Thin Films and Coatings

MS.5.116
Effect of Na-doping on the microstructure in $Cu(In,Ga)Se_2$ thin-film solar cells

L.A. Pfaffmann[1], A. Kast[1], D. Litvinov[1], E. Müller[1], W. Hempel[2], M. Powalla[2,3], D. Gerthsen[1]

[1]Laboratorium für Elektronenmikroskopie, Karlsruher Institut für Technologie, Karlsruhe, Germany
[2]Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Würtemberg (ZSW), Stuttgart, Germany
[3]Lichttechnisches Institut, Karlsruher Institur für Technologie, Karlsruhe, Germany

lukas.pfaffmann@lem.uni-karlsruhe.de
Keywords: $Cu(In,Ga)Se_2$, sodium-doping, EBSD, STEM, SEM

Polycrystalline chalcopyrites (chemical structure: $A^{I}B^{III}C^{VI}$) thin-films play an important role as solar cell absorbers. Especially solar cells based on $Cu(In_{0.7},Ga_{0.3})Se_2$ layers are particularly promising because they have already reached an efficiency of 20.3% [1].

A typical CIGS-solar-cell layer stack consists of a substrate of glass or flexible foils, coated with Mo as the back contact. The p-n junction is located between the p-type CIGS layer and the transparent n-type window layer, which consists of a CdS buffer layer and the ZnO front contact.

During the fabrication, Na diffuses from the soda-lime-glass substrate into the CIGS layer which has positive effects during the growth process of the absorber layer and the efficiency of the solar cell [2]. Without Na, the formation of a $MoSe_2$ layer [3] is suppressed. This leads to the formation of a Schottky-type electrical contact instead of a contact with ohmic character.

To investigate the effects of Na, three samples with different Na-concentrations in the CIGS layer were prepared by inserting a Na-blocking and Na-doping layer below the Mo back contact as shown in the scanning electron microscopy image Figure 1. Secondary-ion-mass spectroscopy (SIMS) was applied to determine the Na-concentrations in the CIGS layer (0.008 at%, 0.342 at%, 0.523 at%). These samples were compared with a sample prepared by the standard procedure which contains 0.025 at% Na.

To reveal the difference of the microstructure between the CIGS layers, cross-sections were prepared by focused-ion-beam milling in combination with low-energy Ar^+-ion milling. This preparation technique yields thin lamellae for transmission electron microscopy (TEM) and cross-section samples for electron backscatter diffraction (EBSD) measurements with smooth surfaces and without artefacts.

Figure 2 shows high-angle annular dark-field cross-section STEM images of the interface region between the Mo back contact and the CIGS layer for all samples. The measurement of the thickness of the $MoSe_2$ layer, which is important for the electrical contact of the CIGS layer, shows a clear correlation between Na-content and thickness of the $MoSe_2$ layer. Its thickness increases from values below 25 nm for the sample with 0.008 at% Na to values above 150 nm for the sample with the highest Na-concentration.

The grain size was determined by the evaluation of EBSD maps from cross-sections (see Figure 3) and by etching the solar cell on top. The average grains size increases from 1.0 m (0.008 at% Na), to 1.1 (0.025 at%), to 1.5 (0.342 at%), to 4.3 (0.523 at%) demonstrating again a strong influence of the Na-concentration. The EBSD maps also reveal the crystallographic orientation of the grains and facilitate the characterization of grain boundaries. A slight preference of the [010] grain orientation (green colour) perpendicular to the surface of the cross-section can be recognized in Figure 3 with increasing Na-content which is particularly obvious in the sample with the highest Na-content.

Clear effects of the increasing Na-concentration on the microstructure could be revealed. However, apart from the sample with the lowest Na-content, all other samples are characterized by efficiencies between 14,44 % and 15,10 % indicating that the increase of the grains sizes do not have a pronounced effect of the efficiency.

1. P. Jackson, D. Hariskos, E. Lotter, S. Paetel, R. Wuerz, R. Menner, W. Wischmann and M. Powalla, Prog. Photovolt: Res. Appl. 19 (2011) pp. 894–897
2. U. Rau, Advances in Solid State Physics 44 (2004) pp. 27-39
3. J. H. Sco_eld, A. Duda, D. Albin, B.L. Ballard, P.K. Predecki, Thin Solid Films, 260 (1995) pp. 26-31

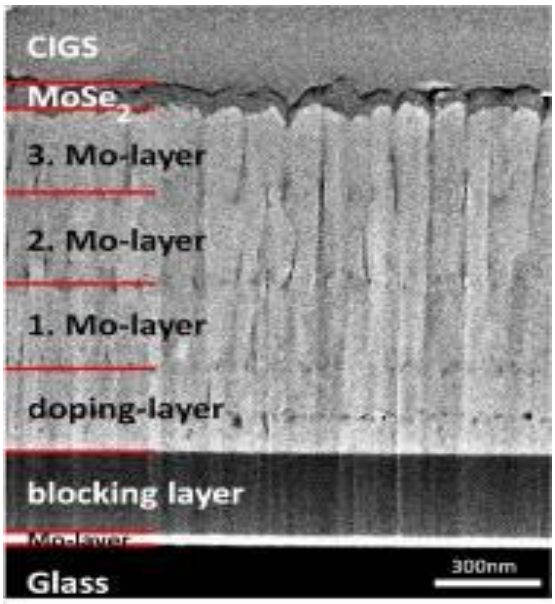

Figure 1. Scanning electron micro-graph of a cross-section of the modified back-contact

