

Strain and defects induced by chemical gradients in CIGSSe absorber

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$\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ (CIGSSe) is one of the most promising absorber material for use in thin film solar cells since high cell efficiencies can be achieved at relatively low production costs. Depending on the fabrication process CIGSSe absorbers typically show inhomogeneities [1] and chemical gradients which strongly influence the performance of the resulting solar cell. The CIGSSe solar cells investigated in the present study were processed by a stacked elemental process comprising sputtering of precursor films and formation of the chalcopyride by rapid thermal processing [2]. In order to increase the open circuit voltage of the final cell, the CIGSSe formation process is performed in a sulfur containing ambient resulting in a partial replacement of Se by S in a surface-near layer. In this paper the origin of extended defects below the surface of the absorber is studied and related to lattice misfit resulting from the chemical gradient.

Fig. 1 shows HRTEM images of typical defects that occur in the top 50 – 100 nm of CIGSSe absorbers. In order to illustrate that these defects are present in actual solar cells the cross-sectional images were taken from complete cell stackings containing a conventional CdS buffer (Fig. 1a) and an In_xS_y buffer (Fig. 1b, Cd-free cell concept) on top of the CIGSSe absorber. Apart from planar defects, like stacking faults, considerable strain contrast can be seen in the images pointing to the presence of dislocations. Similar contrast features have been observed by Abou-Ras [3] below the CIGS- In_xS_y interface of a solar cell fabricated by a completely different process.

In order to learn more about the origin of these defects CIGSSe absorbers without buffer layers were studied in cross-section and plan-view geometry. As can be seen from the cross-section TEM bright-field image Fig. 2a the defect band and considerable strain contrast are already present before addition of a buffer layer. Moreover, the surface is rough and shows small surface steps (Fig. 2b). Plan-view TEM images reveal Moiré-fringes in almost all the grains of the CIGSSe absorber (Fig. 2c). The Moiré-fringes are mainly of translational type indicating the superposition of two lattices with slightly different lattice spacing as expected for an epitaxial misfit system that is partially relaxed by misfit dislocations.

Chemical analysis by EDX line scans in cross-section geometry (Fig. 3a) shows that the highly defective subsurface region roughly coincides with a chemical gradient in the group V elements Se and S. Across the top ~ 100 nm the Se concentration decreases significantly while the S concentration increases correspondingly. A similar gradient, however closer to the surface and less pronounced, occurs for the group III elements In and Cu. In fact, Yan et al. [4] observed a defective surface layer for S-free CIGS absorbers deposited by sequential PVD and attributed the defects to a chemical gradient in the group III sublattice.

Fig. 3b summarizes the main findings of the study. Taking into account only the gradient in the S/Se concentration the misfit can achieve values up to -4.5% corresponding to a complete replacement of Se by S. Based on the observed concentration gradients estimated values of the critical thickness for strain relaxation via dislocations are well below 100 nm independent of the grain orientation and type of misfit dislocation (60° , Lomer) assumed in the calculation. Thus the formation of extended defects and the observation of translational Moiré-fringes in plan-view TEM images can be nicely understood as resulting from partial relaxation of misfit strain introduced by the S gradient.

References

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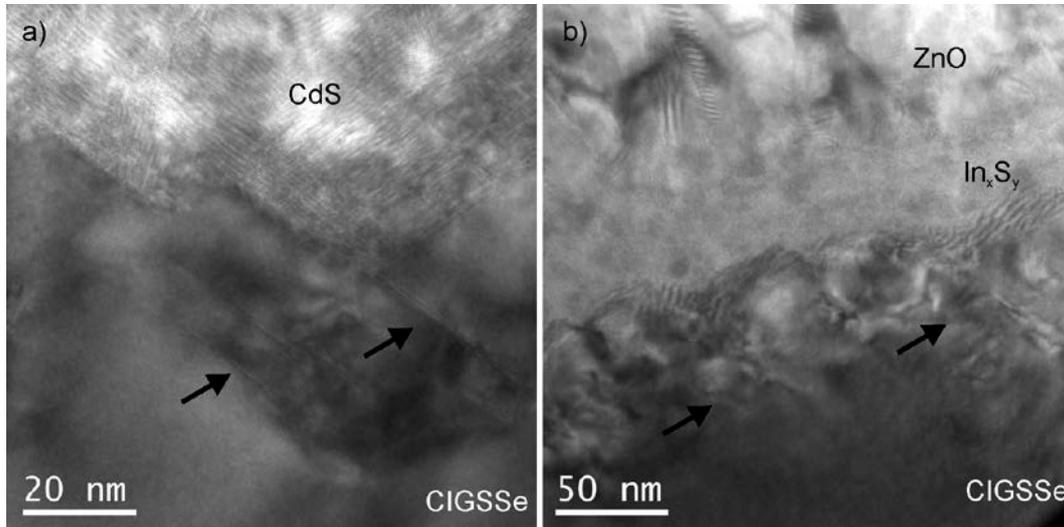


Fig. 1: a) CIGSSe absorber with epitaxial CdS buffer layer showing planar defects (arrows) and strain contrast in the absorber below the interface, b) CIGSSe absorber with In_xS_y buffer layer showing similar defect structures (arrows).

