Tail states and the efficiency of solar cells

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In an ideal semiconductor the density of states is zero for energies between the band edges. However, every real semiconductor shows tail states extending into the band gap. To learn about the tail states, optical absorption measurements are performed. Photoluminescence provides an excellent tool to measure the absorption coefficient down to very low absorption values,[1] i.e. deep into the band gap. Essentially, this is because it is easier to measure the emission of very few photons than the absorption of very few photons. Recently, we have shown that the method is also applicable to thin films.[2] In various thin-film materials, tails show an exponentially decaying behaviour away from the band edges, which is described by the Urbach energy. An example is given in Fig. 1a). Tails can be caused by band gap fluctuations, due to composition variations [3] or due to bond length fluctuations,[4] or by electrostatic fluctuations.[5]

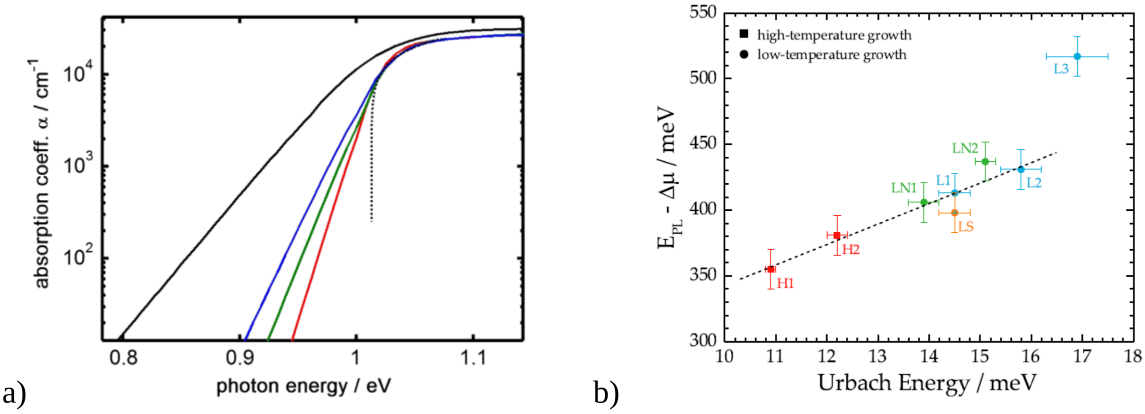

Fig. 1 a) absorption coefficient of CuInSe$_2$ films (Cu-rich in colour, Cu-poor in black), the ideal semiconductor absorption is shown by the dashed line. From [6] b) Correlation between band tails and quasi-Fermi level splitting loss for various Cu(In,Ga)Se$_2$ absorbers with and without alkali treatments. From [7]

A correlation between the Urbach energy and the V_{OC} loss, i.e. the difference between the band gap and the open-circuit voltage of a solar cell, has been demonstrated over a range of different PV technologies.[8] The recent improvements in the record efficiencies of Cu(In,Ga)Se$_2$ solar cells[9-11] have been achieved by alkali post deposition treatments[12] which improve the open-circuit voltage. Early experiments revealed that the treatments influence the surface of the absorber and the interface with the buffer.[12] However, we could recently demonstrate that the treatment improves the electronic quality of the absorber bulk as well: we observe an equivalent improvement of the quasi-Fermi level splitting in bare absorbers with and without treatment.[13] No deep defects have been observed in these absorbers.[14] They provide, therefore, a model system to study the influence of tails states on the open-circuit voltage. A clear correlation between Urbach energy and quasi-Fermi level splitting loss is shown in Fig. 1b). Most samples fall on a linear dependence, which is very similar to the one observed in literature.[8] Sample L3 is one without any alkalis and clearly has additional limitations than the band tails. If the quasi-Fermi level splitting/open-circuit voltage loss is determined by the bulk properties and the bulk is good enough that the limitations are due to tail states, then the values fall on the line. If other loss mechanisms are added, the V_{OC} loss will be higher.

The question arises by what mechanism the tail states limit the open-circuit voltage. It has been shown in the past that tail states lead to a loss in V_{OC} because of a shift of the energy maximum of the radiative recombination.[15,16] However, the observed V_{OC} loss is much higher than this shift caused by radiative recombination. But tail states also increase the non-radiative recombination. The open circuit voltage V_{OC} is given by [17]

$$V_{oc} = \frac{E_A}{e} - \frac{Ak_BT}{e}\ln\left(\frac{j_{00}}{j_{sc}}\right)$$

with E_A the activation energy of the main recombination rate, A the diode ideality factor, j_{00} the reverse saturation current prefactor, j_{SC} the short-circuit current, e the elementary charge, k_B Boltzmann constant and T the temperature. In the case where V_{OC} is limited by bulk recombination, E_A is the energy of the radiative recombination and reflects the shift of the energy due to tail states. But the room temperature V_{OC} depends critically on the diode ideality factor. In kesterite solar cells we have seen a correlation (although with strong scatter) between the diode factor and the shift of the radiative recombination away from the band gap, indicating that increasing Urbach energies increase the diode factor and thus the V_{OC} loss because of non-radiative recombination. Preliminary results on chalcopyrites, based on the absorbers shown in Fig. 1b, show no trend for the H-samples, but decreasing optical diode factor[18] with decreasing Urbach energy for the L-samples.

In summary: In the best solar cells most detrimental recombination paths, such as interface or deep trap-assisted recombination, are eliminated. The remaining path is then recombination through tail states. This recombination will have a slight influence on the energy of radiative recombination, which is the first (small) contribution to increasing V_{OC} loss. The main contribution is however the increase in non-radiative recombination, which is reflected in the reduced quasi-Fermi level spitting and the increased diode ideality factor with higher Urbach energy.

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