Volume 22, Issue 1: KUS: 1256: 62-67: 12082024: 2025

KHULNA UNIVERSITY
STUDIES

journal homepage: www.kus.ku.ac.bd

Research article

Impact of Alkali Post Deposition Treatment on Chalcogenide-based CIGSSe Solar Cells through Solution-based Method

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ABSTRACT

Solution-based fabrication methods for high efficiency CIGSSe [Cu(In,Ga)(S,Se)$_2$] solar cells have been extensively studied as the preference to vacuum-based fabrication methods. We employed an environmentally conscious solution-based deposition technique to fabricate thin films of CIGSSe. Despite significant research on non-vacuum (solution- processed) CIGSSe solar cells, compared to vacuum-based solar cells, their power conversion efficiency (PCE) remains lower. Additionally, numerous solvents employed in solution-based precursors are not environmentally friendly. We have developed a distinctive technology called solution-processed alkali (Sodium, Na) post-deposition treatment (PDT), which utilizes de-ionized (DI) water in ambient air. The presence of additional Na inclusions was found to significantly enhance the photovoltaic performance. The favorable effects of extra treatment were systematically investigated using several characterization approaches. Defect passivation had a positive impact, leading to PCE above 11% (in the absence of an anti-reflection coating layer).

ARTICLE INFO

Article timeline:
Date of Submission:
12 August, 2024
Date of Acceptance:
17 January, 2025
Article available online:
13 February, 2025

***Keywords*:**
CIGSSe
Thin Film
Post deposition treatment (PDT)
Defect passivation

Introduction

The excellent photovoltaic features of chalcopyrite based CIGSSe solar cells materials, including the highest absorption coefficient (~10^5 cm^{-1}) nature (Ramanujam & Singh, 2017) in the range of the visible spectrum region, better substantiality, and tunable bandgap properties of the absorbers with changing Ga/(Ga+ In) or Se/(S+Se) ratio, resulted in significant study into these solar cells over a long period (Bär et al., 2004, Han et al., 2005). Applying vacuum-based deposition techniques, including sputtering and co-evaporation with a sequentially post-selenization process, CIGSSe absorbers were fabricated for the most efficient (23.35%) solar cell. (Nakamura et al., 2019). However, the three-stage thermal evaporation technique used to produce the best-performing CIGSSe solar cells discussed above is costly, needs a vacuum facility, and requires significant maintenance costs. Therefore, a solution-based process that can be conducted in an air environment shows potential as an alternative to the vacuum-based approach (Mina et al., 2022, Jung et al., 2022, Kim et al., 2019).

Recent enhancements in the performance of CIGSSe solar cells have resulted in the incorporation of alkali elements in the PDT process. (Mina et al., 2023) At first, it was thought that the movement of Na ions from SLG (soda lime glass) to the CIGSSe absorber enhanced the PCE through changing the structural characteristics of the film as it formed. However, the growth of a CIGSSe layer on a Na-free substrate and the subsequent addition of Na showed a significant increase in PCE. (Rudmann et al., 2004, (Rudmann et al., 2005) Further research into alkali treatment in CIGSSe was prompted by this beneficial impact of Na device performance. The accumulation of Na during development is believed to hinder the interfusion of chemical compounds, resulting in a more prominent gradient band structure. (Ishizuka et al., 2009). Hedström et al., unveiled that the CIGSSe absorbers crystal structure and device performance are significantly better when grown on an SLG substrate compared to borosilicate glass (Hedstrom et al., 2002). The inclusion of Na is the cause of this phenomena, since it causes to a rise in all parameters, resulting to an overall enhancement in device performance.

