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The performance of $CuInSe_2$ monograin layer solar cells with variable indium content

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Abstract

The recent results on the characterization of $CuInSe_2$ monograin layer solar cells are presented. The influence of different Cu/In ratio on solar cell characteristics was studied. It was determined that device-quality $CuInSe_2$ monograin powder could be grown from CuIn precursor alloys with a composition between $0.9<Cu/In<1$. For absorber material, these powders were post-treated in sulphur vapour. The cells based on these absorbers showed efficiencies up to 9.5%. However, the quantum efficiency measurements revealed a significant loss in the long-wavelength range of photons $\lambda>800$ nm. The derivative of QE with respect to wavelength showed two peaks at the energy values of ~1.4 eV and ~1.03 eV, which proves that these sulphurised absorber materials consist of two different phases.

Keywords: $CuInSe_2$; Monograin layer; Solar cells

1. Introduction

In recent years an increasing number of studies have been made on polycrystalline $CuInSe_2$ (CIS) thin film production towards its scalability for large area devices at low cost. One possibility to produce solar cells (devices) of practically unlimited area is to use the monograin layer (MGL) design, based on powder materials [1]. In a MGL solar cell all grains of used CIS monograin powder perform as the absorber material of parallel connected micro solar cells. In the production of CIS monograin powder, the chemical nature of the liquid (molten) phase of the used solute material has its impact to the properties of the obtained absorber material. In our previous research the monograin powders were grown in liquid CuSe [2]. The liquid phase of CuSe provides an unlimited source of copper in equilibrium growth process ($CuInSe_2$ (s) − CuSe (l), T=const.) and controls the molecularity of $CuInSe_2$. At the same time, the device properties of CIS solar cells are critically influenced by their deviation from stoichiometric composition [3,4]. The use of alkali metal halides as fluxes facilitates to adjust the Cu/In ratio of grown CIS monograin powders [5]. In this study we focused on the characterization of MGL solar cells based on CIS powders of variable Cu/In ratio grown in molten potassium iodide.

2. Experimental details

2.1. Growth and characterization of $CuInSe_2$ powders

The monograin powders of CIS were synthesised from CuIn alloys of different Cu/In concentration ratios (0.5–1.1) and elemental Se in potassium iodide (KI) as a solvent material at 1000 K in evacuated and closed quartz ampoules. After the growth, KI was dissolved in deionised water and removed by washing. The shape and surface morphology were studied by high-resolution scanning electron microscopy (SEM) LEO SUPRA 35. The structural properties of the as grown powders were studied by X-ray diffraction. The composition of powders was determined polarographically. The electrical resistance was determined by pressing individual grains between two indium contacts. The ohmic behaviour of indium contacts has been proven by linearity of I–V measurements. The conductivity type was determined by the hot probe method.

All the as grown powders were post-annealed in sulphur vapour at 800 K for 18 h and used as the absorber materials in MGL solar cells. More processing details could be found in Ref. [5].

2.2. The performance and characterization of MGL solar cells

For MGL formation a monolayer of unisize CIS powder crystals covered with chemically deposited CdS was sedimentated into a

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thin layer of epoxy resin so that the contamination of the upper part of crystal surfaces with epoxy was avoided. After the polymerization of epoxy, *i*-ZnO and conductive ZnO:Al were deposited by RF-sputtering. The solar cell structure was completed by the evaporation of 1–2 μm thick In grid contacts onto the ZnO window layer. After glueing the structures on glass substrates, the back contact area of crystals covered with epoxy was opened by etching with concentrated H_2SO_4 and following abrasive treatment. Back contact was made by graphite paste.

Photovoltaic properties of graphite/$CuInSe_2$/CdS/ZnO structures (see Fig. 1) were characterized by *I–V* measurements under 100 mW/cm^2 illumination at room temperature. Spectral response measurements were performed using a computer-controlled SPM-2 monochromator and a 100 W halogen lamp. For bias-dependent measurements the Autolab PGSTAT-30 together with a lock-in amplifier was used.

