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Further developments in CIS monograin layer solar cells technology

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Abstract

This paper reviews recent studies and technological developments on different materials and technologies for monograin layer (MGL) photovoltaics (PV) solar cells conducted at Tallinn University of Technology. It is shown that in spite of improvements in technical parameters of MGL solar cells resulting from research in adsorber layer materials and surface modification, several problems have to be solved before determining the prospects of design.

Keywords: CuInSe2; Solar cells; Monograin layers

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1. Introduction

$CuInSe_2$ (CIS) materials with direct bandgap and a high absorption coefficient have received considerable attention as one of the most promising materials for second-generation solar cells [1,2]. They exhibit high long-term stability and can keep a relatively stable performance. These materials have also remarkably stable electrical properties over a wide range of stoichiometry. Further success of CIS material-based solar cells use will strongly depend on the production cost of the CIS layer, since the production of this layer carries a significant part in the overall

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module cost. The relative high cost of the CIS layer production is connected with the expensive vacuum technologies used for deposition of layers. In order to reduce process complexity and costs of solar cells and to achieve further commercial success of CIS material based photovoltaics, as a prerequisite, the ability to produce a CIS layer on a large scale and at a low cost has to be provided. The aim of the report is to summarize the results of research during the last year on the technological development of monograin layers (MGL) and technical parameters of the developed solar cells. We showed in [3] that the isothermal recrystallization of initial powders in different molten fluxes appears to be a relatively simple, inexpensive and convenient method to produce powder materials with an improved crystal structure and reduced concentration of defects. The powders developed are characterized by single-crystalline structure of grains, uniform chemical and narrow granulometric composition. This makes these materials very beneficial for MGL use. MGL has both high photoelectric parameters of monocrystals and advantages of polycrystalline materials: (1) low cost and simple technology of materials and devices; (2) possibility of making devices of a practically unlimited area; (3) possibility of nearly 100% use of materials. Due to the peculiarities of the technology of MGL solar cells, the most complicated technological problem in MGL technology is the possibility of contamination of monograin surfaces with an organic resin used in MGL formation. Thus, in our first publication on MGL solar cells [4], it was concluded, that "… the low efficiency of currently developed monograin layer solar cells is connected with the materials' defects and chemical composition and also with insufficient cleaning of the surfaces of the crystals in the monograin layer".

2. Experimental

CIS powder materials were synthesized from Cu–In alloy and Se in molten fluxes. The growth temperature varied in the range of 800–1025 K. Crystals of the synthesized powder were of a uniform round shape, with smooth surfaces. Crystal size could be controlled by the temperature and duration of the recrystallization process and by the chemical nature of the flux used in the growth process. More details about this process can be found elsewhere [3].

After the removal of the flux material, the as-grown powders were post-treated in selenium and/or sulphur vapour for surface restoration and defect structure improvement. Sulphur treatment leads to a higher bandgap surface region on CIS crystals. This region with a larger bandgap near the surface of the absorber crystals, where the p–n junction is formed, allows us to yield devices with higher open-circuit voltages (V_{oc}) [5]. The bulk composition of powders was determined by energy dispersive spectroscopy (EDS). Surface composition was studied by X-ray photoelectron spectroscopy (XPS). The shape and surface morphology were studied with the help of high-resolution scanning electron microscopy (SEM) LEO SUPRA 35 and chemical and phase compositions using polarographics and mass-spectrometric chemical analyses, EDS and X-ray diffraction (XRD).

A monolayer of chemically treated powder crystals was embedded in epoxy resin for MGL formation. The technology is described in detail in [6]. CdS was deposited onto the surfaces of crystallites released from epoxy resin surfaces of crystallites from a chemical bath. For cell completion, i-ZnO and conductive ZnO:Al were deposited by RF-sputtering. Photovoltaic properties of graphite/$CuInSe_2$/CdS/ZnO structures were characterized by the *I–V* measurements under $100\,mW/cm^2$ illumination. Spectral response measurements were performed with the help of computer-controlled SPM-2 monochromator and a 100 W halogen lamp. For the bias-dependent measurements, we used Autolab PGSTAT-30 together with a lock-in amplifier. All temperature-dependent measurements were made with the help of a closed-cycle He cryostat ($T = 10-300\,K$).