Moreover, it was observed that the electrical characteristics increased only until the Na atom density reached roughly 10^{15} cm^{-3}, irrespective of whether the inter-diffusion of Na occurred from SLG or was introduced by other methods. (Holz et al., 1994) Granata et al. proposed that when the Na atomic concentration became closer to 1%, the devices performance

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DOI: https://doi.org/10.53808/KUS.2025.22.01.1256-se

significantly degraded and the optimum atomic concentration was in the range of 0.05% to 0.5 % (Granata et al., 1997). Furthermore, Contreras et al., conducted a groundbreaking study at the NREL (national renewable energy laboratory), where they explored the effects of doping with additional alkali components. They found that extra inclusion of potassium (K) and cesium (Cs) also enhanced the open circuit voltage (V_{oc}) significantly, but Na had the notable improvement on the overall device performance (Contreras et al., 1997). However, the alkali element incorporation under selenium (Se) ambient conditions have significant positive impacts on the solar cell performances: forming copper (Cu) and gallium (Ga) depilated surface and enhancing Cd_{Cu} antisites, facilitating the formation of the thinner cadmium sulphide (CdS), suppressing potential fluctuations, increasing bandgap with possible secondary phase formation and defect passivation at grain boundary (Chirilă et al., 2013). The alkali-PDT technique was carried out employing a high vacuum-based approach and may be subsequently adapted to an aqueous solution-based procedure. The alkali PDT impact was found to be highly efficient in defect passivation, leading to enhanced device performance.

Hence, we implemented an additional alkali treatment method for the solution-based spray pyrolysis technique. This study presents the fabrication process of the CIGSSe absorbers involved the use of PDT, which was applied using an aqueous spray pyrolysis technique. Finally, we achieved the ultimate PCE of 11.18% with Na inclusion CIGSSe absorbers.

Experimental Section

Materials and Method

The Molybdenum (Mo)-coated SLG's with a thickness of 500 nm were employed as a substrate and were gently dried with compressed nitrogen (N_2) flow after being ultrasonically cleaned for five minutes in an ethanol solution. For aqueous precursor solution preparation, all the metallic salts of $CuCl_2$ (98%), $InCl_3$ (99%), $Ga(NO_3)_2$ (99%), and $CS(NH_2)_2$ are dissolved in 50 ml de-ionized water (DI water) with a molar stoichiometric ratio of 0.7:0.8:0.2:4.0 and a molality of 40 mmol/L and sprayed on Mo-coated SLG substrate.

Synthesis of CIGSSe absorber and solar cell fabrication

The spray was conducted for a duration of 10 minutes at a substrate temperature (T_{sub}) of 430 ºC (the designated hot plate temperature) in an ambient air condition. The earlier report provides a comprehensive description of the spray pyrolysis procedure. (Jung et al., 2022) Finally, in order to carry out alkali PDT, we prepared a 50 ml solution by dissolving NaCl in DI water with a molar proportion of ($NaCl:CS(NH_2)_2 = 5:2$). We then sprayed this solution for a duration of 4 minutes at a temperature of 350 ºC. The spray deposition process incorporated nitrogen gas with a purity of 99% as a carrying gas, which was flowed at an average speed of 2 liters per minute (LPM). After the spray deposition process was completed, the sprayed absorbers were exposed to the selenium (Se) environment by being kept at 550 oC for 30 minutes in a graphite box with 1 gram of Se pellets. The graphite box was inserted into a quartz tube, and a flow of N_2 gas was circulated throughout the tube. In order to finalize the device structure, conventional chemical bath deposition (CBD) was employed to deposit a CdS buffer layer (~50 nm). The complete device structure was subsequently accomplished by the deposition of intrinsic ZnO (~60 nm) and tin-doped indium oxide (known as indium-tin oxide or ITO) (~350 nm) layers via a radio RF-DC magnetron sputtering method (Enkhbat et al., 2023, Lee et al., 2022, Kim et al., 2019)

Solar Cells' Characterization

To conduct current density versus voltage (JV) measurements of the selected devices, a source meter named Keithley 2400 was employed according to the air mass (AM) 1.5 and a Xe lamp of 1000 Wm^{-2} of spectrum illumination. To carry out the external quantum efficiency (EQE) measurement the system including a source (Xe lamp), built in monochromator, processor, and lock in signal amplifier was employed within the wavelength region of 360 nm to 1180 nm. Calibration was conducted using a Si-reference cell prior to the measurements. The near-infrared (IR) fluorescence range lifetime spectrometer (C12132, Hamamatsu) was used to carry out photoluminescence (PL) and time-resolved PL (TRPL) measurements under 300K with a 532 nm excitation wavelength laser. The admittance spectroscopy (AS) measurements were carried out using an L-C-R meter (model no. E4980A) to investigate the defect formation. By changing the measurement temperature from 300K to 90K, frequency ranges from 20 Hz to 2 MHz and an AC bias-voltage of 30 mV was implemented. Finally, a potentiostat (model no. PGSTAT302N) was used to carry out electrochemical impedance spectroscopy (EIS). It had a frequency range of 100 mHz to 2 MHz, a root-mean-square amplitude of 0.02 V, and a frequency variation of 10 per decade. (Mina et al., 2023, Lee et al., 2022, Kim et al., 2019)