3. Results and discussion

3.1. Material properties

The properties of $CuInSe_2$ monograin powders grown in potassium iodide solvent were characterized in details in Ref. [5]. The obtained results could be summarized as follows: the single-phase powder crystals were synthesised from Cu–In precursor alloys with Cu/In ratios between 1 > Cu/In > 0.7. Selenium content in the grown powders increased almost linearly with the decreasing Cu/In ratio. The conductivity of the materials decreased with increasing In content. The samples with nearly stoichiometric or slightly In-rich compositions showed *p*-type conductivity and exhibited PL spectrum with dominant peak at 0.93 eV. The change of conductivity type was observed in the region of Cu/In ratios of 0.67–0.71. The samples with Cu/In < 0.7 exhibited two broad bands in PL curve with the peak positions at 0.86 eV and 0.93 eV. In the further studies (unpublished in Ref. [5]) we found that XRD patterns (Fig. 2.) of stoichiometric or slightly In-rich as grown powders showed very sharp reflections, spectra revealed the presence of a single phase, corresponding to the $CuInSe_2$ chalcopyrite compound. In XRD spectra for the materials with the Cu/In ratio less than 0.77, the (101), (211), (301) reflection peaks disappeared while the reflection peaks (220/204) and (312/116) were shifted to the right side. In Ref. [6] the similar behaviour in XRD spectra was attributed to the appearing of a new phase – $Cu_2In_4Se_7$ – in the system. In Cu-rich materials there were no additional reflections in XRD spectra. This confirms that the single-phase $CuInSe_2$ chalcopyrite material was formed in the Cu-rich growth process.

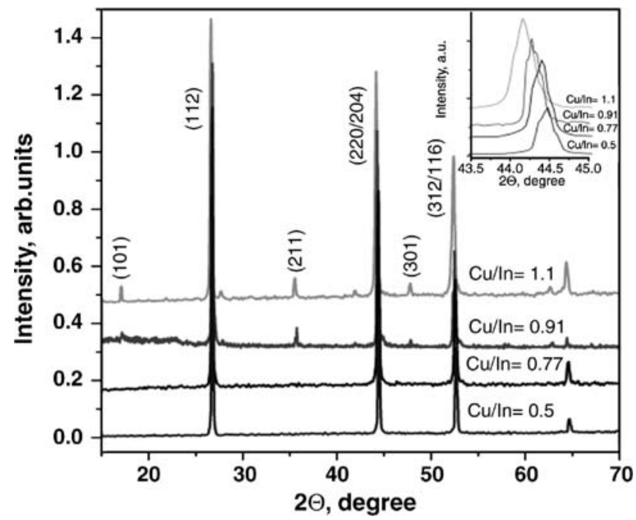

Fig. 2. XRD patterns of as-grown $CuInSe_2$ monograin powders from CuIn precursor alloys with different Cu/In ratios. Shift of the peak (220/204) with change in composition is shown in the upper right corner.

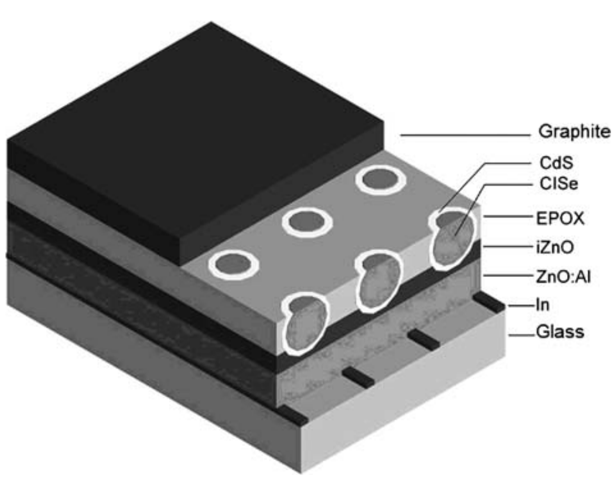

Fig. 1. Schematic illustration of the $CuInSe_2$ monograin layer solar cell structure.

3.2. Device characterization

Fig. 3a and b shows the open circuit voltage (V_{oc}) and the short circuit current density (J_{sc}) of MGL solar cells in dependence on the Cu/In ratio of precursor Cu–In alloys. In Fig. 3 the dashed lines mark the concentration limits of the Cu–In alloy composition that leads to the growth of In-rich single-phase $CuInSe_2$ absorber materials. Solar cells based on the absorber layers prepared from slightly In-rich (Cu/In = 0.9) and stoichiometric (Cu/In = 1.0) CuIn alloys exhibited the open circuit voltages up to 500 mV, fill factors (FF) around 60% and efficiencies around 9.5%. As the monograins of CIS in the MGL design of solar cell are separated from each other with epoxy, the active area of a MGL solar cell forms approximately 60% from the total area. So, the calculated maximum efficiencies of 9.5% show the efficiencies of the active working areas of the best MGL solar cells. The high In content (Cu/In < 0.7) of absorber material reduced the open circuit voltage and decreased the current density about 5 times. The completed cell structures from absorber materials with remarkably In-rich CIS composition (Cu/In < 0.7), displayed non-ideal *S*-shaped *I–V* characteristics with fill factors (FF) less than 25%. Ref. [4] attributed this behaviour to the breakdown in electrical field required to ensure the effective separation of photogenerated electron-hole pairs. The value of FF can be low also if serial resistance is too high. A sharp decrease in V_{oc} values was noticeable if Cu-rich Cu–In precursor alloys (Cu/In = 1.1) were used.