Sodium doping of solution-processed amine-thiol based CIGS solar cells by thermal evaporation of NaCl

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Abstract
Poor crystallinity, high degree of porosity and rough surfaces are the main drawbacks of solution-processed CIGS absorbers resulting in lower power conversion efficiencies when compared to vacuum-based CIGS solar cells. Therefore, promoting absorber grain growth is key to further improve solution-based solar cell performance. The effect of alkali elements such as Na in CIGS absorbers is generally recognised to have beneficial effects not only on the absorber opto-electronic properties but also on the grain growth. In this work, thermal evaporation of a thin layer of NaCl prior to selenisation resulted in absorbers with significantly larger CIGS grains than previously seen with Na diffusing directly from the soda-lime glass substrate. NaCl is non-toxic, abundant and readily available compound that has not been typically used as an evaporation source, but rather as an additive into CIGS precursor solution. The effect of Na on these solution-processed CIGS devices was primarily observed in the spectacular morphological changes leading to improved carrier collection and minority carrier lifetimes, but less on the absorber doping. Transmission electron microscopy (TEM) revealed voids forming around large CIGS grains upon NaCl addition and these had a negative effect on inter-grain carrier transport. Nonetheless, the resulting device performance doubled from 5% to 10% with addition of Na using this doping approach; however, a compromise between the optimum grain growth and optimum electronic properties had to be made. This study demonstrates a novel, simple and effective Na-doping strategy for CIGS absorbers and reveals the current limitations of the Na-doping in solution-processed atmospherically deposited cells.

KEYWORDS
amine-thiol, CIGS, NaCl, grain growth, sodium doping, solution-processing
INTRODUCTION

Cu(In,Ga)Se₂ (CIGS) solar cells are currently the best performing commercially deployed thin film photovoltaic (PV) technology. To further reduce manufacturing costs, development of a large-scale atmospheric processing method of CIGS solar cells and modules is highly desirable. In recent years a wide range of solution-based approaches have been investigated, including a variety of precursor materials, solvents, deposition techniques, and annealing methods. However none of the vacuum-free methods resulted in CIGS absorbers with comparable quality to the vacuum-based ones, with device efficiencies still lagging behind. Inferior quality was often attributed to the presence of voids, impurities, and large number of grain boundaries (GBs). Carbon and oxygen from the solvent or additives can impede the grain growth and remain in the final film causing performance deterioration. The most efficient solution-based method to date uses a highly toxic and explosive solvent hydrazine, and therefore has limited potential for large scale industrial application.

The solution-processing method presented in our as well as other groups’ previous work is a very promising approach which takes the benefits of the hydrazine method but using a safer and more environmentally friendly solvent system. This approach consists of dissolving metal chalcogenides in 1,2-ethylenediamine/1,2-ethanedithiol (EDA/EDT) solvent mixture of 10/1 v/v ratio. After the full precursor dissolution, the separate solutions were combined in specific ratios targeting final composition of Cu₀.₉In₀.₁Ga₀.₃Se₂. This solution was subsequently sprayed, in ambient atmosphere, onto Mo-coated substrates in a total of six layers corresponding to approximately 2–2.5 μm of precursor thickness. Further details on the precursor solution preparation and deposition can be found elsewhere. Eagle XG (Corning) glass substrates were used to ensure no additional Na was added to the precursor from the substrate. Mo/Mo-N/Mo multi-layers were deposited onto the substrates by DC magnetron sputtering at a base pressure lower than 3 × 10⁻⁶ Torr. The Mo-N served as a diffusion barrier against excess MoSe₂ formation and was shown to be crucial in improving performance in our solution-processed CIGS solar cells. The final Mo multilayer thickness was approximately 1 μm with sheet resistance of ~0.4 Ω/sq. NaCl layers were thermally evaporated onto the as-deposited CIGS absorber inside a homemade thermal evaporation system. The evaporation was performed at a base pressure below 3 × 10⁻⁶ Torr, applying current of 60 A to a tungsten boat containing NaCl. The substrates were placed directly above the source at a distance of 15 cm. NaCl layers of different thicknesses ranging between 15 and 150 nm were evaporated onto the CIGS substrate, as shown in Figure 1.

The layer thickness during the evaporation was controlled using a quartz crystal microbalance. The absorbers were subsequently seleniumised in a closed SiC-coated graphite box at 550°C and 200 Torr for 70 min, using 900 mg of Se in a rapid thermal processing (RTP) system. To minimise any ‘accidental’ Na-doping, the RTP oven and the graphite box were cleaned by high temperature and low pressure annealing under flowing nitrogen and mechanical scrubbing of the quartz annealing tube to remove residual selenium between each run.