Results and Discussion

We investigated the impacts of Na PDT on absorber growth and solar cells performance by varying the alkali percentage. Figure 1 shows the field effect-scanning electron microscopy (FE-SEM) images of without (w/o) PDT-treated and different Na (%) PDT-treated CIGSSe absorbers.

The CIGSSe film has a rough texture, and grain growth occurs. Generally, for a spray pyrolysis case, the absorber film shows a rough surface pattern. However, the incorporation of Na PDT into CIGSSe absorber films results in a decrease in surface irregularity and boosting up the grain sizes. The surface roughness of (Na8% PDT) CIGSSe is much passivated than that of other CIGSSe films. Furthermore, the compacted grains sizes and growth mechanism of (Na8% PDT)-CIGSSe enhancing the crystallinity with comparing CIGSSe film. The greater grain sizes of the (Na8% PDT) CIGSSe absorber would decrease charge recombination at the grain borders. (Jung et al., 2022, Wang et al., 2017)

Figure 2 represents the x-ray diffraction (XRD) patterns of CIGSSe and different Na (%) PDT- CIGSSe absorber films.

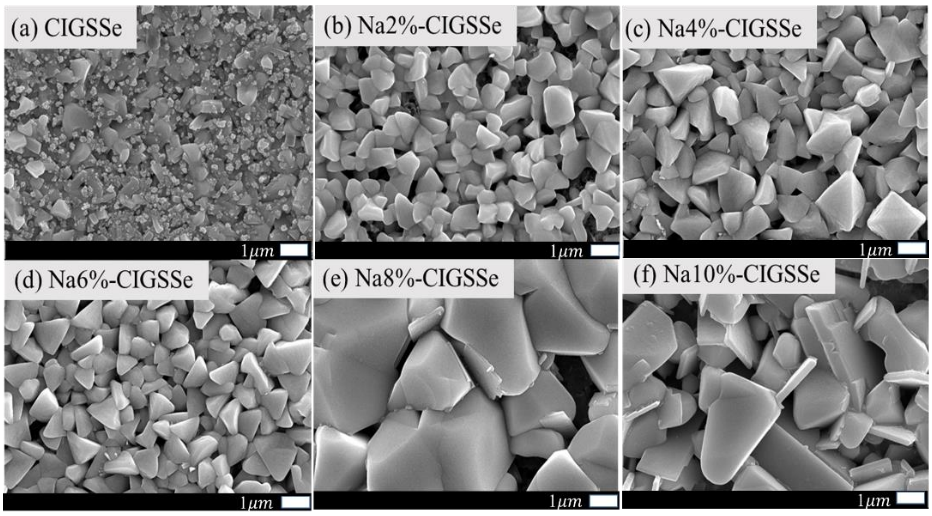

Figure 1: FESEM images of CIGSSe (a) and different Na (%) PDT CIGSSe absorbers (b-f).

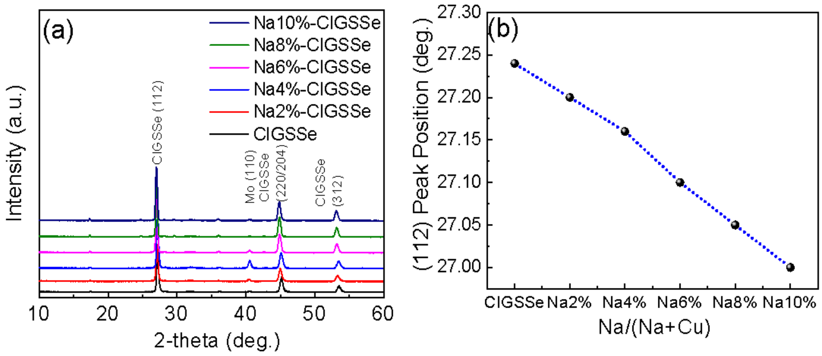

Figure 2: (a) XRD spectrum and (b) (112) peak shift (deg) of CIGSSe and different Na (%) PDT CIGSSe absorbers.

