Band to band photoluminescence emission revealed in post annealed Cu2ZnSnS4 solar cells

Gansukh, Mungunshagai; Martinho, Filipe Mesquita Alves; Mariño, Simón López; Espindola Rodriguez, Moises; Engberg, Sara Lena Josefin; Hajijafarassar, Alireza; Stamate, Eugen; Hansen, Ole; Schou, Jørgen; Canulescu, Stela

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Presenting author:
Mungunshagai Gansukh¹

Contact email address for presenting author:
mugan@fotonik.dtu.dk

List of co-authors:
Filipe M. Martinho², Simón L. Mariño², Moises E. Rodríguez³, Sara Engberg¹, Alireza Hajijafarassar², Eugen Stamate², Ole Hansen², Jørgen Schou¹, and Stela Canulescu¹

List of affiliations:
¹Department of Photonics Engineering, Technical University of Denmark, 4000 Roskilde, Denmark.
²DTU Nanolab-National Centre for Nano Fabrication and Characterization, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark
³Department of Energy Conversion and Storage, Technical University of Denmark, 4000 Roskilde, Denmark.

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Abstract

Post annealing is frequently used for improving the device performance of the kesterite solar cells. The rise in the efficiency has been mainly attributed to elemental interdiffusion such as Na, Cd, Cu, and Zn[1]–[3]. In particular, at the CdS/CZTS interface, the interdiffusion between Cd and Zn was shown to reduce the conduction band offset resulting in a more favourable band alignment[2]. In the bulk, the Cu-Zn disorder and Na diffusion are affecting the device parameters[1], [3]. A drop in the efficiency occurs at an annealing temperature higher than 300°C and/or longer annealing times[2]. Since most studies on post annealing were carried out on complete cells, it is difficult to assess which effects are responsible for the performance behaviour.

In order to decouple the different contributions, we have performed systematic studies at three different stages during sample fabrication. We studied the effect of post annealing on the CZTS absorber, CZTS/CdS heterojunction, and CZTS/CdS/Al:ZnO complete device. The post annealing was carried out in nitrogen atmosphere in a temperature range varying from 125°C to 325°C. The efficiency of the complete cells increases at a temperature as low as
150°C, and it drops above 300°C. Our findings reveal a band to band (BB) photoluminescence (PL) emission from annealed CZTS/CdS and complete devices which did not occur when annealing only the CZTS absorbers. Additionally, BB PL position and bandgap derived from EQE measurements correlate with each other. The BB PL peak reaches a maximum for solar cells annealed at 275°C, which coincides with the lowest $V_{OC}$ deficit (see Figure 1 a, b). The BB emission has been reported previously in CZTS polycrystalline powders at room temperature[4]. We will discuss the effect of post annealing in terms of efficiency and BB emission by comparing post annealing at different stages.

![Figure 1](image1.png)

**Figure 1.** Room temperature photoluminescence spectra (a) and $V_{OC}$ deficit compared to the ratio of the band to band (BB) to the band to tail (BT) peak intensity (b) after post annealing full cells.


