Effect of thermal annealing in vacuum on the photovoltaic properties of electrodeposited Cu$_2$O-absorber solar cell

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Received: 24 October 2013 / Received in final form: 15 April 2014 / Accepted: 15 April 2014

Abstract

Heterojunction solar cells were fabricated by electrochemical deposition of $p$-type, cuprous oxide (Cu$_2$O) absorber on sputtered, $n$-type ZnO layer. X-ray diffraction measurements revealed that the as-deposited absorber consists mainly of Cu$_2$O, but appreciable amounts of metallic Cu and cupric oxide (CuO) are also present. These undesired oxidation states are incorporated during the deposition process and have a detrimental effect on the photovoltaic properties of the cells. The open circuit voltage ($V_{OC}$), short circuit current density ($j_{SC}$), fill factor (FF) and power conversion efficiency ($\eta$) of the as-deposited cells are 0.37 V, 3.71 mA/cm$^2$, 35.7% and 0.49%, respectively, under AM1.5G illumination. We show that by thermal annealing in vacuum, at temperatures up to 300 °C, compositional purity of the Cu$_2$O absorber could be obtained. A general improvement of the heterojunction and bulk materials quality is observed, reflected upon the smallest influence of the shunt and series resistance on the transport properties of the cells in dark and under illumination. Independent of the annealing temperature, transport is dominated by the space-charge layer generation-recombination current. After annealing at 300 °C the solar cell parameters could be significantly improved to the values of $V_{OC}$ = 0.505 V, $j_{SC}$ = 4.67 mA/cm$^2$, FF = 47.1% and $\eta$ = 1.12%.

1 Introduction

Cuprous oxide (Cu$_2$O) is one of the first known semiconducting materials. Although its photovoltaic (PV) property was very early recognized [1], the technological advancements towards a Cu$_2$O-based solar cell were only sporadic. Presently, Cu$_2$O attracts increased attention, driven by the need for abundant and environmentally-friendly materials for PV and by newly introduced technological approaches for solar cell fabrication. In a recent study, Cu$_2$O appears as one of the most intriguing among 23 inorganic absorbers for abundant and affordable electricity supply, based on the dual constraints of material supply and lowest cost per watt [2].

Indeed, Cu$_2$O is abundant, non-toxic and can be prepared by non-vacuum techniques, such as thermal oxidation of Cu sheets and electrochemical deposition (ECD). It is a native $p$-type semiconductor, due to a high concentration of negatively-charged copper vacancies [3]. Its direct bandgap of $\sim$2 eV is quite large for an ideal match of the solar spectrum, but still allows for a theoretical maximum power conversion efficiency of $\sim$20% for a single junction under AM1.5 illumination [4]. This is combined with a high absorption coefficient for energies above the bandgap ($10^6$ up to more than $10^8$ cm$^{-1}$) [5], high majority carrier mobility (in the range of 100 cm$^2$/Vs) [6,7] and large minority carrier diffusion length (up to several micrometers) [8,9]. Early investigations showed that Cu$_2$O Schottky barrier-type solar cells lead to poor PV performance [8] and pointed out the need for heterojunction or homojunction architectures. Since the $n$-type doping of Cu$_2$O is extremely difficult due to the mechanism of dopant self-compensation [10], research efforts focused inevitably on heterojunctions. Many $n$-type window layers have been tested for this purpose, such as In$_2$O$_3$ [11,12], SnO$_2$ [11], CdO [11,13], Cu$_2$S [14], TiO$_2$ [15], Ga$_2$O$_3$ [16] and ZnO, with the last two being the most promising.

Indeed, in 2006, an efficiency of more than 2% was achieved by sputter-depositing a thin ZnO layer on a bulk Cu$_2$O substrate, produced by thermal oxidation of a Cu...
sheet at temperatures exceeding 1100 °C and process duration of several hours [7]. Through optimization of the thermal oxidation process and appropriate ZnO doping with Mg, the efficiency increased to 4.3% for bulk Cu2O cells [17,18]. Recently, record efficiency of 5.38% was reported through the use of Ga2O3 n-layer [16]. However, the demand is to turn from bulk to thin film absorbers, which require significantly less material and lower fabrication cost. To this end, ECD of Cu2O has a large potential as it takes place close to room temperature (about 50–60 °C) and from aqueous solution. In addition, ECD is easily up-scaleable, high throughput and roll-to-roll compatible. However, the maximum achieved efficiency of solar cells with thin film, ECD-grown Cu2O in combination with ZnO remained for long limited at 1.28% [19]. Only very recently did the efficiency jump to 2.65% by employing a tin-doped ZnO layer, formed by atomic layer deposition and a substrate-type of solar cell [20].

