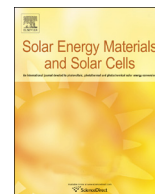




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Influence of iron on the performance of CIGS thin-film solar cells

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ABSTRACT

In the last years steel foil has become an attractive candidate for use as a flexible substrate material for Cu(In_xGa_{1-x})Se₂ thin-film solar cells (CIGS). It is stable at the high temperatures present during CIGS processing and is also commercially available. However, one disadvantage is the diffusion of substrate elements into the CIGS layer, which are detrimental for the performance of solar cells. We found a direct correlation between the iron (Fe) content in the CIGS layer and corresponding solar cell parameters. A deep defect related to Fe impurities could be detected by admittance spectroscopy measurements. The solar cell parameters could be well fitted by simulation with recombination at an acceptor like deep defect in the bulk of the CIGS layer. The simulated density of deep defect states correlates nicely with the Fe concentration in the CIGS layer. From this we conclude that Fe replaces an In (or Ga) site in the CIGS lattice and creates an Fe_{In}²⁺ (or Fe_{Ga}²⁺) deep acceptor state in the bulk of CIGS layers, which is detrimental already at a low concentration in the sub ppm range. The simulations enabled us to estimate the maximum Fe concentration in CIGS layers which is tolerable without disturbing the performance of high-efficiency CIGS solar cells.

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1. Introduction

Steel foil is one of the most attractive substrates for the production of flexible CIGS devices. It withstands high temperatures, has a coefficient of thermal expansion (11 ppm/K at about 550 °C for ferritic stainless steel and 13 ppm/K for mild steel) matching to that of CIGS (8–9 ppm/K). So far CIGS solar cells with a maximum efficiency of 17.7% and 15.45% have been processed in the lab [1] and in production [2] on stainless steel, respectively. For enamelled steel a maximum cell efficiency of 18.6% was reported [3]. But the maximum cell efficiency on steel is still lower than the maximum efficiency of 20.8% [4] and 20.4% [5] obtained on rigid glass substrate and flexible polyimide foil, respectively. One reason is the diffusion of detrimental substrate elements, such as Fe, Ni, Al and Mn into the CIGS layer during the high temperature processing of CIGS, as they deteriorate CIGS cell efficiency [6]. Among these, Fe and Ni were found to be the most critical elements for CIGS solar cells [6]. Another subject is the different supply of Na on flexible substrates compared to soda lime glass substrates. Sodium plays a crucial role, as it extremely influences the band gap grading [7], which is one particular essence for reaching high cell efficiencies [8]. To counteract

the negative influence of Fe and other detrimental substrate elements, metallic barrier layers like Cr [9], Ti [10] or metallic compounds like TiN can be used. Alternatively, steel substrates can be coated with insulating barrier layers like SiO_x [11], Al₂O₃ [12], ZnO [13] or enamel [3] to suppress the diffusion of detrimental substrate elements. Another possibility is to reduce the diffusion of Fe by growth of the CIGS layer in a low temperature CIGS process [1], as diffusion is thermally activated.

So far it has been demonstrated that diffusion of Fe into the CIGS layer is negative for solar cell performance [6,9–16], but systematic studies quantifying the maximum critical Fe concentration c_{crit} which is tolerable in CIGS layers for solar cells application are rare. Only Jackson et al. [6] report a value of $c_{crit}=7$ ppm, which was determined by calibrated Secondary Ion Mass Spectrometry (SIMS), a method which is able to measure Fe concentration down to the ppm range.

