Combining optical and electrical spectroscopy to unravel the effect of Sb doping on CIGS solar cells

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1) Context / Study motivation

Among the thin film solar cells, those based on a chalcopyrite $Cu(In,Ga)Se_2$ (CIGS) absorber layer are the most efficient. A way to lower the manufacturing cost of CIGS thin film solar cells is to use flexible polymer substrates instead of glass substrates. Because such substrates do not stand high temperature during absorber deposition, the efficiency of the cells remains slightly lower (18.7% [1]) compared to CIGS on glass substrates (20.3% [2]). Partial compensation of this efficiency loss might be accomplished by Sb doping [3] of the absorber, which is reported to have a positive effect on the morphology of this layer.

2) Description of approach and techniques

In this work experiments were performed on cells deposited on soda lime glass substrate, adding a thin Sb layer onto the Mo back contact prior to the CIGS absorber deposition. The results are compared with those for cells without Sb layer using the same process. Two series of cells are tested, a first series had a varying thickness of Sb layer (8, 12 nm). For the second series the substrate temperature was varied, while the Sb layer thickness was kept fixed at 10 nm. By using optical and electrical spectroscopic techniques the defect structure of Sb doped CIGS solar cells and the influence of substrate temperature is investigated.

Photoluminescence provides information on shallow-level defects. The spectra are investigated as a function of temperature (10–80K) and optical excitation power. For a correct determination of the activation energy of the defects, the band gap of the absorber layer is measured as a function of temperature by Fourrier-Transform near Infrared Spectroscopy in photocurrent mode. Measurements are performed in the temperature range of 10-300K. For the electrical characterization Deep-Level Transient Spectroscopy (DLTS) and Admittance Spectroscopy (AS) are performed in the 4-300K range. Inspired by our study of the N1 signal on these samples, which can be assigned to a non-ideal ohmic, RC like back contact, we recorded DLTS spectra with normal and inverted pulses, leading to the conventional and complementary signal, respectively [4].

3) Results / Conclusions / Perspectives

Fourier-Transform near infrared photocurrent measurements demonstrate that the band gap of Sb-doped samples (at 5K E_g = 1,180 eV) is larger than for undoped samples (5K E_g = 1,166 eV) (fig 1). The relation $\alpha^2 \sim (E_g - E)$ for direct band gap materials is used to determine the gap energy. As temperature increases, the band gap energy decreases.

The PL spectra of all the cells show broad optical transitions. A blue shift with increasing excitation power of the peak energy of the PL spectra and a red shift with increasing temperature (larger than the decrease in band gap energy) is observed (fig 2). This indicates that the CIGS absorber is highly compensated and that potential fluctuations in the valence and conduction band strongly influence the optical spectra [5, 6]. The shape of the emission spectra slightly changes with excitation wavelength.

Samples made on lower substrate temperature show a more pronounced peak at low energy (between 0,9 and 0,94 eV) (fig 3). This can be attributed to an incomplete diffusion reaction of Cu at low substrate temperature, whereby the ratio of Cu/In can be altered [7]. A variation in the Cu/In ratio can lead to a change in the type of defects dominating the luminescence signal and may change the number of luminescence peaks [8]. On the spectra of samples doped with Sb, peaks can be better distinguished.

DLTS spectra of Sb-doped cells exhibit two features not encountered for non-doped cells: 1) instead of one peak (N1) below 200K, two negative peaks are visible and 2) samples without Sb undergo complete carrier freeze-in around 20 K, while samples with Sb do not exhibit complete freeze-in down to 4 K (fig 4). The first result indicates an extra non-Ohmic contact in the solar cell structure [4]. The second suggests the introduction of a very shallow acceptor by Sb doping.

AS measurements provide additional information on the carrier freeze-in. Only in Sb doped samples an extra admittance step at very low temperature is observable, in non-doped samples this step is not seen (fig 5). From these data, the activation energy of the intrinsic and the extra Sb-doping-related acceptor defects can be estimated.

Electrical and optical spectroscopic characterization indicates that Sb addition to CIGS solar cells, besides a possible positive influence on the morphology, also has an impact on the electronic structure of the absorber layer. The possible introduction of a shallow acceptor opens new perspectives of controlling the electronic properties of CIGS.