3. Results and discussion

3.1. Modification of composition of monograin powders

Additional thermal treatments in different atmospheres and etching in different etchants were used to modify the composition of the developed monograin powders. The results of EDS analysis of selenium treated materials exposed to selenium vapour at up to 725 K for 15 min did not show any changes in the molecularity of material but indicated to the loss of selenium from materials at temperatures higher than 370 K. Sulphur treatments of powders lead to the formation of a higher bandgap surface region on CIS crystals as it was reported in [5].

Additional chemical treatments with different etchants (HCl, KCN, KOH in ethanol and NH_3) showed differences in the behaviour of etchants to materials with different composition (Cu- and In-rich). NH_3 treatment of Cu-rich CIS absorber material led to the depletion of the surface of materials of copper and selenium and resulted in reduced values of the parameters of solar cell structures. KCN dissolved copper preferentially from the surface of absorber and as a result, the fill factor of solar cells improved.

3.2. MGL solar cells

The MGL consists of a one-crystal-thick layer of grains of the monograin powder embedded in an organic resin (Fig. 1).

Current–voltage (*I–V*) dependences of MGL solar cells show values of V_{oc} up to 500 mV and fill factors up to 60% (Fig. 2, Table 1). The value of V_{oc} is close to the typical values of V_{oc} for CIS thin film cells. The low values of fill factor are connected with insufficient cleaning of open surfaces of crystals in the MGL as it was shown by electron beam-induced current (EBIC) studies (Fig. 3). The temperature dependence of open-circuit voltage (V_{oc}) gives a barrier height for the junction $\Phi_p = 1034\,meV$ (Fig. 4). This is close to the typical value for CIS.

$CuInSe_2$-based monograin cells show typically lower V_{oc} and fill factors than those of polycrystalline $CuIn_xGa_{1-x}Se_2$ (CIGSe)-based solar cells. Moreover, they have

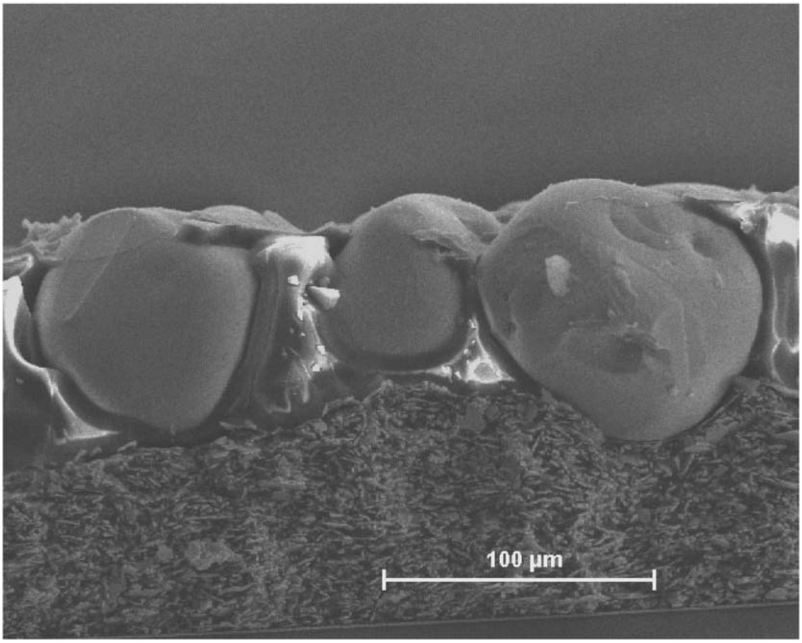

Fig. 1. SEM photo of cross-section of MGL solar cell.

