

# Local versus global electronic properties of $\text{Cu(In,Ga)}\text{S}_2$

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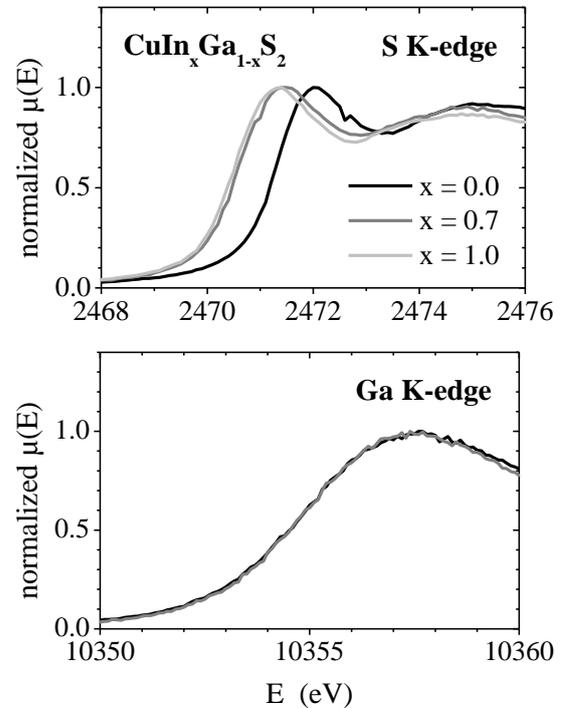
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Thin film solar cells based on  $\text{Cu(In,Ga)(Se,S)}_2$  have reached record conversion efficiencies well above 20% thus closing the gap to silicon based technologies. The properties of the material can be specifically tuned by adjusting the material composition. For example,  $\text{Cu(In,Ga)}\text{S}_2$  crystallize in the chalcopyrite structure where each Cu, In and Ga cation has four S first nearest neighbors while each S anion is bonded to two Cu and two group-III (In or Ga) atoms. The lattice constants change linearly with In to Ga ratio between those of the ternary end members. Similarly, the band gap of  $\text{Cu(In,Ga)}\text{S}_2$  changes continuously from 1.5 eV for  $\text{CuInS}_2$  to 2.4 eV for  $\text{CuGaS}_2$ . Interestingly, this change is mostly caused by a shift of the conduction band minimum while the valence band maximum remains nearly unaltered.

Unoccupied electronic states can be accurately probed by near edge X-ray absorption fine structure (NEXAFS) spectroscopy, where an absorbed photon excites a core level electron into an empty conduction band state according to dipole transition rules. One would thus expect that a shift of the conduction band minimum due to a change of the In to Ga ratio in  $\text{Cu(In,Ga)}\text{S}_2$  leads to a shift of the X-ray absorption edge positions as measured by NEXAFS.

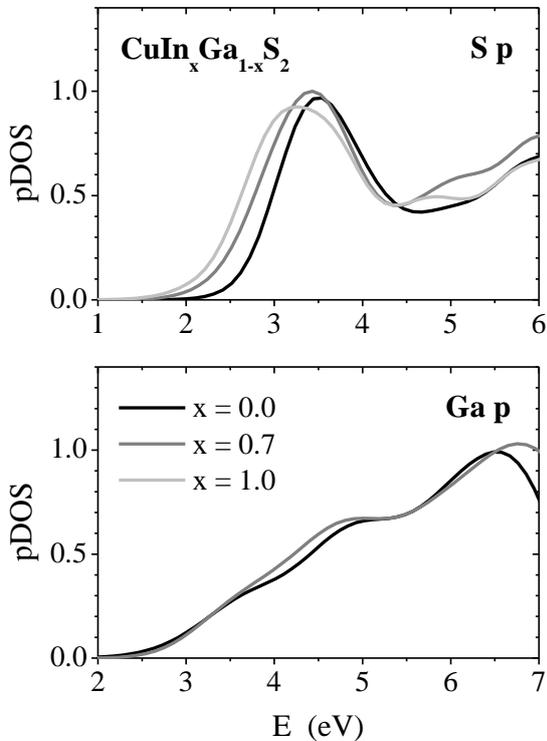
Solar cell grade  $\text{CuIn}_x\text{Ga}_{1-x}\text{S}_2$  thin films with  $x = 0, 0.7$  and  $1$  where studied by NEXAFS at the Cu, Ga and S K- and  $L_{3-}$  edges and at the In  $L_{3-}$  and  $M_{4,5-}$  edges [1]. As an example, Fig. 1 shows the S and Ga K-edge spectra as a function of excitation energy. As expected, the S K-edge position shifts to lower energies when the Ga content of the material and thus the band gap is decreased. A similar behavior is also observed for the S  $L_{3-}$  edge. In contrast, no change is observed in the position of the



**Fig. 1:** Measured absorption coefficient  $\mu(E)$  versus the X-ray energy  $E$  for the S and Ga K-edges of  $\text{CuIn}_x\text{Ga}_{1-x}\text{S}_2$ .

Ga K-edge in Fig. 1 or any of the other cation edges [1]. This means that although the band gap and thus the energy of the conduction band minimum change, only the anion absorption edges exhibit a corresponding shift whereas the cation absorption edges remain unchanged.

To unravel the origin of this unexpected behavior, we performed density functional theory calculations of the electronic states of  $\text{CuIn}_x\text{Ga}_{1-x}\text{S}_2$  for different  $x$  including 0, 0.7 and 1 [2]. The alloys were modelled with special quasi-random structures and the projected partial densities of states (pDOS) were calculated using a screened hybrid Heyd-Scuseria-Ernzerhof exchange-correlation potential. Figure 2 plots the pDOS of the S and Ga  $p$  states of the conduction band which correspond to the unoccupied states sampled at the S and Ga K-edge as shown in Fig. 1. Clearly, the S pDOS shifts with changing composition



**Fig. 2:** Calculated pDOS versus energy  $E$  of  $p$  states on S and Ga atoms for the conduction bands of  $\text{CuIn}_x\text{Ga}_{1-x}\text{S}_2$ .

while the Ga pDOS remains unchanged in excellent qualitative agreement with experiment. Similar agreement between the measured NEXAFS spectra and the calculated pDOS is also obtained for the other absorption edges [2].

The explanation for this behavior of the absorption edge positions can be found in the atomic-scale structure of  $\text{Cu}(\text{In,Ga})\text{S}_2$  alloys [2]. All cations are surrounded by four S atoms independent of composition. Furthermore, it was shown by extended X-ray absorption fine structure spectroscopy that the element-specific bond lengths remain nearly constant over the whole compositional range despite the significant change of the lattice constants [3]. The first nearest neighbor structural environment of Cu, In and Ga is thus nearly independent of composition and the *element-specific local* electronic states remain almost unchanged. Since the core level electrons are excited predominantly into unoccupied states of the absorbing atom itself, the absorption process is sensitive to these local electronic states. As a consequence, the cation absorption edges do not shift with changing composition. In contrast, the first nearest neighbor environment of the S anions contains two Cu and two group-III atoms and thus changes with changing In to Ga ratio. Consequently, the S absorption edges shift with varying composition. The observed change of the band gap thus arises from a changing spatial average of the nearly unaltered local states rather than from a change of the states themselves [2].

## References

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