The most common approach is the NaF post-deposition treatment (PDT) where a thin layer of NaF (20–40 nm) is typically evaporated after the 3-stage CIGS growth. As this treatment is applied after the CIGS growth, it does not modify significantly the absorber microstructural properties. Sutter-Fella et al. reported that when NaF was evaporated onto solution-processed copper zinc tin sulphide (CZTS) devices prior to selenisation, the beneficial effects of Na were observed on electronic as well as morphological properties of the devices. In this work, NaCl was chosen as the Na source because of its low cost, benign nature, and ease of thermal evaporation with lower thermal budget, as compared to NaF. A thin layer of NaCl was evaporated onto the as-deposited CIGS absorbers and the effects of different NaCl layer thicknesses on the device electronic and morphological properties were studied.

EXPERIMENTAL DETAILS

2.1 CIGS absorber and solar cell preparation

Individual metal chalcogenide precursor solutions of 0.2 M concentration were prepared by dissolving indium sulphide (In₂S₃), copper sulphide (Cu₂S) and gallium together with selenium powder (Ga + Se) in EDA/EDT solvent mixture of 10/1 v/v ratio. After the full precursor dissolution, the separate solutions were combined in specific ratios targeting final composition of Cu₀.₉In₀.₁Ga₀.₃Se₂. This solution was subsequently sprayed, in ambient atmosphere, onto Mo-coated substrates in a total of six layers corresponding to approximately 2–2.5 μm of precursor thickness. Further details on the precursor solution preparation and deposition can be found elsewhere. Eagle XG (Corning) glass substrates were used to ensure no additional Na was added to the precursor from the substrate. Mo/Mo-N/Mo multilayers were deposited onto the substrates by DC magnetron sputtering at a base pressure lower than 3 × 10⁻⁶ Torr. The Mo-N served as a diffusion barrier against excess MoSe₂ formation and was shown to be crucial in improving performance in our solution-processed CIGS solar cells. The final Mo multilayer thickness was approximately 1 μm with sheet resistance of ~0.4 Ω/sq. NaCl layers were thermally evaporated onto the as-deposited CIGS absorber inside a homemade thermal evaporation system. The evaporation was performed at a base pressure below 3 × 10⁻⁶ Torr, applying current of 60 A to a tungsten boat containing NaCl. The substrates were placed directly above the source at a distance of 15 cm. NaCl layers of different thicknesses ranging between 15 and 150 nm were evaporated onto the CIGS substrate, as shown in Figure 1.

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Colombara et al. showed that background sodium contamination from routine annealings in presence of SLG or Na salts acts as a parallel doping source and has significant influence on the CIGS device performance.\textsuperscript{28} CIGS solar cells were completed by depositing approximately 80 nm of CdS by chemical bath deposition (CBD) from CdSO\textsubscript{4}, NH\textsubscript{4}OH and thiourea precursors. This was followed by RF sputtering of intrinsic ZnO and Al doped ZnO (AZO) with a thickness of 80 and 500 nm, respectively. Finally, a 500 nm thick silver grid was thermally evaporated on the top of the TCO using a mask. Cells of an area of 0.25 cm\textsuperscript{2} were delimited by mechanical scribing. All devices were thermally annealed in an air-circulating furnace at 180°C for 5 min, which typically results in a small improvement of device performance by passivation of CIGS/CdS interface.\textsuperscript{29}

\section{2.2 CIGS absorber and solar cell characterisation}

Scanning electron microscope (SEM) surface and cross-section images of the absorber microstructure were acquired using the JEOL JSM-7800F FE-SEM equipped with the Oxford Instruments energy dispersive X-ray spectroscopy (EDX) detector used for elemental composition determination. X-ray diffraction (XRD) data were collected using a Bruker D2 Phaser diffractometer equipped with a Lynxeye™ detector and Cu-Kα source. The current density–voltage (JV) characteristics were measured using AM1.5G simulated sunlight from ABET solar simulator under 1000 W/m\textsuperscript{2}, calibrated with a Si reference cell. The external quantum efficiency (EQE) spectra were obtained at 0 V bias with 5 nm spectral resolution using a Bentham PVE300 system. Capacitance–voltage (CV) and drive-level capacitance profiling (DLCP) data were acquired using a Keysight E4990A impedance analyser. The voltage was swept from \(-1\) to 1 V at a frequency of 100 kHz at room temperature. Spectrally resolved photoluminescence (PL) and time-resolved photoluminescence (TRPL) were performed using an in-house constructed measurement system equipped with a single excitation laser source of 640 nm wavelength. The laser excitation was pulsed at 40 MHz to measure a detectable PL signal. The wavelength was scanned from 900 to 1200 nm with a 1 nm step size. TRPL was conducted on the same measurement spot, with the wavelength selected based on the material bandgap (\(\sim\)1.055 nm) with a laser pulse frequency of 20 MHz. Transmission electron microscopy (TEM) was carried out using FEI Tecnai F20 (S)TEM equipped with an Oxford Instruments X-Max 80 silicon drift (SDD) EDX detector. The TEM lamella was prepared by Focused Ion Beam milling using Helios G4 PFIB UXe DualBeam Microscope equipped with Xe plasma source.

