

Efficiency limitations in thin film solar cells based on $\text{Cu}_2\text{ZnSnS}_4$

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$\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTS) thin films for solar cells are of interest due to strong light absorption, stability and high abundance and non-toxicity of constituent elements. However, CZTS devices have only reached efficiencies of up to 12.6% and current research is focused on understanding reasons for device limitations. Segregation of secondary phases can be an issue, and non-ideal interface formation. However, the current understanding is that high concentration of bulk defects, causing potential fluctuations and band tailing, is the limiting factor. Highest concentration is seen for Cu_{Zn} and Zn_{Cu} defects [1], in agreement with calculated low formation energy over a wide range of chemical compositions for the defect complex $\text{Cu}_{\text{Zn}} + \text{Zn}_{\text{Cu}}$ [2]. Since these defects are relatively shallow, it is unclear if other defects, such as Sn_{Zn} and associated defect complexes, predicted to be deeper in the band gap [3], are instead limiting performance. Another issue is the decomposition of CZTS at high temperature in vacuum [4], related to the instability of Sn(IV)[5]. It is not clear if this instability affects properties of CZTS processed at the higher pressures typically used.

At Uppsala University, a CZTS synthesis route based on compound sputtering and annealing in elemental vapors is used. Variation of chemical composition such as S/Se ratio, exchange of Sn with Ge and annealing conditions is used as a tool to understand defect-related materials- and device properties. Since it is difficult to maintain high sulfur partial pressure in an annealing furnace, we studied influence from partial pressure through an annealing time series including monitoring pieces of SnS_2 that transformed into SnS when the partial pressure dropped over time [6]. The material and device properties after short annealing were very different from those seen after longer annealing times typically used in our baseline anneal. In particular, higher open circuit voltage was obtained for short annealing and this appeared correlated to an increase in the band gap as seen from quantum efficiency and photoluminescence (fig 1).

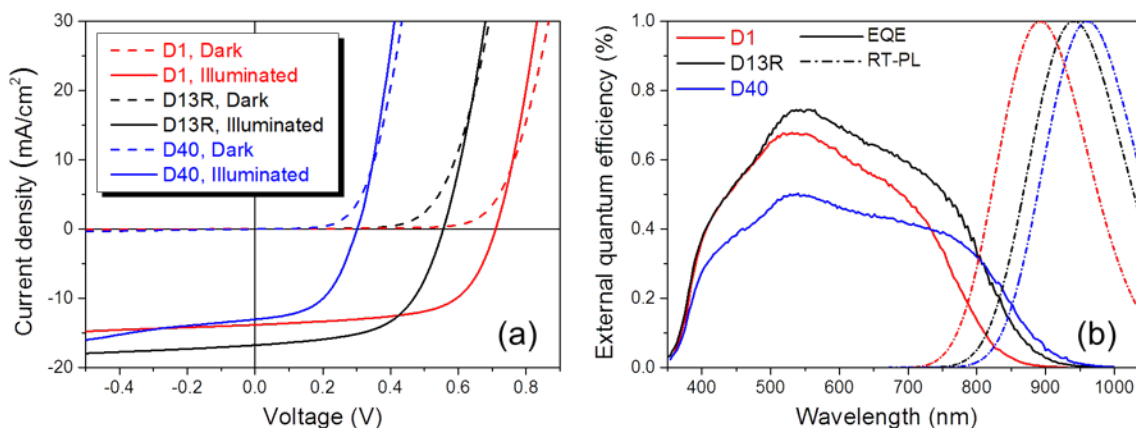


Figure 1: (a) Current-voltage characteristics and (b) External quantum efficiency (solid line) and the RT-PL spectra (dash line) of the CZTS solar cells; (D1) 1 min anneal, loading SnS_2 ; (D13R) 13 min anneal, no loading SnS_2 ; (D40) 40 min anneal, loading SnS_2 . From reference [6].

What could cause such a large shift in band gap? Cu-Zn disorder is one possibility, where reversible band gap changes are well established as a function of annealing above or below the critical temperature for the order-disorder transition. If the observed change in band gap is due to a difference

in the degree of disorder – what is the connection between disorder and sulfur partial pressure during annealing at high temperature? And if not – what other defects are responsible for the change?

Front and back contacts for CZTS are also studied with focus on energy band matching at the hetero-interface using atomic layer deposition buffer layers [7] and chemical stability of the back contact. Post deposition air-annealing can give dramatic improvements of devices, but can also increase disorder due to quenching from temperatures above the critical temperature. In this presentation, reasons for efficiency limitations in CZTS will be described, with focus on the contribution from bulk defects.

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