Buffer-free Cu(In,Ga)Se$_2$-solar cells by near-surface ion implantation

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ABSTRACT

High-efficiency Cu(In,Ga)Se$_2$ thin-film solar cells typically include CdS buffer layers deposited in a chemical bath. In this work, Cu(In,Ga)Se$_2$ devices are presented in which the CdS buffer layer was omitted completely. Instead, low-energy ion implantation of group-II-elements (Cd, Zn, and Mg) is applied in order to establish an n-type surface layer in p-type Cu(In,Ga)Se$_2$ absorber layers. Therefore, thermal annealing procedures were developed which lead to a full recovery of the implantation induced defects and simultaneously minimize the diffusion of the dopants. Such a treatment is shown to provide high-quality p–n junction functionality and buffer-free Cu(In,Ga)Se$_2$ thin-film solar cells with open-circuit voltages close to 600 mV and efficiencies exceeding 10 %.

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1. Introduction

The chalcopyrite semiconductor Cu(In,Ga)Se$_2$ (CIGSe) is successfully applied as light-absorbing material in thin-film solar cells, which exhibit record efficiencies above 20 % in laboratory [1]. Thin-film solar cells are based on p–n-heterojunctions and, thus, on the charge carrier separation at the interface between p- and n-type semiconductors. High-efficiency CIGSe thin-film solar cells commonly use a thin chemical-bath-deposited (CBD) CdS buffer layer as an n-type partner to the p-type CIGSe absorber layer. The use of the CBD-CdS buffer in the layer structure is undesirable from a technological as well as an environmental perspective. Therefore, the basic understanding of the buffer functionality and the replacement of the CBD-CdS buffer layer by a non-toxic alternative buffer have been subject to numerous studies in the last decade (reviewed in [2,3,4]). However, the alternative buffer devices still exhibit lower efficiency, reproducibility and stability compared to that of the standard CBD-CdS buffer devices.

High-efficiency CdS-CIGSe solar cells are found to be limited in efficiency by recombination either in the space charge region [5,6] or the quasi-neutral region [7]—thus, they can be assumed to exhibit very low interface recombination. Such low interface recombination rates can be reached either by a very low interface defect density or by driving the Fermi-level close to the

conduction band at the interface [8]. The latter implies the surface of the CIGSe absorber layer to be inverted to n-type in contrast to the p-type absorber volume. This so-called surface inversion induces a lower concentration of recombination partners (holes) for the minority carriers of the absorber volume (electrons) at the interface and, therefore, leads to low recombination rates despite the presence of a considerable concentration of interface defects. A similar situation can be obtained, if a surface layer of the CIGSe absorber material is artificially inverted from p-type to n-type. As the minority carriers in such an inverted layer (holes) are not expected to contribute significantly to the photo current [8], this layer should be as thin as possible (< 50 nm) [9]. Indeed, device simulations have shown an effective surface inversion to be able to maintain high diode-quality performance also in the presence of a high concentration of interface defects [9].

It can be assumed that a doping profile based on intrinsic doping on such small length scales will not be controllable due to the complexity of the deposition process and the strong self-compensation of the material [10]. Extrinsic n-type doping has been suggested from the theory to be most promising using group-II-elements in Cu-poor CuInSe$_2$ material [11], but is also expected to be very inefficient due to strong self-compensation. N-type doping of p-type CIGSe has also been successfully performed in experiment using the group-II-elements Cd and Zn [12–14].

In this contribution, low-energy ion implantation of group-II-elements is applied as a method to effectively introduce the type-inversion of a very thin surface layer of the CIGSe absorber. In this

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context, an annealing procedure has to be developed that efficiently reduces the damage caused by ion implantation in the CIGSe material and simultaneously minimizes the diffusion of the implanted ions. Finally, buffer-free CIGSe solar cells are produced and investigated as an alternative to conventional CIGSe solar cells with CBD-CdS buffer.

2. Experimental methods

CIGSe absorber layers were deposited on Mo-coated soda-lime glass by multi-stage co-evaporation as described elsewhere [15]. The composition was analyzed by means of X-ray fluorescence and yielded slightly Cu-poor stoichiometry ([Cu]/([Ga]+[In])=0.9) and an average Ga-content of approximately [Ga]/([Ga]+[In])=0.3.

Subsequently, ion implantation into the absorber surface was performed at room temperature using ^{114}Cd, ^{64}Zn, ^{24}Mg and ^{132}Xe ions. If not stated otherwise, an ion energy of 20 keV was applied leading to an ion range of 11, 14, 29 and 10 nm for the above elements, respectively. All results shown here correspond to a maximum ion concentration of approximately 2 at% (corresponding to ion fluences in the order of 10^{15} cm^{-2}). Depth profiles of the implanted elements were simulated using the Monte-Carlo-code *Stopping and Range of Ions in Matter* (SRIM) [16], as also described in [9]. Using the simulation data given above, a total sputter yield of around 2 nm or below was calculated by SRIM.

