nmNaF and CIGS-0NaF, likely because the reduced Ga/(In+Ga) gradient is common to both. Because SEM images of CIGS thin films show an increase in grain size and a reduction in roughness with increasing NaF thickness (in the 0–30nm range) prior to selenization of Cu(In,Ga) [11], crystal growth is clearly not the only factor determining carrier dynamics. Added Na to CIGS-30nmNaF grains may either create similar defects to those in CIGS-0NaF grains or more extreme defects, which become quenching centers that lead to rapid excited carrier recombination.

It is worth pointing out that the time constant of the minority carrier dynamics (nonradiative decay) was hundreds of picoseconds, which is much shorter than the lifetime (radiative decay) of the CIGS measured by time-resolved photoluminescence [26]. Such a long carrier lifetime has been correlated with high-quality CIGS in minimal air exposure and subsequently high efficiency of CIGS solar cells [26]. CIGS samples were exposed to the atmosphere during sample transfer between different labs, almost a week time. However, the performance of the device for the samples were tested again prior to the laser study and yielded the same results.

In summary, we see a clear correlation between Na concentrations, the Ga/(In+Ga) depth profile, minority carrier lifetime, and the performance of the device. Due to the concomitant change in both the Ga/(In+Ga) depth profile and minority carrier lifetime with NaF thickness, it is difficult to elucidate the electronic impact of Na on grain interior and grain boundary. Future work will include ungraded, coevaporated CIGS with varying Ga/(In+Ga) and Na incorporation methods (e.g., NaF PDT) to provide further insight into the electronic impact of sodium.

4. Conclusions

In conclusion, we present ultrafast carrier dynamics with varying Na concentrations in polycrystalline CIGS and the impact of added Na on minority carrier lifetime. As revealed by our pump-probe data, Na incorporation decreases carrier recombination after the carriers are captured in CIGS energy states and then relaxed into the lowest energy state, leading to

elongation of the carrier recombination processes. Such long lifetimes of excited carriers in the presence of Na can be directly correlated with a high-energy conversion efficiency.