With the increase of Na (%)-PDT, the dominant XRD (112) peak of CIGSSe shifts to a lower angle, indicating that the lattice parameter has increased and that Na has been incorporated into the Cu-site. An increase in the quantity of Na (%)-PDT could potentially improve the lattice parameters of the CIGSSe absorbers, which is in accordance with the findings reported in other literature (Jung et al., 2022). The graphs in Figure 3 show the JV and EQE of the CIGSSe and Na (2% to 10%) PDT CIGSSe solar cell devices.

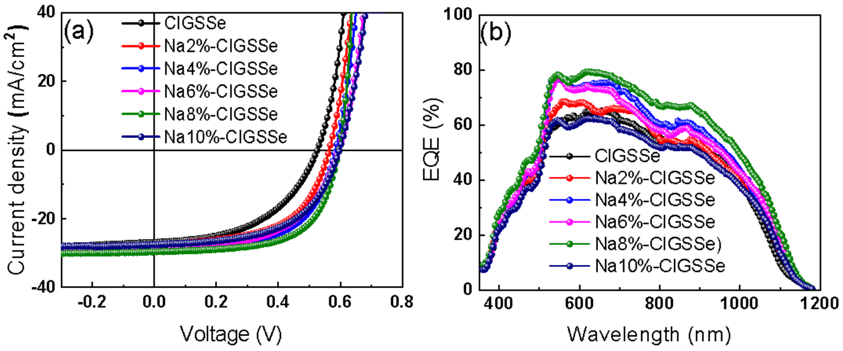

Figure 3: (a) JV and (b) EQE graphs of CIGSSe and different Na (%) PDT CIGSSe solar cells.

The introduction of Na PDT into CIGSSe absorbers increases all device parameters, leading to an increment in the PCE from 7.38% to 11.18% at the optimal Na-8% PDT condition. Furthermore, adding more Na (%) PDT leads to a decrease in PCE to 9.03%. It is reported that Na inclusion into CIGSSe enhances the current density (J_{sc}), fill-factor (FF), and strong contribution to the V_{oc} improvement (Pianezzi et al., 2014, Salome et al., 2014). The detailed device parameters are enlisted in Table 1.

Table 1: Device parameters of CIGSSe and different Na (%) PDT CIGSSe solar cells

Items	**CIGSSe**	**Na2%-CIGSSe**	**Na4%-CIGSSe**	**Na6%-CIGSSe**	**Na8%-CIGSSe**	**Na10%-CIGSSe**	**Unit**
V_{oc}	0.54	0.57	0.58	0.59	0.60	0.59	**V**
J_{sc}	26.91	27.88	28.23	28.74	29.63	27.54	**mA/cm^2**
Fill Factor	50.81	55.10	58.23	60.42	62.92	55.63	**%**
Efficiency	7.38	8.75	9.57	10.24	11.18	9.03	**%**

Furthermore, the increased V_{oc} is commonly associated with improved positive (p-type) conductivity of the bulk layer (Bob et al., 2012). The EQE results of the Na 8%-PDT CIGSSe device show an enhancement of the spectrum over the 550 nm region compared to the pure CIGSSe device. This analogy demonstrates that the absorbers' bulk defect is substantially more passivated than untreated Na PDT CIGSSe solar cells. (Mina et al., 2022) Figure 4 shows the PL and TRPL measurements of the same devices as characterized before.

