

II-VI semiconductors and derivated kesterites structures for photovoltaic conversion

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CuZnSnSSe (CZTSSe) semiconductor devices are nowadays one of the approaches to achieve thin film solar cells of the third generation. However, up to now, they do not allow to reach power conversion efficiencies as high as the ones obtained with similar absorber materials such as CuInGaSSe, typically 12% instead of 22%: more precisely, the limited open-circuit voltage (V_{oc}) commonly reported on CZTS based solar cells is still an important issue and remains a main drawback for the former compounds, made from earth-abundant elements. This is probably due to the presence of strong potential fluctuations which are induced by a large amount of intrinsic point defects.

As predicted by the density functional theory calculations, the major part of these point defects in CZTSSe compounds is coming from the exchange between Cu and Zn which induces Cu_{Zn} and which are stabilized by the formation of self-compensated defect clusters (see S. Chen, X.G. Gong, A. Walsh, S.H. Wei, Phys. Rev. B 79, 165211 (2009); S. Chen et al. Phys. Rev. B 81,245204 (2010)). A high concentration of these neutral defect complexes locally induces a band gap shift of the conduction and valence band edges, directly responsible for potential fluctuations and consequently for the V_{OC} reduction due to the induced band tailing.

This band tail is studied here by optical spectroscopy, combining three types of measurements, namely emission spectra compared to photoluminescence excitation spectroscopy, emission spectra as function of excitation power, and time resolved photoluminescence spectra. All these data converge to show that both the bandgaps and the band tail of localized states just below are depending on the order/disorder degree in the Cu/Zn cation sublattice of the quaternary structure: in the more ordered structures, the bandgap is increasing by about 50 meV and the energy range of the band tail is decreased from about 110 meV to 70 meV.

The impact of this localized states band tail on the admittance response is also considered. The admittance model which was developed shows that the potential fluctuations can well explain the anomalous stretching of the capacitance step which is observed, and that they have to be considered to precisely extract the energy trap position.

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