References

- [1] A.M. Gabor, J.R. Tuttle, D.S. Albin, M.A. Contreras, R. Noufi, A.M. Hermann, High efficiency $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ solar cells made from $(\text{In}_x\text{Ga}_{1-x})_2\text{Se}_3$ precursor films, *Applied Physics Letters* 65 (1994) 198-200.
- [2] J. Hedstrom, H. Ohlsen, M. Bodegard, A. Kylner, L. Stolt, D. Hariskos, M. Ruckh, H.-W. Schock, Thin film solar cells with improved performance, in: *Proceedings of 23rd IEEE Photovoltaic Specialists Conference*, Louisville, 1993, pp. 364-371.
- [3] D. Rudmann, A.F. de Cunha, M. Kaelin, F. Kurdesau, H. Zogg, A.N. Tiwari, G. Bilger, Efficiency enhancement of $\text{Cu}(\text{In,Ga})\text{Se}_2$ solar cells due to post-deposition Na incorporation, *Applied Physics Letters* 84 (2004) 1129-1131.
- [4] F. Pianezzi, P. Reinhard, A. Chiril, S. Nishiwaki, B. Bissig, S. Buecheler, A.N. Tiwari, Defect formation in $\text{Cu}(\text{In,Ga})\text{Se}_2$ thin films due to the presence of potassium during growth by low temperature co-evaporation process, *Journal of Applied Physics* 114 (2013) 194508.
- [5] P. Jackson, D. Hariskos, R. Wuerz, W. Wischmann, M. Powalla, Compositional investigation of potassium doped $\text{Cu}(\text{In,Ga})\text{Se}_2$ solar cells with efficiencies up to 20.8%, *Physics Status Solidi RRL* 8 (2014) 219-222.
- [6] Z. Zhang, W. Witte, O. Kiowski, U. Lemmer, M. Powalla, H. Hölscher, Influence of the Ga content on the optical and electrical properties of $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ thin-film solar cells, *IEEE Journal of Photovoltaics* 3 (2013) 823-827.
- [7] M.A. Contreras, L.M. Mansfield, B. Egaas, J. Li, M. Romero, R. Noufi, E. Rudiger-Voigt, W. Mannstadt, Improved energy conversion efficiency in wide bandgap $\text{Cu}(\text{In,Ga})\text{Se}_2$ solar cells, *Conference Record of the IEEE Photovoltaic Specialists Conference*, Seattle, 2011, article number 6185837, pp. 000026-000031.
- [8] M.A. Contreras, L.M. Mansfield, B. Egaas, J. Li, M. Romero, R. Noufi, E. Rudiger-Voigt, W. Mannstadt, Wide bandgap $\text{Cu}(\text{In,Ga})\text{Se}_2$ solar cells with improved energy conversion efficiency, *Progress Photovoltaics: Research Applications* 20 (2012) 843-850.
- [9] S. Ishizuka, A. Yamada, M.M. Islam, H. Shibata, P. Fons, T. Sakurai, K. Akimoto, S. Niki, Na-induced variations in the structural, optical, and electrical properties of $\text{Cu}(\text{In,Ga})\text{Se}_2$ thin films, *Journal of Applied Physics* 106 (2009) 034908.
- [10] P.S. Vasekar, N.G. Dhere, Effect of sodium addition on Cu-deficient $\text{CuIn}_{1-x}\text{Ga}_x\text{S}_2$ thin film solar cells, *Solar Energy Materials and Solar Cells* 93 (2009) 69-73.
- [11] J. Eid, H. Liang, I. Gereige, S. Lee, J.V. Duren, Combinatorial study of NaF addition in CIGSe films for high efficiency solar cells. *Progress Photovoltaics: Research Applications* 23 (2015) 269-280.
- [12] S.-H. Wei, S.B. Zhang, A. Zunger, Effects of Na on the electrical and structural properties of CuInSe_2 , *Journal of Applied Physics* 85 (1999) 7214-7218.
- [13] A.A. Rockett, The effect of Na in polycrystalline and epitaxial single-crystal $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$, *Thin Solid Films* 480-481 (2005) 2-7.
- [14] J.H. Werner, J. Mattheis, U. Rau, Efficiency limitations of polycrystalline thin film solar cells: Case of $\text{Cu}(\text{In,Ga})\text{Se}_2$, *Thin Solid Films* 480-481 (2005) 399-409.
- [15] S. Siebentritt, L. Gutay, D. Regesch, Y. Aida, V. Depredurand, Why do we make $\text{Cu}(\text{In,Ga})\text{Se}_2$ solar cells non-stoichiometric? *Solar Energy Materials and Solar Cells* 119 (2013) 18-25.