Since ion implantation is accompanied by defect creation, a strong degradation of the solar cell performance is found, if no thermal annealing is applied, as described elsewhere [9]. Therefore, thermal annealing of the implantation defects is performed in a thermal-processing furnace in a rough vacuum (at 3 mbar) or in Ar atmosphere at 1.2 bar subsequent to the ion implantation process. Annealing temperatures up to 500 °C and annealing times up to 30 min were applied. The heating rate was kept constant at 100 K min^{-1}, no active cooling was used.

Finally, complete solar cells were fabricated from such implanted absorbers by depositing the front contact both with and without CBD-CdS buffer and with an RF-sputtered i-ZnO–ZnO: Al double layer [17]. Current density–voltage (j–V) characteristics of the solar cells were measured at room temperature and under standard AM1.5 illumination conditions.

The dopant diffusion during the annealing process was investigated by measuring elemental depth profile using secondary ion mass spectrometry (SIMS) with a depth resolution of about 11 nm. The group-II-ions ^{114}Cd, ^{64}Zn and ^{24}Mg were implanted with increased ion energies of 100, 65, and 24 keV, respectively, in order to lead to ion ranges of about 35 nm for all elements. This ion range was chosen for the SIMS analysis, because it allows the distribution to be well resolved with the given depth resolution of SIMS, but simultaneously, diffusion lengths below 50 nm are still well detectable.

3. Results and discussion

As previously noted and thoroughly described in [9], a thermal annealing procedure is required to efficiently reduce the induced implantation damage. Thus, an annealing procedure is needed that (a) does not degrade the materials solar grade quality, (b) leads to sufficient annealing of the implantation damage, but (c) does not induce a significant diffusion of the dopants. It has been previously shown [9] that the annealing temperature needs to exceed 200 °C in order to reach full recovery of the implantation damage. In order to investigate the influence of the annealing on the solar cell properties, all solar cells are completed with a CBD-CdS buffer layer in this first stage of experiments.

### 3.1. Thermal annealing of reference absorbers

The performance of solar cells made from unimplanted absorbers is investigated as a function of a post-deposition thermal treatment. The j–V-characteristics of solar cells measured after annealing the absorbers in Ar atmosphere at different temperatures for 30 min and with no holding time (0 min) are shown in Fig. 1(a) and (b), respectively, and compared to a reference cell made from unannealed absorbers. A decrease in all parameters (j_{sc}, V_{oc}, FF) is observed with increasing temperature for both annealing times. This degradation may be related to a loss of selenium from the absorber layer which has been repeatedly observed during high-temperature treatments in inert atmospheres [18,19]. Thus, attempts to anneal under Se containing atmosphere have been made as well. However, such cells often suffered from poor and therefore not reasonably evaluable j–V-characteristics. This unreliability might be due to inhomogeneous supply or condensation of selenium on the absorbers' surface in the annealing furnace. Consequently, annealing in Se containing atmosphere has not been pursued.

For the prolonged annealing time of 30 min, the high-quality cell performance is maintained at a temperature of 300 °C, but it becomes worse at higher values. For the shorter annealing procedure, the cell stays on the reference level at least up to 350 °C as shown in Fig. 1(b). Comparable experiments have been performed for annealing in low-vacuum (≈3 mbar) at these temperatures and dwell times (not shown). Leading to comparable results, the vacuum process is found to be more stable and is therefore chosen as a standard process for investigating the defect annealing in the following.

These investigations show that it is possible to use thermal annealing for post-implantation damage recovery up to temperatures of 300 °C and 350 °C—thus, also giving an upper limit to the temperature range applicable.

3.2. Recovery of the implantation damage

The annealing experiments were repeated after the ion implantation of Xe, which are presumed to induce an amount and distribution of defects similar to Cd implantation (due to the comparable ion mass), but without doing any extrinsic doping effects. The annealing was performed in Ar at the same temperatures and annealing times as above and the respective j–V-curves are shown in Fig. 2(a) and (b), respectively and quantitative details
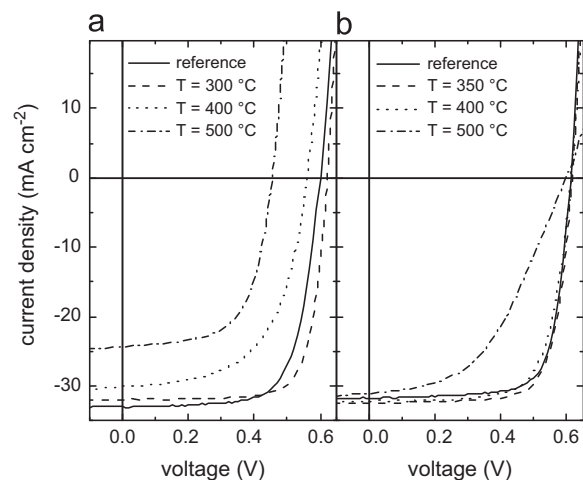
Fig. 1. j–V-characteristics of solar cells with CBD-CdS buffer layer made from unimplanted absorbers annealed in Ar atmosphere at different temperatures for (a) 30 min and (b) with direct cool-down (in the following: 0 min). The curves of the corresponding reference cells are plotted for comparison.