\section{3 RESULTS AND DISCUSSION}

\subsection{3.1 Morphology and composition}

Figure 2 shows the SEM cross-section and surface images of the CIGS absorbers after being selenised in the presence of the evaporated NaCl layer. The significant grain growth seen due to intentional Na-doping on the absorber microstructure is evident. Annealing of the CIGS precursor without any NaCl (0 nm NaCl) in the presence of elemental Se vapours resulted in a poorly crystallised, highly porous CIGS absorber. Slightly larger grains on the surface of the absorber are observed with only 15 nm of NaCl being evaporated; however, the grain growth improved remarkably with 30 and 50 nm of NaCl. Here, some grains extend to the full absorber thickness, which had never been observed for these absorbers when the Na source was SLG. When thicker NaCl layers were evaporated (100 and 150 nm), the absorber grain size started to decrease. The NaCl layer was still present at the end of the selenisation for these two samples and is clearly visible on the surface of the 150 nm NaCl absorber.

To identify absorber composition and residual NaCl present, EDX surface mapping was performed and confirms the presence of 9.2 at% and 19.4 at% of Cl for 100 nm and 150 nm NaCl-coated absorbers respectively, whereas no Cl was detected for any other sample. Table 1 summarises EDX elemental composition of selenised CIGS absorbers and calculated final CGI and GGI ratios for all the films. Absorber composition of the reference sample (0 nm NaCl) is very close to the targeted CGI = 0.9 and GGI = 0.3. However absorbers with NaCl layers show reduced CGI and GGI ratios. These compositional changes are attributed to the effects of Na, which is known to cause absorber grading by hindering In/Ga interdiffusion.\textsuperscript{19,30,31} The morphological observations from the SEM images are in agreement with the XRD patterns of the films presented in Figure 3A.

The peak found at \(2\theta = 31.7°\) in 100 and 150 nm NaCl samples corresponds to the NaCl (200) XRD reflection (JCPDS 78-0751). This peak is not present in any other film confirming SEM and EDX observations. The other visible peaks correspond to the diffraction patterns of Mo, Mo-N and CIGS (JCPDS 42-1120, JCPDS 74-4266 and JCPDS 40-1488 respectively). CIGS has a preferred orientation along the (112) plane of the tetragonal phase and there is no change in dominant crystal orientation when varying the NaCl thickness. The full width half maximum (FWHM) of the dominant CIGS (112) peak was obtained using a peak fitting routine and is plotted in Figure 3B. The FWHM is the highest for the NaCl-free sample and the lowest for the 30 nm NaCl-containing sample.
A lower FWHM (narrowest peak) is indicative of improved crystalline quality and consequently larger grain sizes. The crystalline quality improved rapidly with addition of up to 30 nm NaCl, then started to decrease slowly when higher amounts of NaCl (≥50 nm) were added. Hence, the XRD measurement is consistent with the SEM images of the CIGS crystals showing the smallest grains for 0 nm NaCl and largest for 30 and 50 nm of NaCl. Most recent theories on atomic diffusion and dopant interaction with matrix elements can help to understand why by addition of Na the CIGS grain growth first increases and then starts to decrease when Na was added in excess.
Grain growth is closely related to atomic diffusions which are trig-
gered by sodium dopant addition. Higher Na doping concentrations
were seen to increase Ga diffusion; however, Ga diffusivity decreased
when CIGS had low Cu deficiency because the diffusion occurs
through Cu vacancies.\textsuperscript{31,32} This is consistent with the lower CGI mea-
sured for the 150 nm NaCl sample (Table 1). Several groups have
previously observed a decrease in grain size upon addition of Na;
however, unlike here, the CIGS absorbers were produced by vacuum
techniques.\textsuperscript{33,34} Finally, partial delamination was observed for
absorbers with 30 and 50 nm NaCl, the absorbers with the largest
grains. The delamination of the absorber films with the largest grains
was also reported by Sutter-Fella et al. where NaF layers of various
thickness were evaporated onto CZTS absorbers.\textsuperscript{27}

