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## Efficiency enhancement of Cu(In,Ga)Se<sub>2</sub> solar cells due to post-deposition Na incorporation

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Cu(In,Ga)Se<sub>2</sub> (CIGS) absorber layers for thin-film solar cells were grown without sodium. Na was diffused into some of the absorbers after growth, which led to strongly improved device performance compared with Na-free cells. Efficiencies of 13.3% and 14.4% were achieved at substrate temperatures as low as 400 and 450 °C, respectively. With the post-deposition treatment, the effects of Na on CIGS growth are excluded, and most of the Na is expected to reside at grain boundaries. The dominating cause for Na-induced device improvements might be passivation of grain boundaries. © 2004 American Institute of Physics. [DOI: 10.1063/1.1646758]

High-efficiency thin-film solar cells based on polycrystalline Cu(In,Ga)Se<sub>2</sub> (CIGS) require the incorporation of typically 0.1 at. % of sodium into the CIGS absorber layers. Most often, Na is introduced during CIGS growth by diffusion either from a soda-lime glass (SLG) substrate through the Mo back contact or from a thin Na-containing precursor layer deposited prior to CIGS growth. In the first case, controlled Na incorporation can be difficult due to variations in the properties of the SLG, while in the second, the precursor thickness is crucial, since sufficient Na supply has to be ensured while avoiding delamination. For flexible solar cells, preferred substrates are metal and polyimide foils, which in general do not contain Na and for which low-temperature growth processes are important. Na addition in optimum amounts is needed for optimization of devices grown on such Na-free substrates, which may be automatically fulfilled when Na is in-diffused after CIGS growth.

Several effects of Na on the electronic and structural properties of CIGS have been reported, resulting in enhanced solar cell efficiency due mainly to higher open-circuit voltage ( $V_{oc}$ ) and fill factor (FF). The possible influences of Na can be divided into four categories: (1) Na modifies film growth, (2) Na is incorporated into the CIGS lattice and acts there, (3) Na acts at the grain boundaries, and (4) Na acts indirectly by influencing further parameters such as other impurities. Mainly effect (1), usually in combination with one of the other effects, has been investigated in earlier work. The majority of the Na atoms in CIS and CIGS was shown to reside at grain boundaries of polycrystalline CIGS and not in the bulk of single crystalline CIS,<sup>1–3</sup> which is contradicted by the reported in-diffusion of Na into epitaxial CIGS films.<sup>4</sup> Therefore, it appears likely that effect (2) is of minor importance. However, the incorporation of less than 1% of the available Na into grain interiors could already

suffice to alter the electronic properties significantly. In this letter, we report the controlled incorporation of Na into polycrystalline CIGS absorber layers by post-growth Na in-diffusion and present its consequences on solar cell performance. With this post-deposition treatment (PDT), we exclude effect (1). Since diffusion along grain boundaries is in general much faster than diffusion into grains, we expect to distribute the Na along the grain boundaries and thus to investigate mainly effect (3).

CIGS layers with In/Ga concentration ratios in the range of 2 to 3.5 and of about 2  $\mu\text{m}$  in thickness were prepared on Mo-coated SLG with an intermediate alkali diffusion barrier (Mo/Al<sub>2</sub>O<sub>3</sub>/SLG). The CIGS was deposited by physical vapor deposition of the elements using the three-stage process, as described in more detail elsewhere.<sup>5</sup> Maximum substrate temperatures were 400 and 450 °C for the low-, and 580 °C for the high-temperature process. The PDT consisted of deposition of  $\approx 30$  nm of NaF onto one half of each absorber film at below 100 °C, followed by annealing for 20 min at 400 °C in order to let the Na diffuse into the CIGS. The PDT was applied *in situ* immediately after CIGS deposition. Na-free and NaF-treated solar cells were grown on the same substrate in order to eliminate ambiguities arising from small process variations. Solar cells were processed using CdS deposited in a chemical bath, rf-sputtered ZnO/ZnO:Al, and evaporated Ni/Al grids. No antireflection coating was applied. An “alternative,” more straightforward PDT consisted of NaF deposition during cooldown of freshly grown CIGS films. For structural investigations, we applied the alternative PDT on high-temperature-grown CIGS by interrupting cooldown at 450 °C for 20 min for the codeposition of NaF and Se without a subsequent annealing step.