The need remains to identify the factors that limit the efficiency of ECD Cu2O solar cells and introduce technological processes to address them. The heterojunction interface and the absorber bulk are of paramount importance for the charge carrier separation and collection. Enhanced recombination at the ZnO/Cu2O interface arises due to structural defects and the large conduction band misalignment [21], leading to the degradation of the open circuit voltage and fill factor of the solar cell [22]. Further degradation is caused by current shunts related to a defect-rich heterojunction interface, as well as by the carrier recombination and large series resistance contributions associated with the absorber’s bulk.

Thermal annealing can generally improve the quality of layers’ interfaces and bulk. For potentiostatically-grown Cu2O on Cu and SnO2, annealing in air was shown to promote crystallization, to lower the film’s resistivity and to improve the conversion efficiency of photoelectrochemical cells [23]. On the other hand, the annealing of Cu2O films in air at elevated temperatures was reported to lead to the formation of CuO (cupric oxide) with poor PV properties [23].

In this paper we show that by thermal annealing ZnO/ECD-Cu2O solar cells in vacuum, the crystallinity and composition of the Cu2O absorber film are improved, eliminating the amounts of metallic Cu and CuO in the layer, which are incorporated during the electrochemical deposition. Furthermore, vacuum conditions prevent the oxidation of Cu2O to CuO that arises during annealing in air. Annealed solar cells present increased shunt resistance and lower series resistance, suggesting improvement of the heterojunction interface and absorber’s bulk. The combination of these effects leads to the enhancement of the short circuit current, open circuit voltage and fill factor of the heterojunction solar cells.

## 2 Experimental

### 2.1 Fabrication

The solar cells were deposited on 1 mm-thick glass slides. Apart from the Cu2O absorber, all other films were deposited by sputtering. During the sputter process, the targets and substrate holder were water-cooled at 25 °C. The target-substrate distance was 10 cm and the sputter chamber base pressure in the range of 7 × 10⁻⁶—1.2 × 10⁻⁵ Pa. All oxide films were sputtered from stoichiometric oxide targets. The deposition parameters of the films are shown in Table 1. The film thicknesses and the corresponding sputter rates were extracted from step-height measurements using a surface profilometer.

Firstly, a 400 nm-thick AZO layer was deposited on the glass slide, followed by the deposition of the intrinsic ZnO with a thickness of 40 nm. ZnO covered the whole AZO surface except from a small window at the sample’s edge, which is needed to establish a good contact to the sample during the ECD and later for the electrical measurements. AZO has a resistivity of 1.5 × 10⁻³ Ωcm, while the i-ZnO is highly resistive (>10⁵ Ωcm).

For the ECD of the Cu2O film, an aqueous solution with reagent-grade purified and deionized Milli-Q water was prepared, containing 0.2 M CuSO₄·5H₂O, 3 M lactic acid and 125 mg of ZnO powder, which was stirred for several hours until all grains were fully dissolved. A pH of 12.5 was reached by gradually adding NaOH to the solution. Lactic acid is used to stabilize Cu (II) ions at bath pH higher than 7, while the introduced ZnO powder served as sacrificial material in order to prevent the dissolution of the underlying ZnO layer during ECD and the formation of unwanted impurities, as proposed by Musselman et al. [24]. The reaction solution volume was 200 ml. The aqueous solution was heated under permanent mild stirring at the reaction temperature of 50 °C prior to the immersion of the AZO/ZnO-covered glass substrate (cathode), which was placed vertically in the reservoir. A wound platinum wire with a diameter of 0.5 mm was used as the counter electrode. A negative DC potential of −0.6 V relative to an Ag/AgCl reference electrode was applied.
Fig. 1. Cross section and top view SEM images of the as-deposited heterojunction (a, b) and after annealing at 300 °C (c, d).