### 3.2 | PV performance

To study the effect of the NaCl layer on CIGS solar cell performance,
the above presented absorber films were made into CIGS devices.
The PV performance indicators are plotted in Figure 4. Unlike for the
most significant grain growth, the optimum NaCl thickness for the
best device performance was 15 nm. Adding only 15 nm of NaCl sub-
stantially improved the $V_{OC}$ and $FF$ by on average 100 mV and 11%
absolute, respectively. The increase in $V_{OC}$ and $FF$ are typically
observed consequences of Na-doping of the CIGS absorbers. The
increase in short circuit current density ($J_{SC}$) with the addition of
15 nm of NaCl from an average of 18 to 26 mA/cm\textsuperscript{2} can be attributed
to the enhanced grain growth. The thickness of 15 nm is in the range

| Table 1 | EDX elemental composition (at\%) and absorber CGI and GGI ratios after selenisation with evaporated NaCl layer of various thicknesses |
|---------|---------------------------------------------------------------------------------------------------------------|
| 0 nm    | 15 nm | 30 nm | 50 nm | 100 nm | 150 nm |
| Cu      | 22.5  | 19.6  | 20.5  | 20.4   | 19.0   | 16.5   |
| In      | 17.5  | 19.0  | 18.5  | 18.6   | 17.1   | 15.8   |
| Ga      | 7.0   | 5.9   | 6.1   | 6.0    | 5.7    | 4.9    |
| Se      | 53.0  | 55.5  | 54.9  | 55.0   | 49.0   | 43.4   |
| Cl      | 0     | 0     | 0     | 0      | 9.2    | 19.4   |
| CGI     | 0.91  | 0.79  | 0.83  | 0.83   | 0.84   | 0.79   |
| GGI     | 0.28  | 0.24  | 0.25  | 0.24   | 0.25   | 0.24   |

\textbf{FIGURE 3} (A) X-ray diffraction (XRD) patterns of selenised CIGS + NaCl films and (B) plot of FWHM of the dominant CIGS (112) peak [Colour figure can be viewed at wileyonlinelibrary.com]

\textbf{FIGURE 4} Box plots of photovoltaic (PV) parameters for devices with evaporated NaCl of various thicknesses [Colour figure can be viewed at wileyonlinelibrary.com]
of thicknesses typically used for the evaporation of NaF for high efficiency vacuum-based CIGS solar cells. However the optimum NaCl thickness for the device performance is below the optimum for the CIGS absorber crystallisation at 30 nm. This sample also has the highest $J_{SC}$ among the samples, approximately 29 mA/cm$^2$ on average. This is consistent with the smallest FWHM measured for this sample.

From Figure 4 it is apparent that variations in $J_{SC}$ with increasing NaCl content follow the same trend as the changes in grain sizes. However $FF$ and $V_{OC}$ follow more-or-less an opposite trend causing performance degradation for devices with NaCl layers thicker than 15 nm. In addition, samples with the largest grains (15 and 30 nm NaCl) suffered from partial delamination, which might be related to the grain size or the high amount of Na incorporated. Sudden improvement in device performance was observed for the sample with 150 nm NaCl. Here, a visible NaCl layer remained after selenisation on the absorber surface. It is possible that the remaining NaCl layer served as a chemical barrier to protect the surface from oxidation that leads to the formation of detrimental anion Se-Cu divacancies. In addition, the more compact absorber morphology apparent from the SEM micrograph could have been able to accommodate more Na at GBs which manifested by increased carrier concentration (Figure 6). Increased p-type doping led to an increase in $V_{OC}$ and $FF$ of this device. The remaining highly water soluble NaCl was washed out during the CdS CBD process and therefore did not affect the final device structure.

Figure 5 shows the JV curves and EQE spectra of a representative device for each NaCl thickness. PV parameters for each JV curve are summarised in Table 2. The lower performance of the champion device for the 30 nm NaCl compared to the 15 nm NaCl (PCE of 9.2% as opposed to 10.3%) can be attributed to the reduction in $FF$. The higher series resistance ($R_S$) seen here compared to the other devices could have been caused by delamination observed in this absorber. The bandgap ($E_g$) of the CIGS absorbers was extracted from the peak energy of the derivative of the EQE curves. $E_g$ values will be discussed and compared with an alternative bandgap measurement technique in the following sub-section. The EQE curves show improved photocurrent response especially at long wavelengths with the addition of NaCl. The long wavelength decay is the smallest for the samples with the largest grains (NaCl = 30–100 nm), indicating improved carrier collection efficiency. Although no depth profiles are presented in this work, Na induced interatomic diffusions involving Ga, which might have led to absorber bandgap grading. Back bandgap grading in low diffusion length CIGS such as these would reduce back surface recombination and enhance carrier collection.

