



Effect of ultrasound treatment on CuInSe_2 solar cells

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Abstract

Thin CuInSe_2 films on glass substrate and solar cells were processed using the ultrasound treatment technique (UST). The SIMS measurements on the films showed a strong reduction of the Na-signal after the UST, which is most likely caused by ultrasonically induced chemical reaction of the mobile sodium ions. The change of the solar cell efficiency due to the UST depends on the initial efficiency. For the cells with efficiencies below 10% relative improvements of up to 50% are observed. On the contrary, the cells with higher efficiencies remain stable after the UST. In addition, parameters of CuInSe_2 cells affected by the UST show the relaxation. © 2000 Published by Elsevier Science Ltd.

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Since the early 80s, CuInSe_2 has been intensively investigated and it is now one of the most promising materials for the next generation of thin-film solar cells. Due to a low-cost deposition technique and the use of large-scale substrates, the material is expected to challenge the predominance of silicon on the photovoltaic market. The high potential of CuInSe_2 is demonstrated by the manufacturing of solar cells with efficiencies up to 18.8% on a laboratory scale [1]. However, large area devices produced in industrial environments still struggle with the 10% mark. Thus a primary task of the current research and development is to identify the loss processes and to define the new methods for device optimization.

In this study we explored the potential of ultrasound treatment (UST), a new approach to defect engineering [2], for the optimization of CuInSe_2 solar cells. Ultrasonic vibrations generated into a crystal can stimulate different defect reactions and specifically promote the diffusion of mobile point defects. The UST is widely used for the optimization of electronic devices, such as thin-film transistors, IR photo-detectors and light-emitting diodes [2]. The positive effect

of the UST on solar cells was first reported by Iskanderov et al. [3]. The authors observed a spectacular increase in efficiency by up to 5% in absolute value, after treating the ribbon polycrystalline silicon cells with ultrasound. Koshka et al. developed an empirical model that qualitatively explains the UST stimulated redistribution of atomic hydrogen in thin polycrystalline Si films on glass for thin-film transistors [4]. In this material hydrogen is crucial for the passivation of dangling bonds at the grain boundaries. However, after conventional hydrogenation a substantial part of the hydrogen is trapped and electrically inactive. The authors demonstrated that the UST promotes the release of hydrogen from these traps and stimulates the hydrogen diffusion to the grain boundaries where it reacts with dangling bonds.

In polycrystalline CuInSe_2 the element Na is considered to play a key role for the film performance. Na is mainly concentrated at the surface and at grain boundaries and can be detected with high spatial-resolution Auger electron spectroscopy [5]. According to the calculations of Wei et al., Na partly replaces Cu and increases the band gap of the absorber layer and as a consequence the open circuit voltage of the solar cell [6]. Since the solubility of Na in CuInSe_2 is limited, a separated NaInSe_2 phase is formed at the surface or at the grain boundaries when the Na concentration reaches stoichiometric quantities. Kronik et al. suggested

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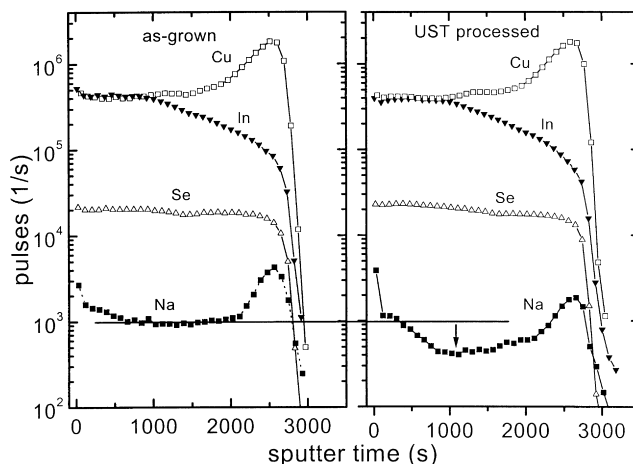