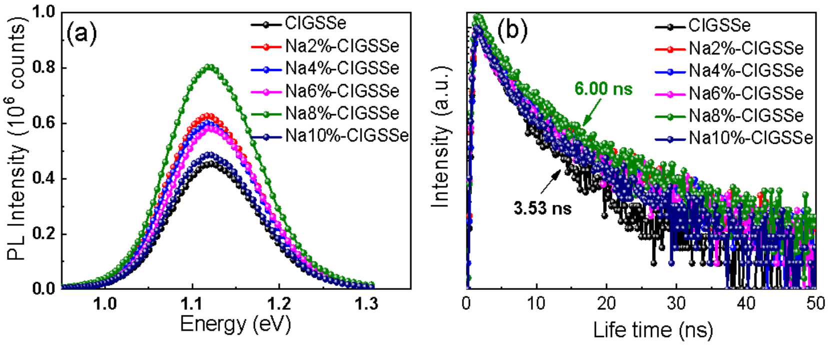

Figure 4: (a) PL and (b) TRPL spectrum of CIGSSe and different Na (%) PDT CIGSSe solar cells under 532 nm excitation wavelength.

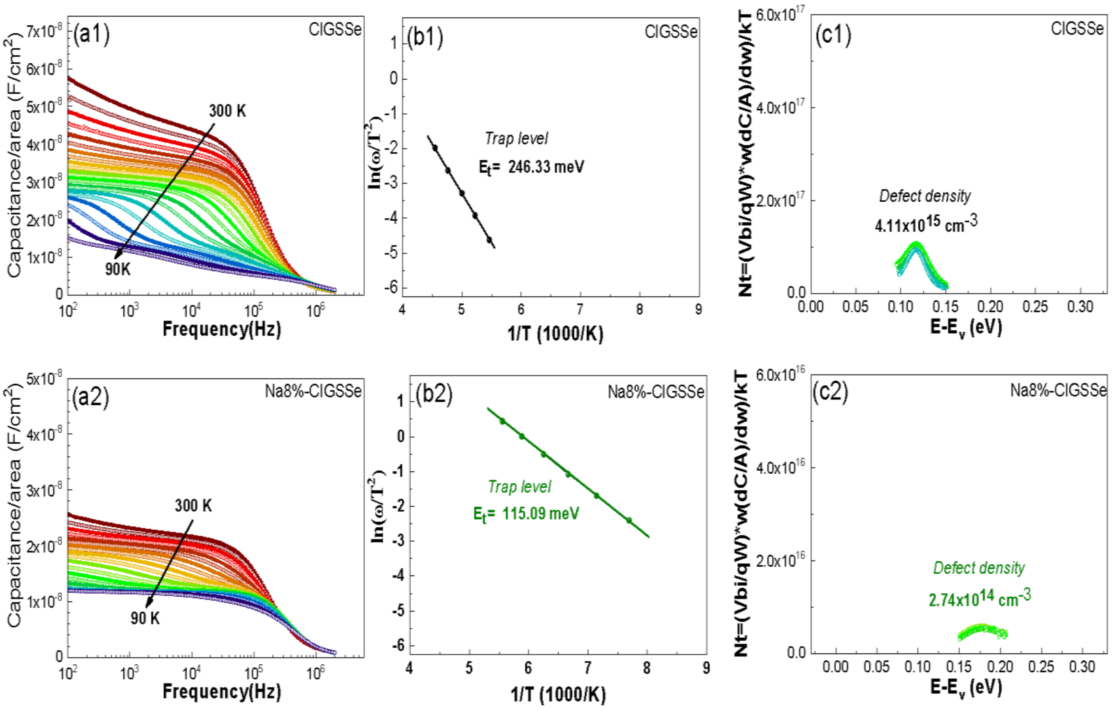

Figure 5: AS analysis of CIGSSe and Na8%-CIGSSe solar cells. (a1, b1, c1) and (a2, b2, c2) are capacity/area-frequency responses (300 K-90 K), trap level and density estimation of CIGSSe and Na8%-CIGSSe solar cells, respectively.

