Boosting the Open Circuit Voltage of Cu2ZnSnS4 Solar Cells by a Lattice-Matched CeO2 Layer and Theoretical Understanding of Interface Defects

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Publication date:
2017

Document Version
Peer reviewed version

Link back to DTU Orbit

Citation (APA):
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The open circuit voltage of state-of-the-art Cu$_2$ZnSn(S,Se)$_4$ solar cells with a low S content appears to be limited by bulk recombination. Therefore, at the current stage of development, the standard CdS buffer layer of Cu(In,Ga)Se$_2$ solar cells is sufficient for obtaining a high-quality heterointerface with Cu$_2$ZnSn(S,Se)$_4$. Conversely, pure-sulfide Cu$_2$ZnSnS$_4$ solar cells are plagued by interface recombination, possibly due to a combination of an unfavorable band alignment with CdS, a large lattice mismatch with CdS, and unfavorable properties of the Cu$_2$ZnSnS$_4$ surface. As a consequence, the open-circuit voltage deficit and efficiency are consistently inferior in Cu$_2$ZnSnS$_4$ solar cells than in Cu$_2$ZnSnSe$_4$ solar cells.

In this work, we tackle the interface recombination problem of Cu$_2$ZnSnS$_4$ solar cells by a combination of theory and experiment. First, we verify by density functional theory that detrimental states within the band gap are expected on Cu$_2$ZnSnS$_4$ surfaces, but not necessarily on Cu$_2$ZnSnSe$_4$ surfaces. This means that band alignment is not the only important parameter when searching for a new buffer material for Cu$_2$ZnSnS$_4$ solar cells. Instead, an ideal buffer material should also remove the native defect states from the Cu$_2$ZnSnS$_4$ surface (passivation role) and form a high-quality interface with Cu$_2$ZnSnS$_4$ without introducing new defect states (by lattice matching and epitaxial growth).

To solve those problems, we propose and test experimentally CeO$_2$ as a novel buffer layer material in Cu$_2$ZnSnS$_4$ solar cells. The major advantage of CeO$_2$ is its nearly perfect lattice match with Cu$_2$ZnSnS$_4$ (0.4%), in contrast to the poor lattice match of CdS (7%). CeO$_2$ is a non-toxic compound that is already used in the fields of catalysis and solid oxide fuel cells. Ce is more earth-abundant than Sn and about as earth-abundant as Cu and Zn (source: U.S. Geological Survey Fact Sheet 087-02).

Here we demonstrate that CeO$_2$ can be easily grown on Cu$_2$ZnSnS$_4$ by chemical bath deposition. For growth temperatures as low as 50°C, we observe epitaxial growth of CeO$_2$ on Cu$_2$ZnSnS$_4$ by transmission electron microscopy. Furthermore, CeO$_2$ films show good surface coverage, low spurious phase content, and a nearly optimal band alignment with Cu$_2$ZnSnS$_4$ as measured by x-ray photoemission spectroscopy.
We then make a first attempt to include CeO$_2$ in the Cu$_2$ZnSnS$_4$ solar cell architecture by inserting a thin CeO$_2$ layer between Cu$_2$ZnSnS$_4$ and the usual CdS buffer. The result (over four solar cell batches up to 7% efficiency) is a reproducible open circuit voltage boost compared to the baseline case with a pure CdS buffer layer. The efficiency is also improved in three batches out of four. We argue that this is due to formation of a less defective heterointerface with a lower recombination velocity. By examining the calculated band structure of CeO$_2$, we discuss why CeO$_2$ can be an excellent thin passivation layer for Cu$_2$ZnSnS$_4$ but cannot be used as a stand-alone buffer layer.