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Composition dependent characterization of copper indium diselenide thin film solar cells synthesized from electrodeposited binary selenide precursor stacks

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ABSTRACT

$CuInSe_2$ solar cells were prepared from electrodeposited and annealed stacks of indium selenide and copper selenide on molybdenum ($Mo/In_2Se_3/Cu–Se$). In comparison to a simultaneous electrodeposition of all elements at once the electrodeposited binary selenide stack leads to larger grains and lattice coherence length if annealed under the same conditions (30 min at 550 °C). Absorbers with atomic Cu/In ratios <1, 1 and >1 and their corresponding solar cells were characterized. An incomplete reaction in case of the Cu-poor precursor caused a Cu-deficient layer at the back contact of the absorber leading to the formation of a reverse electronic barrier reducing fill factor and short circuit current and thus the solar power conversion efficiency. Photoluminescence measurements showed a strongly compensated semiconductor for the Cu-poor absorber and an incomplete charge carrier collection was identified by quantum efficiency measurements under reverse bias. The reverse electronic barrier, the high compensation and the incomplete carrier collection could be avoided by Cu-rich growth conditions. The appearance of an excitonic transition in photoluminescence indicated a high semiconductor quality in this case. It was linked with a high quantum efficiency resulting in a local short-current density of 38.3 mA/cm^2. Temperature-dependent *JV* measurements identified interface recombination as the limiting recombination loss mechanism for the Cu-rich grown solar cell reducing the open-circuit potential and decreasing the conversion efficiency. The solar cell prepared from the precursor with Cu/In ≈ 1 had similar properties as the Cu-poor device without the reverse electronic barrier at the back contact but instead dominating interface recombination. It reached a best solar power conversion efficiency of 5.5%.

1. Introduction

The highest performance of thin film solar cells has been reached with the compound semiconductor $Cu(In,Ga)Se_2$ [1]. Electrodeposition followed by selenization is a low-cost and material-efficient method for the fabrication of this semiconductor and its underlying compound $CuInSe_2$ (CIS) [2,3]. In principal the following three routes can be applied for the electrodeposition of CIS precursors [4]: (i) co-electrodeposition of all elements (Cu, In, Se) at once in the deposition process [5]; (ii) electrodeposition of a precursor stack consisting of indium selenide and copper selenide (In–Se, Cu–Se) [6–8]; (iii) electrodeposition of a metal(-alloy) precursor stack (Cu, In, Cu–In) [9,10]. A combination of these routes is also possible (e.g. a Cu/In–Se stack) [11]. The co-electrodeposited precursor in route (i) is nano-crystalline. Previous experiments have shown that its recrystallization during the annealing process can be insufficient and the grain size in the absorber stays below 100 nm [12]. Such a small grain size is undesirable, because the numerous grain boundaries can act as non-radiative recombination centers reducing the solar cell performance. Absorbers prepared from metal stacks in route (iii) can peel during the selenization process due to the profound volume expansion of the layer with the incorporation of selenium [13]. An electrodeposited precursor stack of binary selenides according to route (ii) is expected to solve the issues of low recrystallization

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and peeling. Experiments on the selenization of sputtered precursors have also resulted in a considerable shorter selenization time if the precursor does not consist of metal layers exclusively but contains a layer of indium selenide [14]. In co-electrodeposited precursors the thermodynamically stable CIS phase is already present and the reduction of the number of grain boundaries is the only driving force for recrystallization. In binary selenide precursors the favorable thermodynamic reaction between the precursor phases provides an additional driving force. The densities of the binary selenide are close to the density of CIS and the volume expansion during annealing is reduced in comparison to metal stack precursors.

Hermann et al. studied the synthesis of CIS from an electrodeposited stack of Mo/Cu/In–Se/Cu–Se [6–8]. They successfully prepared smooth, single-phase CIS absorber layers. No solar cell prepared from an electrodeposited stack of In–Se and Cu–Se has been reported so far.

Only a few solar cells prepared from an In–Se/Cu–Se precursor by the use of vacuum methods have been published. Anderson et al. deposit the precursor by Migration Enhanced Epitaxy and anneal it under Se flux [15]. The finished solar cell has a power conversion efficiency of 5.1%. Park et al. prepared the precursor stack by physical vapor deposition and obtained a best efficiency of 5.4% [16].

This work presents the first CIS solar cell prepared from an electrodeposited precursor of In–Se and Cu–Se. Different growth compositions are studied and their limitations are given.