The highest PL spectrum of Na8%-PDT CIGSSe device implies that optimum PDT is effective to lowering the charge recombination center and mitigate the non-radiative recombination of the bulk. Consequently, the Na PDT plays a significant impact to improve the device performance. (Mina et al., 2023). Along with this characterization further those devices were analyzed by TRPL to study the minority carrier life-time. The life time increased from 3.53 ns to 6.00 ns for the Na8%-PDT CIGSSe device the maximum carrier times indicate that the defect at the absorber/buffer interface as well as bulk site has been extensively passivated by optimal Na inclusion. (Jung et al., 2022, Mina et al., 2023). Figure 5 shows the AS results of the w/o PDT treated and Na8%-PDT CIGSSe devices. The trap levels (shallow and deep levels) are estimated to be (246.33 meV and 115.09 meV) for CIGSSe and Na8%-PDT CIGSSe devices, accordingly.

However, the defect density decreases from 4.11×10^{15} cm^{-3} (for CIGSSe) to 2.74×10^{14} cm^{-3} (Na8%-PDT CIGSSe). The trap level and defect density lowering by Na PDT allows to enhance the PCE of the device (Mina et al., 2023). However, some research finding proposed that Na is beneficial to mitigate donor type In_{Cu} antisite defects at grain boundary (GB) region (Forest et al., 2015). Furthermore, some researchers have also suggested that the stability of the defect complexes, such as $2V_{Cu}^{-}+In_{Cu}^{2+}$, is lower due to the formation of Na_{Cu}. . (Wang et al., 2022, Yuan et al., 2016, Maeda et al., 2015)

Conclusion

In conclusion, we have devised an inexpensive and environmentally friendly favorable technique for the fabrication of CIGSSe solar cells. This method involves the use of solution-based fabrication method at ambient air condition to carry out an additional alkali PDT approach. Our findings demonstrated that the incorporation of Na in CIGSSe, substantially enhanced PCE by improving all device parameters, including V_{oc}, J_{sc}, and FF. FESEM and XRD study revealed that crystallization and grain growth modified due to Na PDT and enhancing the PCE improvement. In addition, we studied the beneficial impacts of the additional alkali treatment on device performance by employing several measurement methods, such as PL, TRPL, and AS. Additionally, those techniques revealed that the defect densities as well as trap levels were significantly suppressed in the Na8%-PDT CIGSSe solar cell, contributing to the enhancement of PCE.

Acknowledgement

The Korean Government financed this research under the National Research Foundation of Korea (NRF) and managed by Incheon National University (INU). I express my gratitude to Professor JunHo Kim for his recommendations and guidance about this experiment. I would like to convey my appreciation to the Nano Photoelectronics Devices Lab (NPDL) and INU Research Facility for their assistance with the characterization of the samples. The authors extend their thanks to the Physics Discipline and Khulna University for their support.

Conflict of Interest

The author declare no conflict of interest.

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Supplementary material

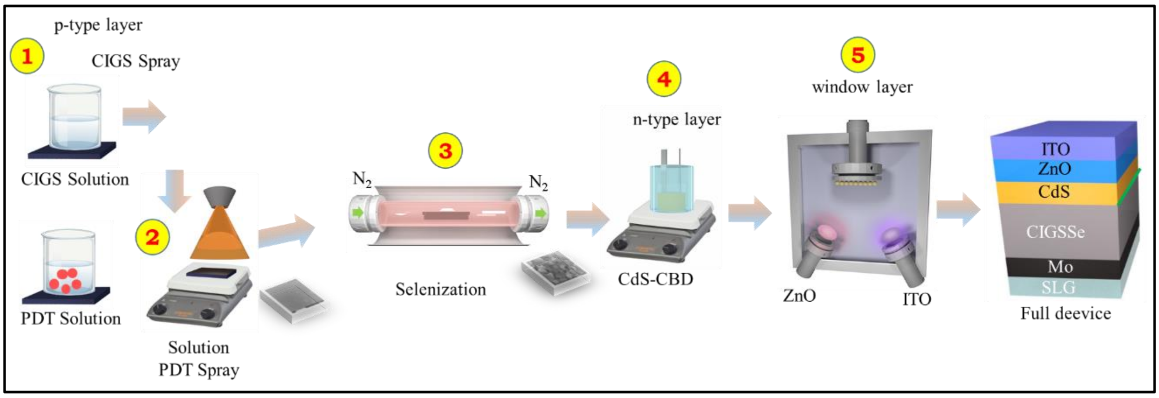

Figure S1. Full device fabrication schematic through spray pyrolysis method.