Fig. 1. SIMS depth profiles of a CuInSe₂ layer. The sputter time of 3000 s corresponds to a depth of 1.5 μm , i.e. the thickness of the layer. While the signals of Cu, In and Se remain constant, the Na-signal is significantly reduced after the UST.

that Na acts as a catalyst for the oxidation of the film surface [7]. Oxygen reacts with donor-like surface states and decreases the band bending. Thus, the sodium appears to be a crucial promoter of the oxygen-passivation of the grain boundaries. Despite Na being mainly accumulated at the surface it is also discussed to change the electrical behavior of the bulk material. It was suggested that Na effectively reduces In_{Cu} donors and thus significantly enhance the effective hole concentration [6,8]. During the processing of the solar cell Na diffuses from the absorber layer into the CdS buffer layer [9]. The idea of this study is to activate Na and to stimulate a redistribution of Na by means of ultrasonic vibrations. Na is highly mobile in CuInSe₂ like hydrogen in silicon. To explore the potential for the optimization of the system we investigated the effect of the UST on the Na distribution and the solar cell efficiency.

We used polycrystalline CuInSe₂ films and solar cells of ZnO/CuInSe₂ heterostructures on glass substrate. The CuInSe₂ absorber layers with a thickness of about 1.5 μm were deposited by sputtering and followed by synthesis with rapid thermal processing. For a homogenous Na doping of the absorber layer, the Na diffusion from the glass substrate was suppressed using an Al₂O₃ diffusion barrier and the film was doped with approximately 0.1 at.% Na. The solar cells with an area of 2 cm² had initial efficiencies between 11 and 12%. After processing the thin films and solar cells were sealed in dry N₂. Details about the sample processing are described elsewhere [10].

For the UST experiments, ultrasound vibrations are generated with a circular 70 mm diameter piezoelectric transducer. The transducer is operated at the resonance frequency of 25 kHz of the radial vibration mode. During the treatment, the thin film or solar cell was pressed with the substrate side against the transducer surface and the vibration amplitude was monitored with a non-contact acoustic probe. The resonance frequency and acoustic amplitude

were software controlled. The treatments were performed at room temperature for a period of 10 min. The thin films were exposed to air only during the UST, after the experiments the samples were stored in dry N₂ atmosphere. Details about a commercially available UST setup can be found in Ref. [2]. The solar cell parameters were determined from the current–voltage (I – V) measurements under 100 mW/cm² illumination intensity. The secondary ion mass spectroscopy (SIMS) measurements were performed with 6 kV O₂⁺ ions in a CAMECA RIBER system.

We first investigated the Na distribution in CuInSe₂ with SIMS since the UST process is known to have a strong effect on highly mobile species. The depth profile of a bare CuInSe₂ thin film is shown in Fig. 1. The abrupt decrease of the signal intensity after the sputter time of 3000 s shows the transition from the CuInSe₂ layer to the substrate at a depth of 1.5 μm . It was not possible to determine the absolute element concentration since the sensitivity factors for the SIMS signals in CuInSe₂ are not available. Thus, we only discuss the relative changes of the signals due to the UST. Comparison of the profiles before and after the treatment reveals a significant change in the Na signal within the layer. While the signals of the matrix elements, i.e. Cu, In and Se, remain unchanged after the treatment, the Na-signal decreases by a factor of two. The decrease varies in different samples, however, the tendency is straightforward: after UST the Na-signal is reduced within the entire sample. In both, the as-grown and the ultrasound treated sample, the Na-signal is enhanced at the surface (one data point). After the treatment, the Na-signal at the surface seems to be increased further. However, non-equilibrium effects distort the SIMS-signals at the surface (~ 20 nm) and do not allow conclusions about the surface concentrations [11]. For this reason we will focus on the decrease of the Na-signal in the bulk.