3.3 | Carrier density and lifetime

To better understand the device performance and the role of Na doping, CV and DLCP measurements at room temperature were performed on these devices. The net acceptor concentration ($N_A$) was obtained from the minima of the doping profiles shown in Figure 6.

The CV measurement and the resulting doping profiles can depend on the amount of Na present in the absorber, however also affected by the morphology. The $N_A$ is clearly the lowest for 30 nm of NaCl, ~$1 \times 10^{15}$ cm$^{-2}$. The highest doping density was measured for the 150 nm NaCl sample, approximately one order of magnitude higher. The width of the depletion region ($W$) at zero bias was estimated from the CV measurement and the values are summarised in Table 3 together with the values for $N_A$ extracted from CV and DLCP measurements.

Depletion width at 0 V bias is significantly larger for the 30 nm NaCl sample than for any other studied sample. A larger depletion width improves the long wavelength charge carrier collection; however, lower doping density results in a weaker electric field across the space charge region (SCR). As opposed to CV, the DLCP method is mostly insensitive to the response from interface states. The net acceptor concentrations extracted from these two methods are compared in Table 3. DLCP doping profiles are shown in Figure S1 in the Supplementary Information. For the undoped and 150 nm NaCl
samples, the CV and DLCP doping profiles have similar minima, indicating that these two samples are dominated by response from the bulk defect states. For all the other samples, DLCP doping profiles minima are shifted to lower values relative to CV. For these samples, DLCP is a better method to quantify the net acceptor concentration in the cell, since these cells contain non-negligible interface states. Higher p-type doping and negligible interface states for the 150 nm NaCl sample is consistent with the hypothesis of lower concentration of divacancy complexes as a result of the residual NaCl layer.

To explain the presence of interface states and unexpectedly low carrier concentrations of all the other Na-doped samples, some assumptions and speculations must be made due to the differences in their morphology. It is suggested that high concentration of Na accumulates along CIGS GBs. Na can also be found in grain interior; however, the concentration is in order of magnitude lower than at GBs due to slower volume diffusion. A study performed by Forest et al. regarding the reversibility of the Na incorporation can be used to infer the presence of interface states. In their study, a series of rinse and heat cycles were performed on a Na-doped sample, resulting in the progressive removal of Na from the grain boundaries. Many Na compounds are soluble in water; therefore, rinsing the absorber in DI water at 60°C typically removes all the Na salts accumulated at the surface. The heat treatment at 200°C allows oxygen to draw Na from the GBs to the surface, where it is washed out in the next cycle. Although this experiment was not intentionally performed here, the samples are very porous and the CdS chemical bath deposition involves immersing the absorbers in an aqueous solution at 60°C for several minutes before the CdS growth starts. The subsequent junction annealing performed in air at 180°C could cause Na to diffuse and create interface states detected by the combination of CV and DLCP measurements. The sample with 30 nm NaCl has the lowest carrier concentration likely because of having largest CIGS grains and consequently lower number of GBs.

Minority carrier lifetime (τ) gives an indication of how fast the minority carriers recombine. The results of the TRPL measurement suggest the highest carrier lifetime of ~6 ns was achieved by adding 30 nm of NaCl, which is also the sample with the largest grains. This value is almost double than for any other Na-doped sample. In vacuum-based CIGS devices carrier lifetime is a good indicator of absorber quality. However in non-ideal devices such as solution-

| NaCl (nm) | 0 | 15 | 30 | 50 | 100 | 150 |
|----------|---|----|----|----|-----|-----|
| PCE (%)  | 5.0 | 10.3 | 9.2 | 6.1 | 8.4 | 9.1 |
| V<sub>oc</sub> (V) | 0.50 | 0.60 | 0.58 | 0.46 | 0.56 | 0.58 |
| J<sub>SC</sub> (mA/cm<sup>2</sup>) | 19.6 | 26.8 | 29.4 | 31.2 | 32.0 | 25.7 |
| FF (%)   | 51.3 | 63.6 | 53.6 | 42.7 | 46.3 | 60.7 |
| R<sub>s</sub> (Ω.cm<sup>2</sup>) | 1.80 | 0.93 | 2.20 | 1.08 | 1.10 | 0.75 |
| R<sub>sh</sub> (Ω.cm<sup>2</sup>) | 149 | 240 | 147 | 132 | 135 | 156 |