- [16] L. Kronik, D. Cahen, H.W. Schock, Effects of sodium on polycrystalline Cu(In,Ga)Se₂ and its solar cell performance, *Advanced Materials* 10 (1998) 31-36.
- [17] U. Rau, K. Taretto, S. Siebentritt, Grain boundaries in Cu(In,Ga)(Se,S)₂ thin-film solar cells, *Applied Physics A* 96 (2009) 221-234.
- [18] Z. Zhang, M. Hetterich, U. Lemmer, M. Powalla, H. Hölscher, Cross sections of operating Cu(In,Ga)Se₂ thin-film solar cells under defined white light illumination analyzed by Kelvin probe force microscopy, *Applied Physics Letters* 102 (2013) 023903.
- [19] C.-S. Jiang, M.A. Contreras, I. Repins, H.R. Moutinho, Y. Yan, M.J. Romero, L.M. Mansfield, R. Noufi, M.M. Al-Jassim, How grain boundaries in Cu(In,Ga)Se₂ thin films are charged: Revisit, *Applied Physics Letters* 101 (2012) 033903.
- [20] M. Takihara, T. Minemoto, Y. Wakisaka, T. Takahashi, Band profile around grain boundary of Cu(InGa)Se₂ solar cell material characterized by scanning probe microscopy, *Conference Record of the IEEE Photovoltaic Specialists Conference*, Honolulu, 2010, pp. 2512-2515.
- [21] W. Li, S.R. Cohen, K. Gartsman, D. Cahen, Ga composition dictates macroscopic photovoltaic and nanoscopic electrical characteristics of Cu(In_{1-x}Ga_x)Se₂ thin films via grain-boundary-type inversion, *IEEE Journal of Photovoltaics* 2 (2012) 191-195.
- [22] R. Herberholz, H.-W. Schock, U. Rau, J.H. Werner, T. Haalboom, T. Godecke, F. Ernst, C. Bleilharz, K.W. Benz, D. Cahen, New aspects of phase segregation and junction formation in CuInSe₂, *Conference Record of the IEEE Photovoltaic Specialists Conference*, Anaheim, 1997, pp. 323-326.
- [23] D. Abou-Ras, R. Caballero, C.A. Kaufmann, M. Nichterwitz, K. Sakurai, S. Schorr, T. Unold, H.-W. Schock, Impact of the Ga concentration on the microstructure of CuIn_{1-x}Ga_xSe₂, *Physics Status Solidi RRL* 2 (2008) 135-137.
- [24] T. Eisenbarth, T. Unold, R. Caballero, C.A. Kaufmann, D. Abou-Ras, H.-W. Schock, Origin of defects in CuIn_{1-x}Ga_xSe₂ solar cells with varied Ga content, *Thin Solid Films* 517 (2009) 2244-2247.
- [25] K. Puech, S. Zott, K. Leo, M. Ruckh, H.-W. Schock, Determination of minority carrier lifetimes in CuInSe₂ thin films, *Applied Physics Letters* 69 (1996) 3375-3377.
- [26] W. K. Metzger, I. L. Repins, M. Contreras, Long lifetimes in high-efficiency Cu(In,Ga)Se₂ solar cells, *Applied Physics Letters* 93 (2008) 022110.
- [27] O.F. Mohammed, D. Pines, J. Dreyer, E. Pines, E.T.J. Nibbering, Sequential proton transfer through water bridges in acid-base reactions, *Science* 310 (2005) 83-86.
- [28] K. Heyne, O.F. Mohammed, A. Usman, J. Dreyer, E.T.J. Nibbering, Structural evolution of the chromophore in the primary stages of trans/cis isomerization in photoactive yellow protein, *Journal of American Chemical Society* 127 (2005) 18100-18106.
- [29] J. Yang, L. Zhang, L. Wang, D. Zhong, Femtosecond conical intersection dynamics of tryptophan in proteins and validation of slowdown of hydration layer dynamics, *Journal of American Chemical Society* 134 (2012) 16460-16463.
- [30] W.K. Metzger, I. Repins, M. Romero, P. Dippo, M.A. Contreras, R. Noufi, D. Levi, Recombination kinetics and stability in polycrystalline Cu(In,Ga)Se₂ solar cells, *Thin Solid Films* 517 (2009) 2360-2364.
- [31] A.O. El-Ballouli, E. Alarousu, A. Usman, J. Pan, O.M. Bakr, O.F. Mohammed, Real-time observation of ultrafast intraband relaxation and exciton multiplication in PbS quantum dots, *ACS Photonics* 1 (2014) 285-292.