Secondary ion mass spectrometry (SIMS) depth profiles of absorbers shielded from exposure to NaF show background Na count rates, as is apparent from the absence of the characteristic peak at the CIGS/Mo interface. Comparable profiles were also obtained from CIGS films deposited on Na-free metal foils. Therefore, we consider these CIGS films as Na free. In contrast, absorbers subjected to either version

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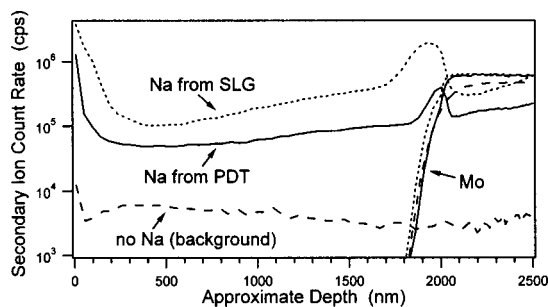


FIG. 1. SIMS depth profiles of Na and Mo in CIGS layers grown at a maximum temperature of 580 °C on Mo/Al<sub>2</sub>O<sub>3</sub>/SLG without Na, and with addition of Na by means of the alternative PDT, and on Mo/SLG where Na diffused from the substrate and no further Na was added. The overall Na concentration in CIGS and Mo is increased due to the PDT, while the shape reflects the changes in grain boundary density. The Na count rate in the Na-free CIGS film corresponds to the background Na rate obtained also from CIGS films deposited on Na-free metal foils.

of the PDT show an increased Na concentration compared with untreated absorbers (see Fig. 1). The distribution of the in-diffused Na in CIGS and Mo resembles the distributions obtained from corresponding “standard” absorbers where Na diffused from the SLG substrate during growth, except that the rise towards the back contact is less pronounced and that the overall concentration is somewhat lower. Hence, Na seems to diffuse quickly enough from the surface into the film to establish an equilibrium distribution, especially since the Na level in the Mo is high as well. Our absorbers grown with the three-stage process at a maximum temperature of 580 °C and with Na present during growth exhibit smaller grain sizes mainly near the back contact compared with Na-free films.<sup>5,6</sup> With the alternative PDT, a reduction of grain size is not observed (see Fig. 2).<sup>7</sup> Hence, a correlation between Na concentration and grain boundary area can explain the reduced Na content of post-deposition-treated absorbers. Furthermore, x-ray diffraction patterns did not reveal a change in texture due to the PDT, and no F could be detected

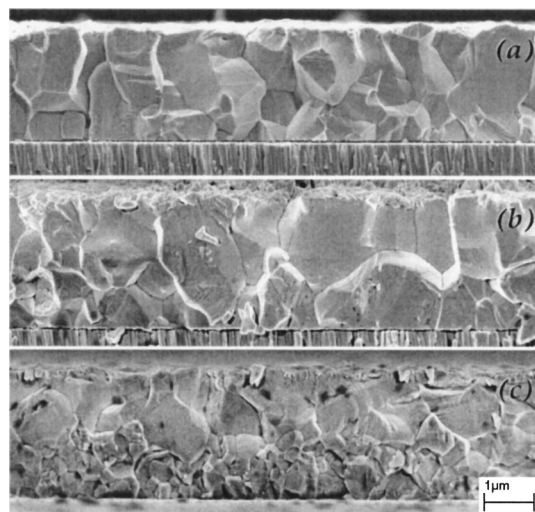


FIG. 2. Scanning electron microscope micrographs of fractured cross sections of CIGS layers grown with the three-stage process at a maximum temperature of 580 °C on Mo/Al<sub>2</sub>O<sub>3</sub>/SLG without Na (a) and with addition of Na by means of the alternative PDT (b), and on Mo/SLG where Na diffused from the substrate and no further Na was added (c). A reduced grain size mainly near the back contact is observable when Na was available during growth, but not when Na was in-diffused after growth.

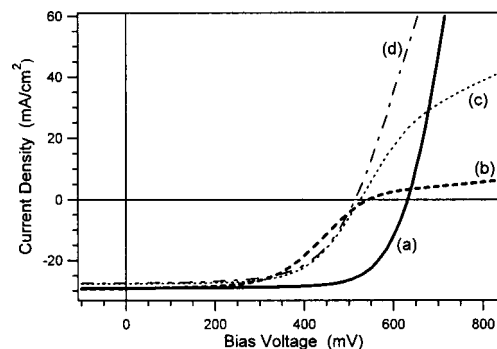


FIG. 3.  $I$ – $V$  characteristics of CIGS solar cells grown without Na at maximum substrate temperatures of 400 °C (curves a and b) and of 450 °C (curves c and d). Absorber (a) was subjected to the full NaF PDT, while absorbers (b) and (c) remained Na-free but were annealed in vacuum. Absorber (d) also remained Na-free but was annealed in Se atmosphere.

in the absorbers with SIMS. Therefore we infer that, in contrast to Na addition at earlier stages, post-deposition Na incorporation does not change the microstructural properties of the CIGS films and results in the distribution of Na mainly along the grain boundaries.