TABLE 2 PV parameters of each J-V curve in Figure 5a
interpreting TRPL data is challenging due to complex charge-carrier dynamics that can lead to overestimating $\tau$. These various contributions to the PL signal may include minority carrier trapping, surface recombination, energetic relaxation of carriers and carrier drift in an electric field.43

Finally, why the performance of the CIGS solar cells with excessively thick NaCl ($\geq 100$ nm) starts to recover owing to a surprising increase in $V_{OC}$ and $FF$, has yet to be answered. The answer to this question is not evident from any previous characterisation technique or from the literature; however, an interesting observation can be made looking at the PL peaks in Figure 7A. PL signals for 15–50 nm NaCl can be fitted with a single peak, but PL signals corresponding to 100- and 150-nm NaCl are both deformed, fitting two distinct peaks. A smaller peak positioned at $E_1 = 1.136$ eV and larger peak with approximately double the PL intensity at $E_2 = 1.187$ eV were fitted for 100 nm NaCl sample. Similarly, a smaller peak at $E_1 = 1.139$ eV and larger ($\sim 4X$ the intensity) peak at $E_2 = 1.191$ eV were fitted under the PL spectra of the 150 nm NaCl sample. These double peak fittings are shown in Figure S2 presented in the Supplementary Information.

Both of these samples still had traces (100 nm) or even a clear layer (150 nm) of NaCl remaining after selenisation. Looking at the PV performance, the 100 nm NaCl device has a large distribution of cell efficiencies ranging from 4.8% to 8.3% due to a large variation in $FF$ and $V_{OC}$. Therefore half of the cells are similar in performance to 50-nm NaCl and the other half to 150-nm NaCl. This last sample has relatively improved PCEs reaching up to 9%, with the narrowest distribution of $V_{OC}$ among the samples, at $\sim 580$ mV. The existence of two PL peaks confirms the theories of atomic interdiffusion discussed earlier, where larger amounts of Na introduced to the CIGS matrix cause higher Ga diffusivities resulting in changes in the bandgap across the absorber depth.19,31,32 In the 100 nm NaCl, sample, the less intense low bandgap peak at $\sim 1.14$ eV corresponds to a Ga-poor phase whilst the more pronounced high bandgap peak at $\sim 1.19$ eV to a Ga-rich phase. Alternative hypothesis could be that during selenisation, Na could have replaced some Cu atoms in the CIGS lattice and form a stable Na(In,Ga)Se$_2$ compound having larger bandgap. Na(In,Ga)Se$_2$ and Cu(In,Ga)Se$_2$ having limited mutual solubility will result in phase separation and the precipitation of a secondary phase on surfaces or GBs.44

It was observed that the bandgaps measured by PL were smaller than those measured using EQE spectra with a particularly big discrepancy in the 50-nm NaCl sample. PL measures the dominating radiative recombination transition, usually related to the bandgap of the material. EQE measured bandgaps between 1.17 eV and 1.2 eV without an apparent trend. However a trend can be seen in PL with bandgap decreasing from 15 to 50 nm NaCl (1.179–1.154 eV) and then the peak splitting occurs and the average $E_g$ increased from 50 to 150 nm (1.154–1.181 eV). This bandgap variation confirms the previous speculations that Na diffusion induces compositional changes in the depth of the absorber. The Na-related compositional

*This is an average value.*

### TABLE 3
Summary of the material bandgap, carrier concentration, depletion width and minority carrier lifetime

| Sample | $E_g$-EQE (eV) | $E_g$-PL (eV) | $N_A$-CV ($\times 10^{15}$ cm$^{-3}$) | $N_A$-DLC (× 10$^{15}$ cm$^{-3}$) | $W$ (nm) | $\tau$ (ns) |
|--------|---------------|--------------|-------------------------------|-------------------------------|--------|---------|
| 0 nm   | 1.203         | –            | 5.3                           | 5.6                           | 263    | 0.50    |
| 15 nm  | 1.198         | 1.179        | 6.6                           | 4.4                           | 270    | 3.48    |
| 30 nm  | 1.170         | 1.166        | 2.7                           | 2.0                           | 361    | 6.04    |
| 50 nm  | 1.175         | 1.154        | 7.0                           | 5.5                           | 248    | 3.93    |
| 100 nm | 1.175         | 1.154        | 4.7                           | 3.9                           | 275    | 3.58    |
| 150 nm | 1.198         | 1.181        | 10.0                          | 10.7                          | 266    | 3.71    |

*This is an average value.*
changes were also observed in various studies on vacuum-processed CIGS and include In/Ga distribution, Na (In,Ga)Se₂ segregation and Cu migration and distribution in the absorber as suggested by Ollkononen et al.45

3.4 Compositional analysis using TEM

To understand the \( V_{OC} \) and FF loss in the device with the largest grains, the composition and structure of the device was studied using TEM in combination with EDX elemental mapping. A TEM bright field cross-section through the best performing cell of the 30 nm NaCl sample is shown in Figure 8.