In the following, some former Fe-related work is presented to give a small overview over literature data concerning Fe. In an early study with Fe-doped CuInSe₂ single crystals [17], Fe²⁺ on an In site was attributed to cause a deep acceptor level with a defect energy of $E_t=400$ meV above the valence band E_v . Neumann et al. [18] found a deep acceptor level at 395 meV in CuInSe₂ single crystals which vanishes after annealing of the single crystal in Se ambient. He attributed the deep acceptor level to Fe²⁺ on In site, which changes its valence state from Fe²⁺ (deep acceptor) to the

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electrically inactive Fe^{3+} due to the oxidizing Se atmosphere. In CuGaSe_2 , a defect energy of $E_t=550$ meV was determined for Fe [19]. In CIGS thin films grown on stainless steel substrates, an Fe-induced deep defect with $E_t=440$ meV above E_V was found with Deep Level Capacitance Profiling (DLCP) measurements [15]. This value corresponds well to the value of $E_t=400$ meV measured in CIS single crystals [17]. With electron paramagnetic resonance (EPR) measurements, Fe-related paramagnetic active defect levels were found in Fe doped CuInSe_2 [20] and CuGaSe_2 [21] single crystals. Furthermore, Ni^+ was found to cause a paramagnetic defect in CuGaSe_2 single crystals [21,22]. Ni and Fe are the two metallic impurities which are most detrimental for CIGS solar cells [6]. The Ni^+ signal, an active recombination centre, was shown to be light-sensitive [22], even at a Ni concentration of 0.5 ppm. Therefore, even very low concentrations of Ni in the sub-ppm range are harmful for chalcopyrites as was also found by Jackson et al. [6]. Hence CIGS is not tolerant against impurities, but is a semiconductor nearly as sensitive to impurities as silicon [23]. The question often arose, if Fe impurities accumulate at grain boundaries (GB). From energy-dispersive X-ray spectrometry (EDX) performed in a transmission electron microscope, it was deduced that there is probably no significant difference in the Fe concentration in the bulk of the CIGS grains compared to the GBs [6]. However, recent Atom Probe Tomography (APT) measurements have clearly proven that Fe is homogeneously distributed in CIGS grains and GBs, whereas Na accumulates at the GBs [24,25].

In this study we used mild steel substrates to investigate the influence of Fe on the solar cell parameters, as the diffusion of Fe is more pronounced on mild steel as compared to ferritic stainless steel [11]. By stepwise decreasing the thickness of the Mo layer, the diffusion of Fe was systematically varied to study the influence of increasing Fe content on the solar cell parameters. We show that the simulation programme SCAPS [26] is a powerful tool to explain our electrical measurements with a model of recombination at a deep acceptor-like defect attributed to Fe contamination. SCAPS even allows us to estimate a maximum Fe concentration in CIGS layers which might be tolerated in high-efficiency CIGS solar cells without any loss in efficiency. Hence we can also explain why the constituent materials Cu, In, and Ga need to be very pure to reach maximum cell efficiencies.

2. Experimental details

For the steel substrate we used mild steel sheets with a thickness of $d=500$ μm and a smooth mirror-like surface (average roughness $R_a=18$ nm) to minimize the possible negative effects of surface roughness. The main impurity in the substrate is Mn with a