The SIMS intensity is affected by the element concentration, the ionization probability and the geometry of the

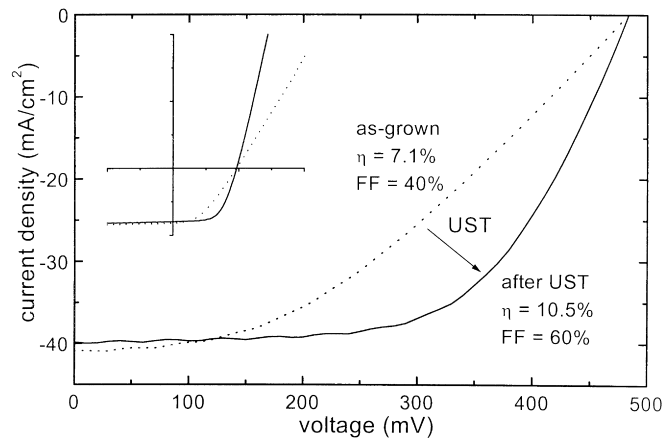


Fig. 2. Solar cell characteristic before (dashed) and after (solid) the UST. The improvement of the efficiency (η) is mainly affected by the increase of the fill factor (FF). The inset shows the complete I – V curves of those cells.

setup. Since all the SIMS measurements were performed under identical alignment, there are two possible reasons that can be responsible for the observed Na reduction. The first possibility is the reduction of total Na concentration. The sink for the extracted Na could be located at the surface. Indeed, the Na-signal, which is decreased throughout the layer after the UST, is only weakly changed at the top 200 nm of the film, i.e. the upper layer seems to contain more Na than the back side of the layer. However, to retrace the decrease of the Na-signal only to a redistribution of Na the SIMS-signal of the top layer has to increase significantly. Since this cannot be observed we favor the second possibility. The second option is attributed to a change of the ionization probability of Na due to the restructuring of the local chemical bonds. It implies a variation of a chemical

state of Na triggered by the UST processing. This so-called matrix-effect can be explained in terms of the bond-breaking model of the ionization of sputtered particles [12]. As a rule of thumb the increase of the polarity of the chemical bond increases the ionization probability. Assuming the matrix-effect takes place, the decrease of the SIMS signal is caused by a change of the sodium atoms from a high-polarity state to a low-polarity state. Different chemical Na-compounds in CuInSe_2 were reported recently. Heske et al. characterized two different species of Na on the surface of CuInSe_2 , which they denoted as “metallic” and “reacted” [13]. Since the “metallic” Na state is considered to be less polar than the “reacted” one, an enhanced creation of this species could explain the UST change in the SIMS profiles. Considering that the Na-signal decrease is observed all over the film thickness (Fig. 1), the chemical reaction of Na may take place at grain boundaries in the entire CuInSe_2 layer.

It is reasonable to assume, that the change of the Na state also affects the parameters of CuInSe_2 solar cells. In the following part we focus on the effect of ultrasound on the cell efficiencies. A part of the investigated cells was exposed to air and degraded prior to our UST experiments. Those cells initially had efficiencies between 11 and 12%, however, after long-term storage the efficiencies were well below 10%. An I – V curve of such a cell with 7.1% efficiency is shown in Fig. 2. After the treatment the efficiency increased to 10.5%, which corresponds to a relative increase of almost 50%. Obviously the treatment could reverse the degradation process. However, the upper limit of the improvement was given by the efficiency of the non-degraded cell, i.e. the efficiencies did not exceed 11% after UST.