Different layers constituting the cell are clearly indicated on the image. The image shows large CIGS grains; however, the individual grains are separated by extensive voids. The presence of voids causes the Mo layer to be uncovered at certain places or covered with only small grains. The presence of such extensive voids in the absorber might hinder the photo-generated carrier transport between the grains and limit the carrier collection at the contacts from the grains isolated by the void. Moreover, the CdS deposited by CBD forms not only on the surface of the absorber, but also inside it, which is corroborated by the elemental maps of Cd presented in Figure 9. The CdS enveloping each grain separately creates a local p-n junction, leaving the photo-generated carriers trapped inside the grain as they cannot be collected at the contacts. The combination of these effects is likely the cause of the deterioration of the FF seen in the devices with large grains (30 to 100 nm NaCl).

The elemental maps (Figure 9) show the distributions of the constituent elements of various layers in the CIGS device. It can be seen that Cd is not only present around each CIGS grain, but also in the Mo back contact. Cd is generally known for diffusing to the surface of CIGS absorbers during the CBD process. Moreover, Cd diffusion into the MoS₂ layer was seen by Gherson et al.23 Cd diffusion into the absorber and towards the back contact is enabled by the presence of voids in the absorber. However Cd diffusion into the Mo back contact is not typically observed and should not occur in a good quality and dense Mo grain structure. This suggests that the Mo back contact might be of poor quality with GBs allowing for accumulation of Cd and other impurities. The sheet resistance of 0.4 \( \Omega \)/sq. for \( \sim 1.1 \mu \text{m} \) thick Mo/Mo-N/Mo back contact gives a back contact resistivity of \( 4.4 \times 10^{-5} \Omega \cdot \text{cm} \), which is one order of magnitude higher than a typical Mo resistivity. The Mo-N barrier layer has a similar grain morphology and conductivity to Mo. Impurities in Mo such as oxygen suggested by its elemental map in Figure 9 would increase back contact resistivity as well as the oxygenated columnar GBs would promote MoSe₂ formation, which is also accelerated in the presence of Na.47 Excessive MoSe₂ formation along Mo GBs caused local delamination on the samples with the largest grains (30 and 50 nm NaCl).

Mo and S EDX peaks overlap; therefore there is a combined elemental map for these two elements. Its signal in the CIGS absorber indicates that not all the sulphur from the precursors was replaced by Se during the selenisation and consequently the final absorber is not a pure selenide phase but rather a mixed Cu(In,Ga)(S,Se)₂ material. The Ga elemental map shows a strong Ga signal around the grains, indicating Ga segregation and consequently a lower GGI ratio in the bulk CIGS. The Na signal is included as well; however, Na is a light element and EDX detection of such light elements is very limited and therefore the Na signal is very weak. But according to this map, the Na signal seems to overlap with the strong Ga signal outside CIGS grains. The EDX map also shows presence of oxygen around the grains and its signal is overlapping with the Ga signal, suggesting formation of gallium oxide phases. To quantify the device composition, four different areas of the device were analysed: inside the grain, at GBs and in the Ga segregate. The areas are marked by blue rectangles in Figure 8 and the composition of each is summarised in Table 4.

The EDX compositional analysis reveals lower than intended Ga composition inside the CIGS grains (GGI of \( \sim 0.25 \) instead of 0.3). The Ga loss from the bulk is caused by the accumulation of Ga underneath the grains in the void evidenced in Figure 9. In Area 3, Ga is present in an increased quantity but does not form part of the chalcopyrite phase. Large amounts of oxygen are also present in this region, suggesting possible oxidation of the gallium. Partial oxidation and accumulation of Ga was observed by Berner et al., when sodium formate was used as the Na precursor. Ga in the form of Ga₂O₃ is likely no longer available during selenisation as the oxide is very stable.48 Here, the oxygen can come from the air as the spraying procedure is performed at elevated temperatures in ambient conditions. Dimstorfer et al. observed Ga loss in the chalcopyrite phase due to formation of Ga₂O₃ after annealing the CIGSe precursor in air at 400°C.49 Na preferentially located at GBs has a strong affinity for oxygen.43 This can promote the accumulation of the gallium oxide phases around the CIGS grains. The presence of Si and Al found in Area 3 is unexpected and might be a result of TEM sample
preparation or storage. No residual Cl was detected in this device. Several studies were able to detect residual Cl in CIGS films as a result of either NaCl doping or from metal salt (InCl3) precursors using very sensitive SIMS and Auger electron spectroscopy (AES) techniques.27,48,50 Park et al. found a small amount of Cl embedded in a carbon matrix, but most of Cl left the film in form of Cl2 gas, similarly to NaF where F leaves the CIGS film in form of SeF6 vapours.40,50 Two CIGS grains compared in Area 1 and Area 2 have very similar composition with slightly lower Cu and Ga composition than targeted. The GB in Area 4 contains stoichiometric CdS incorporated in during