2. Material and methods

2.1. Sample preparation

The precursors were prepared by electrodeposition from aqueous solutions. The indium selenide layer was electroplated on Mo-coated soda-lime glass substrates ($2.5\times2.5\ \mathrm{cm}^2$) from an electrolyte containing 1.89 mmol/kg (of solvent) $In_2(SO_4)_3$, 1 mmol/kg H_2SeO_3, and 100 mmol/kg K_2SO_4. The pH value of the bath was stabilized at 2 by a buffer prepared from potassium hydrogen phthalate and sulfamic acid. The deposition was carried out under nitrogen atmosphere at 80 °C and -0.60 V (versus a 3 M KCl Ag|AgCl reference electrode) on a rotating disc electrode (RDE) with a rotation speed of 400 rpm. These conditions result in a smooth, shiny gray, and amorphous indium selenide film with an atomic Se/In ratio of 1.5 [17]. The copper selenide layer was plated on top of this film from an electrolyte containing 2.6 mmol/kg $CuCl_2$, 5.9 mmol/kg H_2SeO_3, and 232 mmol/kg LiCl. The pH value was buffered at 3 with potassium hydrogen phthalate and sulfamic acid. The deposition was done at room temperature and -0.30 V on a RDE at a rotation speed of 100 rpm. The plated copper selenide film is black and opaque with an atomic Cu/Se ratio of 0.76 determined by inductively coupled plasma – mass spectroscopy (ICP-MS). In the case of a “stoichiometric precursor” a charge densities of 3.63 $\mathrm{C/cm^2}$ and 3.10 $\mathrm{C/cm^2}$ have been plated for indium selenide and copper selenide, respectively. It has been verified by ICP-MS composition measurements that this ratio of charge densities results in a composition with an atomic Cu/In ratio of 1. Different compositions of the precursor stack were prepared by adjusting the charge density of the copper selenide layer.

For reference purpose a co-electrodeposited precursor has been electroplated at room temperature on a stationary electrode from a bath containing 2.6 mM $CuCl_2$, 9.6 mM $InCl_3$, 5.5 mM H_2SeO_3, and 240 mM LiCl in a pH 3 buffered solution [12].

The precursors were annealed for 30 min at 550 °C in a graphite box with an inner volume of about 20 cm^3 inside a resistance heated quartz tube furnace. 100 mg Se powder was added to the graphite box and the furnace was filled with a mixture of 10% H_2 in N_2 at 10 mbar.

Before processing the absorber to a solar cell, possible copper selenide phases on its surface were removed by etching with a 5% potassium cyanide (KCN) solution for 2 min [18]. Directly afterwards a 60 nm thick CdS layer was deposited by chemical bath deposition [19]. By mistake the CdS layer of the Cu-rich grown sample is slightly thinner (ca. 50 nm). The solar cell was finished by adding a 130 nm intrinsic ZnO layer and a 540 nm thick aluminum doped ZnO layer by sputtering and evaporating a Ni–Al grid for electrical contact.

The electrical performance of the solar cells is compared to a $CuInSe_2$ absorber grown by physical vapor deposition (PVD). A typical Cu-poor three-stage coevaporation process was applied [20,21].

2.2. Characterization techniques

The thin films were characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), Auger electron spectroscopy (AES), and photoluminescence (PL). The EDS spectrum was recorded with a primary electron energy of 20 keV in a system calibrated with a stoichiometric $CuInSe_2$ standard. The XRD diffractograms were recorded with a Cu tube ($K_{\alpha1}$ and $K_{\alpha2}$ lines) in a grazing incidence geometry at an incidence angle of 4°. The XRD peak width was determined from highly resolved diffractograms recorded in a theta–2 theta geometry with a parallel beam. AES measurements were combined with Ar^+ sputtering (3 kV, 3 μA, 45° incidence angle) of the samples to obtain the composition depth profile. The AES spectra were recorded with a primary electron beam of 10 kV and 1 nA on a system calibrated with a stoichiometric $CuInSe_2$ standard. PL measurements were performed at 10 K with the 514.5 nm line of an argon ion laser and an excitation power between 1 mW and 50 mW. After calibrating the system with a lamp of known intensity the same set up was used to determine a quantitative PL spectrum at room temperature.

The finished solar cell with an area of 0.5 cm^2 was characterized by (temperature dependent) current density–voltage (*JV*) measurements and (voltage dependent) external quantum efficiency (*QE*) measurements. *JV* measurements were recorded in a home-built set up using a halogen lamp with a dichroic reflector as illumination source being adjusted to 100 $\mathrm{mW/cm^2}$ with a certified reference solar cell. In a similar set up the solar cell was placed in a cryostat to control its temperature between 100 K and room temperature. *QE* measurements were recorded on a 1–2 mm^2 spot in the middle of the solar cell illuminated with monochromatic light and the intensity calibrated with a certified reference diode. The spectral response was measured by a lock-in amplifier. An apparent *QE* was measured with a reverse voltage bias applied between front and back contact of the solar cell.

2.3. Formulae used for the interpretation of data

2.3.1. Scherrer formula

The Scherrer formula is used to determine the lattice coherence length D of a polycrystalline material from the width of its XRD reflections [22]: $D=\lambda/[\beta_{size}(2\theta)\cos(\theta)]$ where D is the average coherence length, λ is the wavelength of the X-ray radiation, and θ is the diffraction angle. The integral breadth β_{obs} of the XRD reflection for a Pseudo-Voigt profile is determined by the integral breadth β_{size} caused by a finite coherence length and the integral breadth β_{instr} caused by the instrument [23]: $\beta_{size}\approx\beta_{obs}-\beta_{instr}^2/\beta_{obs}$.

2.3.2. Photoluminescence measurements of highly compensated semiconductors

Highly compensated CIGS absorbers show a broad asymmetric PL spectrum [24,25]. The energy of the PL emission maximum depends strongly on the laser excitation intensity I_{exc}. The increase