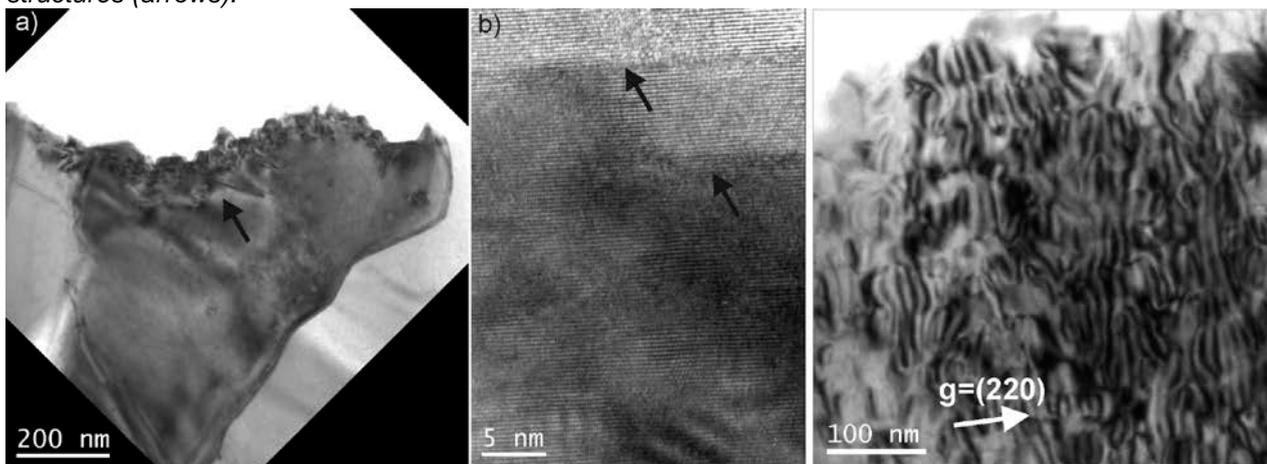


Fig. 2: a) Cross-section TEM bright-field image of a CIGSSe absorber without buffer layer showing surface defects (marked with arrow). b) HRTEM image of the near surface region showing planar defects (arrows) and steps. c) Plan view TEM bright-field image of the sample surface region revealing moiré-contrast across the complete grain.

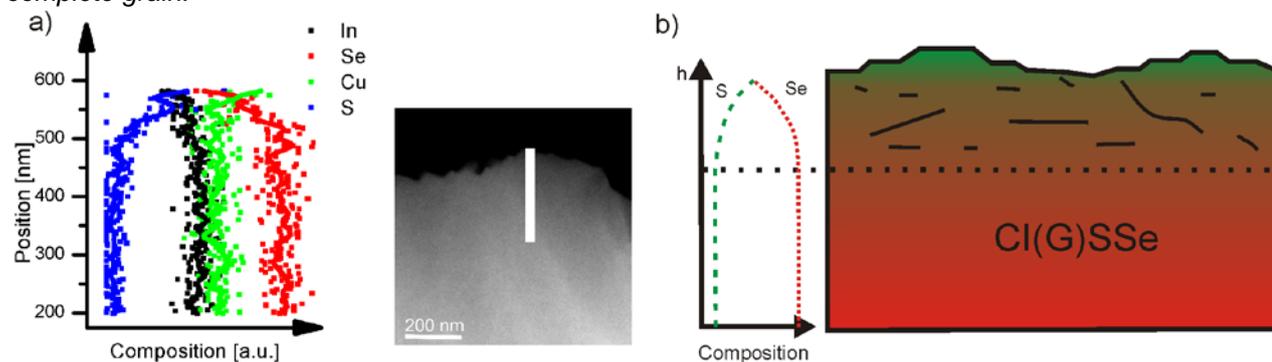


Fig. 3: a) EDX linescan across the highly defective subsurface layer (right: HAADF-STEM image). b) Schematic drawing of the chemical gradient in the CIGSSe absorber below the surface and the resulting microstructure. The S/Se exchange induces strain that partially relaxes and induces near surface defects.