TABLE 4  EDX compositional analysis at four areas of the CIGS absorber visualised in TEM cross-section of Figure 8

| At%    | Area 1 top grain | Area 2 bottom grain | Area 3 under grain | Area 4 GB |
|--------|------------------|---------------------|--------------------|-----------|
| Cu     | 25.0             | 24.7                | 0.6                | 16.7      |
| In     | 21.2             | 21.8                | 0.3                | 14.7      |
| Ga     | 7.4              | 7.4                 | 25.2               | 4.6       |
| Se     | 46.4             | 46.2                | 1.1                | 30.6      |
| O      | —                | —                   | 50.3               | —         |
| Si     | —                | —                   | 17.1               | —         |
| Al     | —                | —                   | 5.5                | —         |
| Cd     | —                | —                   | —                  | 16.8      |
| S      | —                | —                   | —                  | 16.5      |
| CGI    | 0.874            | 0.846               | 0.024              | 0.865     |
| GGI    | 0.259            | 0.253               | 0.988              | 0.238     |
the CBD. Overall this TEM-EDX study confirms that the inferior performance of devices having large CIGS grains can be a result of the formation of extensive voids inside the absorber due to the initial porous precursor film.

4 | CONCLUSIONS

The evaporation of NaCl onto CIGS absorbers in order to enhance the morphological and electrical properties of the devices induced by absorber Na doping was successfully achieved. Depositing NaCl by thermal evaporation is a cheap, non-toxic and previously unexplored method of CIGS doping, with lower thermal budget, compared to NaF. NaCl was also employed as a Na precursor for CIGS, however mostly by direct introduction into the precursor solution in solution-based absorbers. It was shown that NaCl was relatively easy and fast to evaporate under vacuum and its effects on the absorber morphology and performance were similar to those described in the literature for NaF evaporation. It was found that a compromise between the optimum NaCl thickness for CIGS grain growth and the optimum NaCl thickness for the improvement of electronic properties of the material had to be made. The large grain growth is accompanied by the creation of extensive voids in the absorber due to porous nature of the initial precursor film. The voids had detrimental effects on the device performance as they caused delamination and created shunting paths. The voids are particularly problematic as the CdS deposited by CBD forms not only on the absorber surface as for dense films, but also inside the absorber, resulting in less efficient carrier collection. The reversibility of Na incorporation discussed in the literature suggests that part of the Na incorporated at the GBs can effectively be washed out during the CBD, which may also be facilitated by the presence of voids. The presence of oxygen introduced by the ambient deposition technique used to prepare the absorbers can drive Na from the GBs to the surface and create surface traps during the post-CBD heat treatments. Similar doping density for most of the evaporated NaCl thicknesses suggests that addition of Na primarily promoted the grain growth of the absorbers consequently improving the CIGS material quality rather than affected the absorber doping. Finally, bandgap changes and segregation of Ga likely forming gallium oxides in the inter-grain voids were also observed in the presence of sodium.

All these observations have to be taken into account for the further optimisation of this approach of sodium doping of solution-processed CIGS prepared in ambient conditions. In the future work, methods to minimize absorber porosity will be investigated for more efficient Na doping. These will include deposition by ultrasonic spraying allowing for variation in droplet size and varying the precursor solution dilution. In addition, one method suggested to reduce film porosity of CIGS absorbers is by soaking the absorber in a cation solution in order to fill the voids seen in the film. Overall, this method resulted in a device performance of twice that of the Na-free CIGS solar cells, from PCE of 5% to 10% with evaporation of only 15 nm of NaCl. More NaCl produced higher quality CIGS material with greatly improved lifetime. This is a very promising step towards increasing efficiency of sprayed amine-thiol based CIGS solar cells in the future.

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