concentration of 0.24%. Soda lime glass with $d=3$ mm and $R_a=3$ nm was used as a reference substrate. The steel substrates were cleaned with organic solvents in an ultrasonic bath to remove oil residues from rolling. The front side of the substrates were coated with a Mo layer deposited by DC sputtering. The Mo layer served as both a back contact layer and a diffusion barrier layer. Different numbers of single Mo layers (each about 250–300 nm thick) were stacked above a thin Mo layer of 50 nm in order to increase the Mo thickness stepwise from 50 nm to 1900 nm to obtain samples with different concentrations of Fe in the CIGS layer (see Table 1). The back sides of the steel sheet substrates were also coated with Mo to prevent corrosion of the substrate during processing and afterwards. A NaF precursor layer (about 10 nm thick) was deposited as a Na source onto the Mo coated steel substrates prior to the CIGS process. The glass substrate was not covered with the NaF precursor layer, here the Na_2O in the glass substrate acts as the Na source. CIGS absorber layers with a Ga content of $\text{GGI}=[\text{Ga}]/([\text{Ga}]+[\text{In}])\approx 0.3$ were grown by coevaporation of the constituent elements in a single-stage inline process [27] at a substrate temperature of about 600 °C. Solar cells were prepared from the absorber layers by subsequent chemical bath deposition of a CdS buffer layer, RF sputtering of an intrinsic ZnO layer, DC sputtering of a ZnO:Al front contact layer, and electron beam evaporation of Ni/Al contact grids. Cell structuring was done by photo-lithography (total cell area ≈ 0.5 cm^2). Secondary Ion Mass Spectrometry (SIMS) depth profiling was performed at liquid nitrogen temperature on the bare CIGS absorber layers (without CdS and ZnO layer, the window layer was etched with HCl on the eve of the SIMS measurement) by a LEYBOLD SSM 200 system using 5 keV primary Ar^+ ions within a sputter area of 3×2 mm^2 . An Fe-implanted CIGS layer with known ^{56}Fe concentration (dose= 5×10^{14} cm^{-2}) was used as calibration standard to get absolute Fe concentrations from the ^{56}Fe SIMS signal. The ^{23}Na signal was calibrated by measuring a CIGS layer with known Na content. The thickness of the Mo and CIGS layers and the composition of the CIGS layers were measured with X-ray fluorescence spectroscopy (XRF). Grazing incidence X-ray diffraction (GI-XRD) measurements were performed with an incident angle of $\alpha=2^\circ$ and with Cu K_α excitation. Solar cells were characterized by standard current–voltage (I - V) measurements under AM1.5 equivalent illumination. External quantum efficiency (EQE) measurements were done with additional bias illumination by measuring the short-circuit current with spectrally resolved monochromatic light. The active area short current density values were then calculated with the help of the EQE data. Capacitance Voltage (CV) measurements were performed in the dark at room temperature with a frequency of 100 kHz and a modulation voltage of 50 mV. From CV measurements charge carrier concentration profiles were calculated assuming a relative dielectric permittivity of $\epsilon=11.7$ for CIGS. Capacitance-frequency (C - f) measurements were performed with an Agilent E4980A LCR metre.

Table 1
Solar cell parameters of CIGS cells on mild steel substrates with different Mo thickness $d(\text{Mo})$ and on reference glass substrates (Sample 4 and 10): efficiency η (active area), short-circuit current density J_{sc} (active area as determined from EQE), open-circuit voltage V_{oc} , fill factor FF , all maximum values of each sample. The blank lines separate sample groups from different CIGS runs. Reverse saturation current density J_0 and diode ideality factor A as derived from dark J - V curves. Fe and Na concentration and signal intensity of ^{55}Mn in the CIGS layer as measured by SIMS.

Sample ID	Symbol in Fig.	$d(\text{Mo})$ (nm)	η_{max} (%)	$J_{sc}(EQE)$ (mA cm^{-2})	V_{oc} (mV)	FF (%)	J_0 (mA cm^{-2})	A	[Fe] (ppm)	Mn55 (cps)	[Na] (ppm)
1	●	49	0.01	1.1	54	30.9	2.5×10^{-1}	2.2	4387	2369	2921
2	●	566	6.2	19.7	510	62.0	4.8×10^{-4}	2.1	381	284	3064
3	●	1884	10.9	24.2	635	71.1	2.5×10^{-6}	1.7	6	31	1641
4-glass	○	596	13.8	30.1	635	72.4	5.3×10^{-6}	1.7	6	33	405
5	▲	53	0.2	3.3	135	35.1	1.3×10^{-1}	3.1	5441	3477	4028
6	▲	279	4.4	16.1	474	57.3	1.0×10^{-3}	2.1	1165	601	2986
7	▲	1135	9.6	23.1	603	68.6	3.0×10^{-5}	1.8	83	44	2144
8	▲	1689	11.4	24.6	633	73.2	1.5×10^{-6}	1.6	5	20	1683
9	▼	548	7.6	21.1	571	63.2	4.3×10^{-4}	2.2	172	153	2241
10-glass	▼	563	13.8	28.6	654	73.5	2.5×10^{-6}	1.6	3	23	577

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