Fig. 2. Specular XRD measurements of the as-deposited and annealed cell at 300 °C.

for 70 min, using an AUTOLAB potentiostat/galvanostat. After the deposition the sample was removed from the solution and thoroughly rinsed in flowing deionized water to eliminate residual salts and unreacted products from the surface. Then the sample was transferred to the sputtering chamber for the deposition of 20 nm of NiO, followed by Au deposition through a contact mask, to define solar cell areas from 1 to 9 mm².

2.2 As-deposited cell

Figures 1a and 1b show scanning electron microscopy (SEM) images of the cleaved edge and of the surface of the as-deposited heterojunction, respectively (without the top Au contact). The sputtered AZO and ZnO layers have a characteristic columnar structure, while the Cu₂O layer, of approximately 1.7 μm thickness, is compact, rough and features large, flat-top grains, with sizes up to several micrometers. Large grain-size is important in order to keep the charge carrier scattering low and thus improve the absorber’s conductivity and the minority carrier transport length by diffusion or drift. Two groups estimated the latter to be approximately 160 nm for electrodeposited Cu₂O solar cells, much lower than for thermally oxidized Cu₂O [25, 26]. It is admitted, though, that this value is sensitive to the structural properties of the absorber (crystallinity, grain size, defect density) and of the heterojunction quality.

The specular X-ray diffraction (XRD) pattern of the as-deposited multilayer in Figure 2 shows the typical hexagonal ZnO (002) plane reflection at 2θ = 34.25°, with a secondary peak stemming from the (103) planes at 62.6°. In the case of Cu₂O, its structure is cubic with the dominant reflection coming from the (111) family of planes at 36.5°. The same preferred Cu₂O texture was reported by potentiostatic [27–29] or galvanostatic [19, 30] deposition, for solutions with high pH. Indeed, the increase of hydroxyl ion concentration for high bath pH, leads to increased oxygen supply in the film. This favors the growth of planes with high oxygen ion density, such as the (111) family of planes [31]. The XRD pattern also contains Cu₂O peaks of smaller intensities at 2θ = 42.3, 61.4, 29.6, 73.5, 77.6, 52.4 and 92.4° (in descending intensity order), corresponding to the (200), (220), (110), (311), (222), (211) and (400) planes, respectively.

Most importantly, we also observe reflections from metallic Cu at 2θ = 43.2, 50.2, 74.2 and 90.1°, which correspond to the fcc (111), (200), (220) and (311) planes, respectively. Finally the peak at 2θ = 53.9° is ascribed to the monoclinic CuO (020) plane reflection. It is therefore
shown that the as-deposited absorber may predominantly consist of Cu$_2$O, but appreciable amounts of metallic Cu and CuO are present. Indeed, the oxidation state of the deposit is very sensitive on the applied ECD potential. For a fixed bath pH, a more negative potential favors the deposition of Cu, a moderate potential the deposition of Cu$_2$O and the least negative the formation of CuO [32]. The limits between the different potential windows are not sharply defined, leading to the possibility that unwanted oxidation states are present in the film. In line with our findings, Septina et al. [29] reported the incorporation of Cu$_{2+}$ and Cu$^0$ impurities during potentiostatic ECD for a wide range of potential values. Also, it is pointed out that traces of these impurities may well be present, even if the corresponding phases cannot be resolved in the X-ray diffractogram [19]. The presence of metallic Cu in the absorber was shown to degrade the PV characteristics [19], while CuO also leads to reduced PV performance compared to Cu$_2$O [28,33].

