

(Photo)electrochemically Induced Surface Transformations at Polycrystalline CuInS₂ Solar Cell Absorbers

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The secondary CuS phase of copper-rich CuInS₂ thin film absorber layers is usually removed by XCN etching (X = Na, K). This treatment would be environmentally problematic in the upscaling of production of these films. We studied an alternative electrochemical treatment of CuInS₂ solar cell absorber films, introduced to remove the segregated CuS phase [1-3]. Its influence on surface topography, chemistry and electronic properties was investigated. The results are examined in order to develop an improved understanding of the electrochemical surface transformation processes.

Photoelectron spectroscopy using synchrotron radiation is performed in a combined electrochemical/UHV surface analysis system at the beamline U49/2 (BESSY II). Different excitation energies are employed to analyse the chemical and electrochemical changes taking place during the transformation of the Cu-S phases (Fig. 1). The recorded valence band spectra indicate the remains of a residual layer of Cu_{2-x}S species on the surface after the electrochemical treatment. A quantitative coverage analysis for the overlayer thickness yields a reduction from 28 to 21 Å. XRD data show that the covellite has been transformed into either Cu₂S in a monoclinic form or intermediates of incompletely reduced Cu-S compounds like Cu_{1.93}S (djurleite) or Cu_{1.96}S (chalcocite). Atomic force microscopy (AFM) measurements showed partial removal of the crust-type overlayer. For electronic characterisation of the modified samples we investigate the behaviour of the photovoltage vs. redox potential in V^{2+/3+}-HCl [4]. The slope of V_{ph} vs. V_{redox} is a measure for surface/interface state densities. Fig. 2 shows that with a slope of ~ 0.4 and a low absolute value of V_{ph} for this treatment, the electronic quality remains limited.

Using a novel additional light soaking treatment in vanadium solution, the behaviour improves considerably (see Fig. 2). AFM and high resolution scanning electron microscopy show a smoothing effect. A further conditioning procedure in vanadium solution gives particularly promising results: the slope of the photovoltage vs. redox potential is increased from 0.38 for the original electrochemical treatment [1,2] to 0.67 for the treatment in a vanadium redox electrolyte reaching the value for KCN etched samples. There is, however, still a voltage limitation compared to KCN treated CuInS₂ which has to be overcome in further work.

References:

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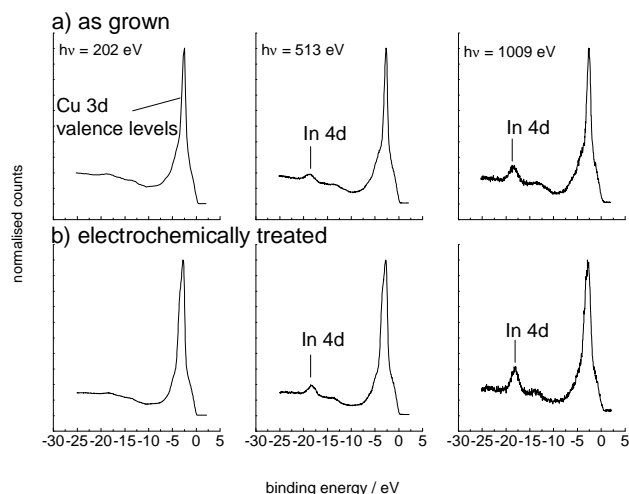


Fig. 1. Valence band spectra obtained for different excitation energies.

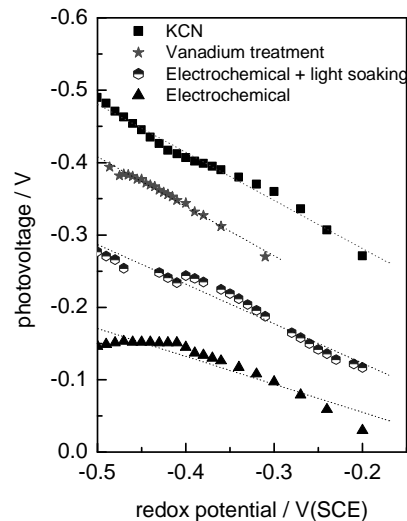


Fig. 2. Photovoltages in redox electrolyte: after KCN, electrochemical, electrochemical + light soaking treatments and the new treatment in vanadium solution.