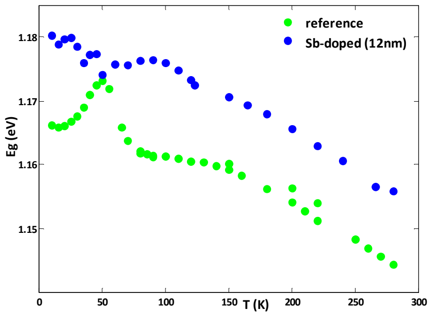

Figure 1: Band gap, measured as the onset of near IR absorption (photocurrent), for Sb-doped and undoped CIGS samples (Series1)

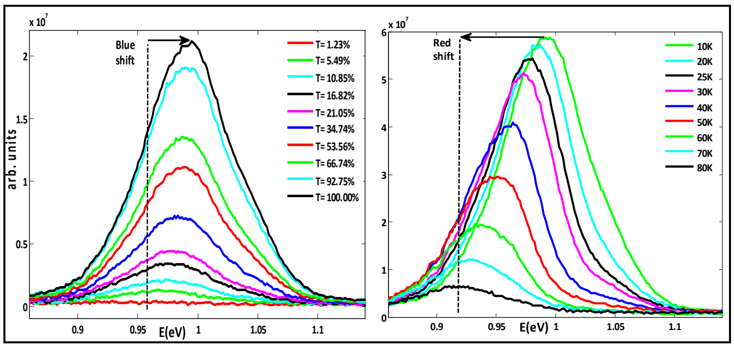

Figure 2: PL spectra of an undoped CIGS cell as a function of excitation power at a temperature of 10 K (left) and as a function of temperature (right). Excitation wavelength is 500nm. (Series2, high substrate temperature)

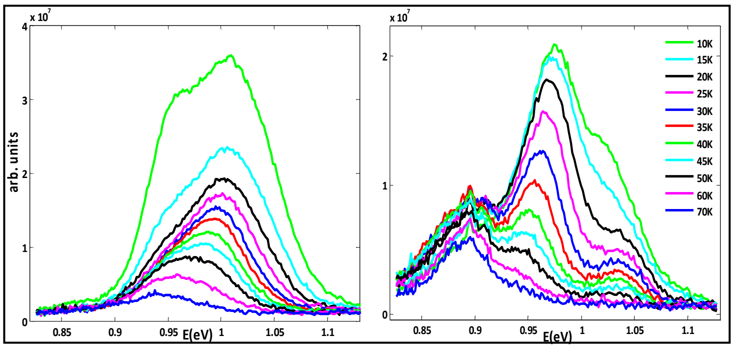

Figure 3: PL spectra of Sb-doped CIGS cell made at high substrate temperature (left) and low substrate temperature (right). Excitation wavelength is 500nm (Series 2)

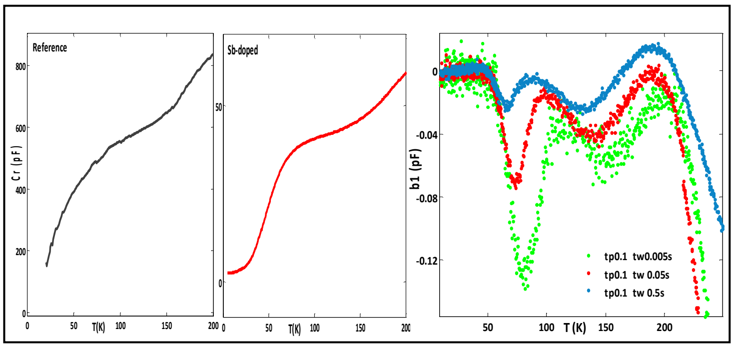

Figure 4: Left: Carrier freeze out of Sb-doped and undoped sampls (Series1) observed in the Cr.
Right: DLTS spectrum of Sb- doped sample (8nm, Series1) at different window times after short pulse (tp=0,1s) from Vr =-1V to Vp= -0,2V

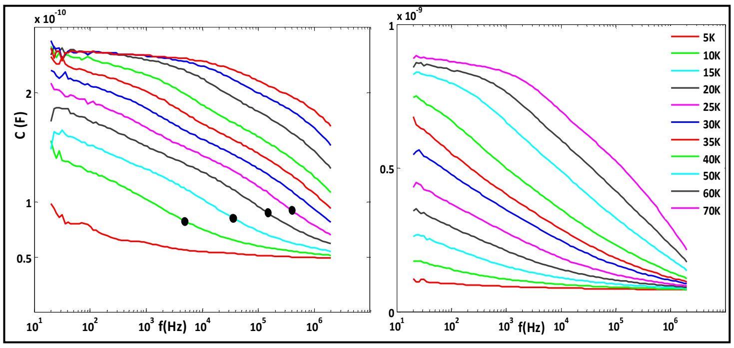

Figure 5: AS spectra of Sb-doped (left) and undoped (right) sample (Series2, high substrate temperature) V_{bias}= -0,3V

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