Figure 3 shows the optical transmittance, $T$, spectrum of the AZO/$n$-ZnO/$p$-Cu$_2$O heterojunction, excluding the glass substrate, measured with a spectrophotometer. From this, the Tauc plot is constructed, i.e. the quantity $(-\ln T \nu)^m$ versus $\nu$, where $\nu$ is the photon energy and $m$ an exponent, the value of which depends on the type of optical transition: $m = 2$ for direct allowed transition and $m = 2/3$ for direct forbidden. The inset of Figure 4 shows the curves for both exponent values, leading to equally good linear dependence at the absorption edge $E_g$. The linear extrapolation to the next temperature. The presented measurements concern a cell area of 6.5 mm$^2$ (as defined by the size of the Au electrode). The current density was, nevertheless, practically independent of the cell area, showing that the current flow is homogeneous throughout the surface of the cell and that the influence of the cell’s edges can be neglected. Also, the photovoltaic properties did not depend on whether a shadow mask was used for illumination or not, showing that the collection of current from outside the cell area is negligible. This is a consequence of the very resistive absorber, restricting lateral carrier transport.

### 2.3 Annealed cell

Figures 1c and 1d show cross section and surface SEM images of the sample after annealing at 300 °C. No significant changes can be observed as opposed to the as-deposited sample (Figs. 1a and 1b). On the other hand, the XRD pattern of the annealed sample in Figure 2 is free of metallic Cu and CuO reflections, i.e. the absorber has acquired the pure Cu$_2$O phase. In parallel, the intensities of the secondary Cu$_2$O peaks relative to the principal (111) peak are notably higher. This is especially the case for the (211), (311), (222) and (400) plane reflections. We assume that this gain in intensity arises from the transformation of the Cu and CuO phases to Cu$_2$O.

The effects of vacuum annealing on the cells’ electrical properties were investigated through dark and illuminated current-voltage ($I$-$V$) measurements. After each annealing step the sample was kept in ambient conditions for 2 days before being measured. This period was necessary in order to obtain stable electrical properties from the solar cells. The dark $I$-$V$s obtained for a 6.5 mm$^2$ area cell as a function of the annealing temperature, are presented in Figure 4 in log $I$ vs. $V$ plots. They are fitted to the one-diode model expression:

$$I = I_0 \left[ \exp \left( \frac{q(V - IR_S)}{n k T} \right) - 1 \right] + \frac{V - IR_S}{R_{SH}}$$

(1)
where $n$ is the diode’s ideality factor, $q$ the elementary charge, $k$ the Boltzmann’s constant, $T$ the temperature in Kelvin, $I_0$ the diode’s saturation current, $R_{SH}$ the shunt resistance and $R_S$ the series resistance. The fit yields in all cases ideality factors close to $n = 2.0$ (Tab. 2), which suggests that transport is dominated by the space-charge layer generation-recombination current as described by the Sah-Noyce-Shockley model [34], with the generation-recombination level located at mid-gap. The parasitic shunt resistance has an important contribution on the transport characteristics at reverse and low forward bias (<0.2 V). It stems from defect-rich junction regions with nearly ohmic behavior, resulting in a practically linear increase of the current with the bias. The value of $R_{SH}$ rises constantly with increasing annealing temperature (Tab. 2). Since low shunt resistance is related to poor heterojunction quality, we conclude that thermal annealing has, indeed, improved the ZnO/Cu$_2$O heterojunction quality, we conclude that thermal annealing has, indeed, improved the ZnO/Cu$_2$O heterojunction quality, we conclude that thermal annealing has, indeed, improved the ZnO/Cu$_2$O heterojunction quality, we conclude that thermal annealing has, indeed, improved the ZnO/Cu$_2$O heterojunction quality, we conclude that thermal annealing has, indeed, improved the ZnO/Cu$_2$O heterojunction quality, we conclude that thermal annealing has, indeed, improved the ZnO/Cu$_2$O heterojunction quality, we conclude that thermal annealing has, indeed, improved the ZnO/Cu$_2$O heterojunction quality, we conclude that thermal annealing has, indeed, improved the ZnO/Cu$_2$O heterojunction quality, we conclude that thermal annealing has, indeed, improved the ZnO/Cu$_2$O heterojunction quality, we conclude that thermal annealing has, indeed, improved the ZnO/Cu$_2$O heterojunction quality, we conclude that thermal annealing has, indeed, improved the ZnO/Cu$_2$O heterojunction quality.

