Impact of potential fluctuations on admittance spectroscopy: The case of $Cu_2ZnSn(S_xSe_{1-x})_4$ thin films solar cells

Frédérique Ducroquet[1], Louis Grenet[2], Raphaël Fillon[2], Henri Mariette[3]

University of Grenoble-Alpes,
[1]CNRS, Grenoble-INP, IMEP-LaHC, 3 Parvis Louis Néel, 38016 Grenoble.
[2]CEA-LITEN,17 rue des Martyrs 38054 Grenoble.
[3] "Nanophysique et Semiconducteurs" group, CNRS/Néel Institute, Grenoble.
Corresponding author: ducroquet@minatec.inpg.fr

All the reports on $Cu_2ZnSn(S_xSe_{1-x})_4$ (CZTSSe) solar cell devices show an open-circuit voltage lower than expected, especially when comparing to $CuIn_xGa_{1-x}(S,Se)_2$ ones, which reduces their power efficiency and delays their development. A high concentration of intrinsic defects in CZTSSe, their stabilization through neutral complex formation and the deep energy position of the dominating acceptors are pointed out to be at the origin of some specific electrical effects (compensating effect linked with a high series resistance at low temperature, potential fluctuations, parasitic charge transport in band tails).

The admittance spectroscopy is a well-established technique to investigate the electrically active defects in solar cell devices. An increase of several orders of magnitude of the series resistance is generally observed on CZTSSe solar cells at low temperature (T<150-200K), which is attributed to carrier freeze-out due to a dominant deep acceptor in the thin film absorber. An additional contribution to the junction admittance results from that and has to be taken into account. In this work, a full modeling of the *ac* admittance response of an asymmetric n^+p junction was developed, considering any degree of absorber depletion. The response of the deep traps lying in the absorber is considered by solving complex small signal Poisson equation. Capacitance calculations are compared to experimental data measured on CZTSSe solar cells fabricated with a 2 steps selenization process, as described in [1].

When considering the response of one single deep acceptor level, the capacitance step *vs* frequency observed on the experimental spectra cannot be accounted properly: indeed, when the trap activation energy is chosen close to that experimentally extracted using the classical Arrhenius plot method, the amplitude step is too small at room temperature indicating that the majority of the dopants are ionized. A better fit of the amplitude step can be obtained by increasing the activation energy; however in that case, the inflection point of the capacitance step is strongly shifted. It can also be noted that simulated data show steeper capacitance steps than experimental ones.

As obtained by the density functional theory calculations, which was used to predict the existence of intrinsic defects in CZTSSe, it was shown that the major part of these point defects are stabilized by the formation of neutral complexes directly responsible for potential fluctuations. The effects of such potential fluctuations were added to the admittance model, by introducing a truncated Gaussian distribution of the energy. The traps and free carriers concentrations are modulated by this energy distribution. With the full modeling including potential fluctuations, a better adjustment is found, giving a good description of the capacitance step amplitude, the stretching and the inflection position.

At high temperatures and low frequencies, an additional contribution is observed, which could be partly attributed to interface states at the interface between absorber and buffer layers which are not taken into account in the model. Another extra response is noted at low temperatures and high frequencies, which could also be visible on the conductance spectrum. This response is characteristic of a dielectric relaxation process and could be related to a charge transport mechanism in disordered materials. Using the concept of transport energy, a charge hopping via localized states of the band tail is suggested to explain the charge transport at low temperature in these CZTSSe solar cells, a high density of neutral complexes near the band tail would enhance this process.

*[1] L. Grenet et al., Solar Energy Mat Solar Cells **126**, 135 (2014).*