- [32] J. Sun, W. Yu, A. Usman, T.T. Isimjan, S. DGobbo, E. Alarousu, K. Takanabe, O.F. Mohammed, Generation of multiple excitons in Ag₂S quantum dots: Single high-energy versus multiple-photon excitation, *The Journal of Physical Chemistry Letters* 5 (2014) 659-665.
- [33] S. Furue, S. Ishizuka, A. Yamada, M. Iioka, H. Higuchi, H. Shibata, S. Niki, S. Cu(In,Ga)Se₂ solar cells and mini-modules fabricated on thin soda-lime glass substrates. *Solar Energy Materials and Solar Cells* 119 (2013) 163-168.
- [34] E. Wallin, U. Malm, T. Jarmar, O. Lundberg, M. Edoff, L. Stolt, World-record Cu(In,Ga)Se₂-based thin-film sub-module with 17.4% efficiency, *Progress Photovoltaics: Research Applications* 20 (2012) 851-854.
- [35] D.F. Dawson-Elli, C.B. Moore, R.R. Gay, C.L. Jensen, Substrate influences on CIS device performance. 24th IEEE Photovoltaic Specialists Conference, 1994, pp. 152-155.
- [36] D. Braunger, D. Hariskos, G. Bilger, U. Rau, H.W. Schock, Influence of sodium on the growth of polycrystalline Cu(In,Ga)Se₂ thin films. *Thin Solid Films* 361-362 (2000) 161-166.
- [37] F. Hergert, S. Jost, R. Hock, M. Purwins, J. Palm, Formation reactions of chalcopyrite compounds and the role of sodium doping. *Thin Solid Films* 515 (2007) 5843-5847.
- [38] K.N. Chauhan, D.M. Riffe, E.A. Everett, D.J. Kim, H. Yang, F.K. Shen, Carrier capture dynamics of single InGaAs/GaAs quantum-dot layers, *Journal of Applied Physics* 113 (2013) 203710.
- [39] O. Voznyy, E.H. Sargent, Atomistic model of fluorescence intermittency of colloidal quantum dots. *Physical Review Letters* 112 (2014) 157401.
- [40] M. Murata, D. Hironiwa, N. Ashida, J. Chantana, K. Aoyagi, N. Kataoka, T. Minemoto, Optimum bandgap profile analysis of Cu(In,Ga)Se₂ solar cells with various defect densities by SCAPS. *Japanese Journal of Applied Physics* 53 (2014) 04ER14.

Figure Captions

Fig. 1. (A) Steady state and (B-C) the corresponding time-resolved transient reflectance spectra at time delays of 2.9–65.5 ps for CIGS-0NaF and CIGS-15nmNaF upon excitation at 1080 nm. The time delays are indicated.

Fig. 2. Simulated differential reflections spectra $\Delta R(\rho) = R(\rho) - R(0)$ of the 1.6 μm CIGS layer on top of the molybdenum-substrate without (A) or with (B) an added 15-nm NaF layer for different densities, ρ , of the electron-hole pairs excited by (150 femtosecond) pulsed laser, changing both real and imaginary parts of the permittivity, $\epsilon = (n + ik)^2$, and corresponding time-resolved differential reflection spectra. (A) The progressive recovery of the refractive index $n(\rho)$ after 1080-nm pump pulse at the negligible recovery of the extinction coefficient, $k(\rho)$, while (B) presents the dominant progressive recovery of $k(\rho)$ at less noticeable changes of the refractive index $n(\rho)$.

Fig. 3. The time-resolved transient reflectance spectra of CIGS-0NaF after 1080-nm excitation. (A) A three-dimensional surface and a corresponding contour plot, (B) transient reflectance spectra at early time delays of less than 3 ps, and (C) transient reflectance spectra with long time delays.

Fig. 4. (A) Dynamics of negative band recovery in CIGS-0NaF and CIGS-15nmNaF and (B) a comparison of the dynamics of the positive band decay and negative band recovery in CIGS-15nmNaF. The solid lines are the best fits of the data points with single- and two-exponential functions for the negative band recovery and the positive band decay, respectively.

Fig. 5. The carrier dynamics of CIGS with different NaF thicknesses from 0 to 30 nm after 1080-nm optical excitation.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5