Solar cells were grown at low (400 and 450 °C) and high (580 °C) maximum substrate temperatures. The  $I$ – $V$  characteristics obtained from these cells are qualitatively similar: While devices processed from Na-free CIGS exhibit a current-blocking behavior at higher forward bias, devices processed from post-deposition-treated CIGS show exponential  $I$ – $V$  curves. The current-blocking effect was found to depend on the availability of Se during annealing and is therefore attributed to an electronic barrier induced by Se loss. The influence on device efficiency  $\eta$  was small (see Fig. 3, curves c and d). The PDT led to improved  $V_{oc}$  and FF, while the short-circuit current ( $J_{sc}$ ) was nearly unaffected (see Table I and Fig. 3, curves a and b). A typical relative increase in efficiency of about 30%–60% can be attributed to the PDT. With absorbers grown at a maximum substrate temperature of 400 °C, an efficiency of 13.3% [ $V_{oc}$ =631 mV,  $J_{sc}$ =29.6 mA/cm<sup>2</sup>, FF=72.1%, area (total)=0.606 cm<sup>2</sup>] was achieved under simulated AM 1.5 conditions for post-deposition-treated CIGS. This efficiency is among the highest reported for such a low substrate temperature.<sup>8–10</sup> The corresponding Na-free absorber yielded a maximum efficiency of 8.2%. With 450 °C substrate temperature, efficiencies improved from 10.4% to 14.4% ( $V_{oc}$ =655 mV,  $J_{sc}$ =30.3 mA/cm<sup>2</sup>, FF=72.8%). The efficiency gain at 580 °C substrate temperature is still considerable (see Table I), although these films have different structural properties. Application of the alternative PDT on high-temperature absorbers led to similar device results.

The main effect of the PDT on solar cell efficiency is a

TABLE I. Change in photovoltaic parameters of CIGS solar cells grown at different maximum substrate temperatures due to post-deposition Na incorporation (relative to corresponding Na-free cells). Absolute values are given in the text.

$T_{sub}$ (°C)	$\eta_{rel}$ (%)	$V_{oc,rel}$ (%)	$J_{sc,rel}$ (%)	$FF_{rel}$ (%)
400	+62	+15	+3	+38
450	+38	+16	+0	+20
580	+40	+13	+3	+19

strong enhancement of  $V_{oc}$  and FF. The magnitude of the improvement in  $V_{oc}$  is similar to the enhancement known from Na diffusing from SLG, where an increase in net carrier concentration and a decrease in resistivity of CIGS by one to two orders of magnitude can explain the improvement.<sup>11,12</sup> From capacitance–voltage measurements, we obtained an increase in net carrier concentration by more than one order of magnitude (from  $\approx 2.4 \times 10^{14}$  to  $\approx 6.5 \times 10^{15} \text{ cm}^{-3}$  for the cells grown at a maximum temperature of 400 °C) due to the PDT, which can be calculated to improve  $V_{oc}$  by about 85 mV.<sup>12</sup> In addition, from in-plane four-point probe measurements on CIGS/ $\text{Al}_2\text{O}_3$ /SLG samples, we obtained a decrease in resistivity by a factor of 80 due to the PDT. Therefore, the similar cell improvements due to Na diffusing during growth and due to Na added after growth could have the same origins. Although we believe that the influence of Na on the structural properties of CIGS during growth is important, the success of the PDT suggests the electronic effects of Na are the dominating cause for Na-induced cell improvements. Since in-diffused Na resides predominantly at grain boundaries, we also expect it to be active there, most likely by passivating defects such as hole traps. However, contributions from intragrain Na cannot be completely ruled out.

In summary, by in-diffusion of Na into Na-free CIGS absorbers, we excluded the influence of Na on absorber growth. Post-deposition-treated CIGS exhibited increased net carrier concentration and conductivity compared to Na-free CIGS, while microstructural properties of the layers appeared to be unaffected. A strong improvement of cell efficiency due to increased  $V_{oc}$  and FF resulted. Efficiencies of 13.3% and 14.4% were achieved at 400 and 450 °C maximum substrate temperature with post-deposition Na incorporation, respectively. These efficiencies are comparable to the highest reported for such low growth temperatures. The dominant reason for Na-induced device improvements in

general is therefore considered to be passivation of grain boundaries, rather than modification of the CIGS growth kinetics.

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