The parasitic resistance values were also extracted from the illuminated $I$-$V$ curves in Figure 5. The $R_{SH}$ is obtained from the inverse of the curve’s slope at $V = 0$ (short circuit condition). We observe again a continuous increase of $R_{SH}$ with the annealing temperature, which becomes especially large after annealing at 300 °C (Tab. 2). The fact that $R_{SH}$ is much lower under illumination than in dark suggests that the shunting paths are photoactive. The cell’s series resistance, as extracted from the $I$-$V$ slope at $I = 0$ (open circuit condition), significantly reduces at 300 °C. The difference between dark and illuminated values is not as strong here as with the case of $R_{SH}$.

Also important is the fact that the characteristic cell resistance, $R_{CH}$, at the point of maximum power, is not significantly modified by the annealing, resulting to a steady improvement of the $R_{SH}/R_{CH}$ ratio (Tab. 2). As a consequence of the considerable increase of $R_{SH}$ and the decrease of $R_S$, an improvement of the fill factor from 37.4 to 47.1% is achieved after annealing at 300 °C (Tab. 2). In parallel, the open circuit voltage, $V_{OC}$, of the cell reaches 505 mV after annealing at 300 °C, steadily increasing from the 370 mV value of the as-deposited state. Likewise, the short circuit current density, $J_{SC}$, increases with the temperature from 3.71 to 4.67 mA/cm$^2$. As a result, the power conversion efficiency, $\eta$, improves from 0.49% for the as-deposited case to 1.12% after annealing at 300 °C (Tab. 2). We note here that further annealing at 350 °C for 1 h resulted to linear $I$-$V$ characteristics for the majority of the cells, which strongly suggests the formation of short-cuts at the heterojunction.

In conclusion, we showed that thermal annealing in vacuum can considerably improve the photovoltaic performance of solar cells with electrochemically-deposited Cu$_2$O. The composition of the annealed absorber is purely Cu$_2$O, with no traces of CuO and Cu, as it is the case for the as-deposited films. The electrical characterization of the solar cells in dark and under AM1.5G illumination showed that the influence of the shunt and series resistance is decreased with annealing and all PV parameters are improved, obtaining a maximum power conversion efficiency of 1.12%.

The authors would like to acknowledge financial support from the Austrian Klima & Energiefonds projects “SAN-CELL” and “CopperHEAD”.

### Table 2. Extracted device parameters from the $I$-$V$ measurements of the solar cells in dark and under AM1.5G illumination.

<table>
<thead>
<tr>
<th></th>
<th>As-dep.</th>
<th>200 °C</th>
<th>250 °C</th>
<th>300 °C</th>
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<tbody>
<tr>
<td>$n$</td>
<td>2.0</td>
<td>1.9</td>
<td>2.0</td>
<td>2.0</td>
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<tr>
<td>$R_{SH}$ (kΩ) – dark</td>
<td>392</td>
<td>590</td>
<td>685</td>
<td>765</td>
</tr>
<tr>
<td>$R_S$ (Ω) – dark</td>
<td>4892</td>
<td>3436</td>
<td>5770</td>
<td>1831</td>
</tr>
<tr>
<td>$I_0$ (10$^{-8}$ A)</td>
<td>11.0</td>
<td>2.8</td>
<td>1.9</td>
<td>1.9</td>
</tr>
<tr>
<td>$R_{SH}$ (Ω) – illum.</td>
<td>4425</td>
<td>5867</td>
<td>6920</td>
<td>14689</td>
</tr>
<tr>
<td>$R_S$ (Ω) – illum.</td>
<td>889</td>
<td>1000</td>
<td>861</td>
<td>599</td>
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<tr>
<td>$R_{SH}/R_{CH}$</td>
<td>3.2</td>
<td>4.6</td>
<td>4.8</td>
<td>9.8</td>
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<tr>
<td>$J_{SC}$ (mA/cm$^2$)</td>
<td>3.71</td>
<td>3.91</td>
<td>4.61</td>
<td>4.67</td>
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<tr>
<td>$V_{OC}$ (V)</td>
<td>0.37</td>
<td>0.44</td>
<td>0.47</td>
<td>0.51</td>
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<td>$FF$ (%)</td>
<td>35.7</td>
<td>35.9</td>
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<td>$\eta$ (%)</td>
<td>0.49</td>
<td>0.62</td>
<td>0.81</td>
<td>1.12</td>
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