The strong improvement of the efficiency is clearly caused by the fill factor upgrading. For the cell presented in Fig. 2 the value increases from 40 to 60%. Analyzing the I – V -curve (inset in Fig. 2), we found that the treatment mainly affects the characteristic

Table 1

Efficiencies (in %) of selected solar cells initially, after UST and after post-UST relaxation. Cells with efficiencies about 11% (1–3) do not react significantly to UST and the relaxation. Cells with efficiencies below 10% were improved (4–8) or deteriorated (9–11) after the UST. Some of cells show a significant post-UST relaxation

Cell #	As-grown	UST	Relaxed
1	11.8	11.7	12.3
2	11.3	11.6	10.9
3	10.6	10.2	10.8
4	8.2	10.5	8.3
5	7.1	10.5	7.9
6	7.8	8.2	8.3
7	9.6	10.0	10.0
8	8.4	9.1	–
9	10.6	8.5	8.5
10	8.2	7.9	3.0
11	9.4	6.2	8.0

under positive voltage bias. Under reverse bias the current is not changed significantly. The strong deviation of the diode characteristic under forward bias indicates a reduction in the series resistance, which predominantly depends on the conductivity of the CuInSe₂ layer. Along with the results from the SIMS measurements we may suggest that the change in the I – V characteristic is linked to the change of the Na state.

Under the experimental conditions applied in this study the positive effect of the UST was found only in degraded cells. Solar cells with efficiencies above 11% (before the UST) were stable under the application of ultrasound. The efficiencies of selected solar cells before and after the UST processing are shown in Table 1. After a few days of storage, the cells were measured again. These “relaxation studies” revealed that some cells were not stable after UST (see Table 1). Specifically, those cells, which significantly improved during the treatment, seemed to be unstable. For example, for the solar cell shown in Fig. 2 a decrease of the efficiency from 10 to 7.9% within one day was observed (cell #5 in the Table 1). To stabilize the efficiency after the first treatment, the process was repeated, however, the degradation of the cell during the post-UST relaxation could not be prevented. Thus, the positive UST effect was partly reversed and the net improvement in efficiency was reduced to relative 10%. In this case the total change was still positive. However, in some cases the relaxation caused a severe deterioration of the solar cell characteristics. One cell (#10 in Table 1) even collapsed after the relaxation. The efficiency went down to as low as 3% after one day of storage. Thus far, we cannot provide a conclusive explanation for this relaxation behavior. However, these processes are crucial for the understanding of the microscopic mechanism as well as for the future application of UST. We can speculate at this point that monitoring of the UST triggered relaxation in the CuInSe₂ solar cells can be a way to accelerate a degradation of potentially faulted devices. As a reference to the Na containing standard cells, we also investigated the UST effect on Na-free cells. For those cells no significant change in efficiency after the UST could be observed. The cells remained stable and did not show any post-UST relaxation. Along with the SIMS results, the fact that the changes in efficiencies occur only in Na containing cells is another strong hint for sodium to be involved in the observed UST effects.

Though we favor a change of the Na state, other ultrasound stimulated processes could also be involved in the change of efficiency since the UST can modify recombination properties of various lattice defects [2]. Ultrasound for example enhances long-time relaxation, which include metastable defects [14]. In CuInSe₂ solar cells, the observed metastability is believed to be caused by lattice relaxation in the absorber layer [15]. However, the observed metastable effects cause a change in the open circuit voltage [16] while we observed the dominant change in the fill factor.

To discuss the potentials of the UST for the solar cell

optimization, it has to be considered that CuInSe₂ cells are not homogenous. Eich et al. reported that the lateral distribution of the open circuit voltage varies between 0.2 and 0.7 V on the scale of the grain size. The average value was 0.5 V [17]. Thus the improvement of the low efficiency parts is essential. As the UST has demonstrated an increase in the efficiencies of degraded cells it appears to be a prospective tool for device optimization. However, the relaxation processes after the treatment have to be analyzed carefully and suppressed for future applications. We conclude that the UST has a strong effect on sodium and on solar cell efficiency. SIMS measurements show a clear decrease of the Na-signal, which we related to a change of the Na chemical state. By applying the UST to solar cells the efficiencies could be increased by up to 50%. However, the positive effect was limited to degraded cells with efficiencies below 10%. Cells with efficiencies above 11% did not change during the UST. Additionally we observed complicated relaxation processes on the time scale of hours.

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