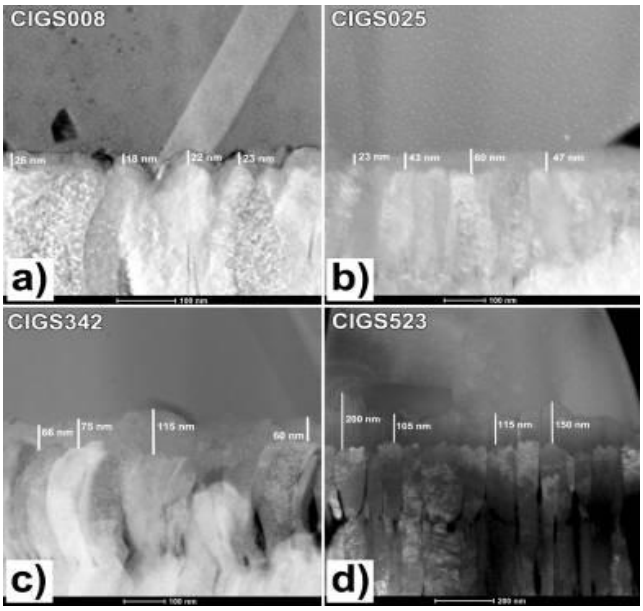

Figure 2. HAADF-STEM images of the Mo/$MoSe_2$/CIGS interface region of the samples with a Na-concentration of a) 0,008 at%, b) 0025 at%, c) 0,342 at% and d) 0,523 at%.

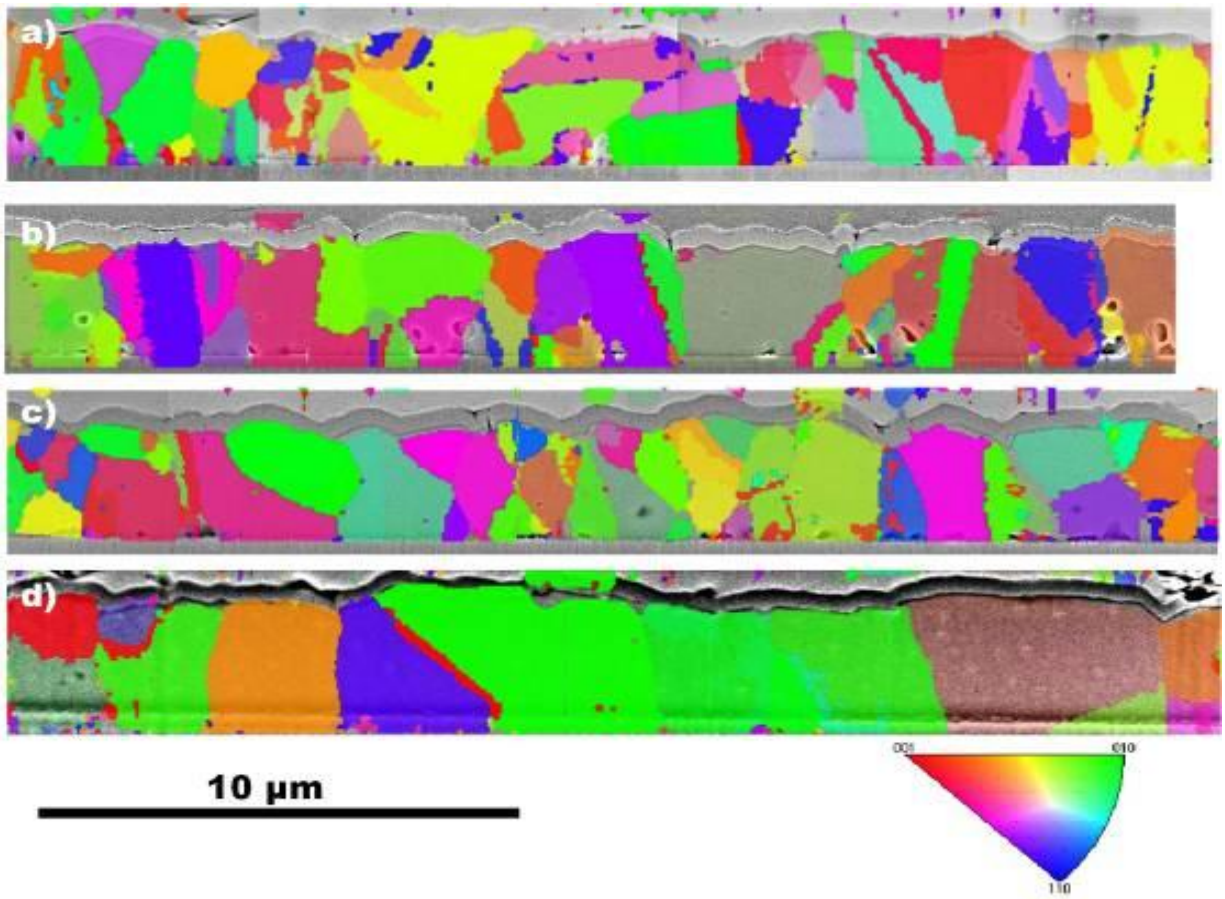

Figure 3. EBSD-maps of the samples with the sodium concentration of a) 0,008 at%, b) 0025 at%, c) 0,342 at% and d) 0,523 at% measured by SIMS. The orientation color scheme is given below the maps.