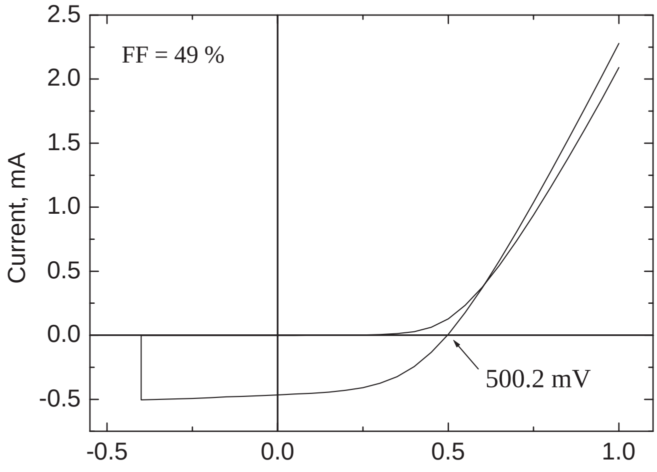

Fig. 2. Typical *I–V* curve of MGL from sulphur-treated $CuInSe_2$ powder. The value of efficiency is not given due to difficulties in determining the precise active solar cell area.

higher values of ideality factors (see Fig. 5). One possible reason for these reduced parameter values is a high recombination rate through interface states. Our studies show that in many cases the Fermi level is pinned at about 200 meV below the

Table 1
Parameters of MGL solar cells from [4] and results of this study (sulphur-treated powders)

Parameter	This study	[4], 2002
V_{oc} (mV)	481	302
Φ_p (mV)	1034	835
FF (%)	58	33.7

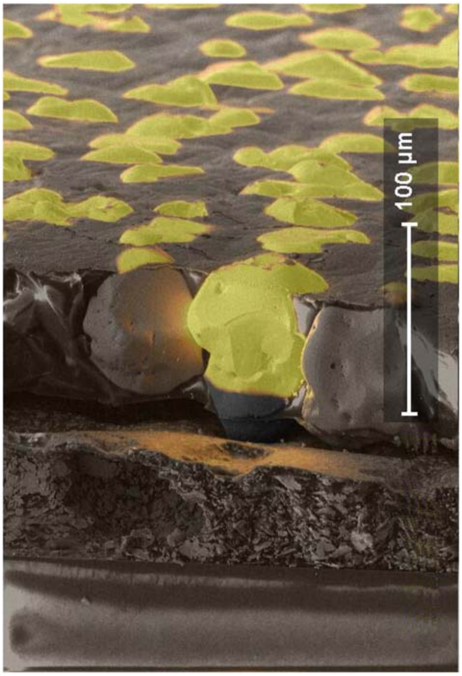

Fig. 3. EBIC picture of surface of MGL.

conduction band edge due to these interface states. It is known that a thin *n*-type inversion layer usually helps reduce interface recombination at the CdS/CIS interface [7]. However, the type inversion adds new problems and does not exploit the benefits of a heterojunction. Another possibility for reducing interface recombination is to use a layer of material with a graded composition, so that heterojunction interface will be formed with a layer of material with a higher bandgap. Widening the bandgap of the absorber leads to a reduced spike at the absorber/buffer interface. Usually, a $CuInGaSe_2$ layer or the so-called ordered vacancy compound (OVC) layer is used for this purpose [8]. Intermixing at the interface can then help to close the recombination path over the reduced barrier if the band discontinuity is spread over a certain distance. In our MGL cells, it is very difficult to form an OVC layer on the surface of grains and therefore we used sulphur treatment to increase the bandgap of the absorber surface. Extrapolation of the V_{oc} (T) curve to 0 K (see Fig. 4) confirms

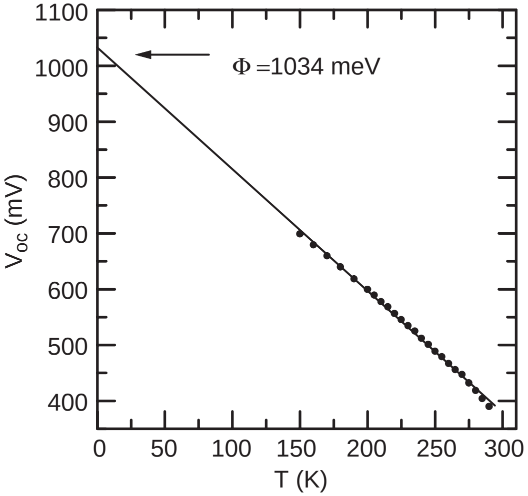

Fig. 4. V_{oc} vs. T for sulphur-treated $CuInSe_2$ monograin layer solar cell.

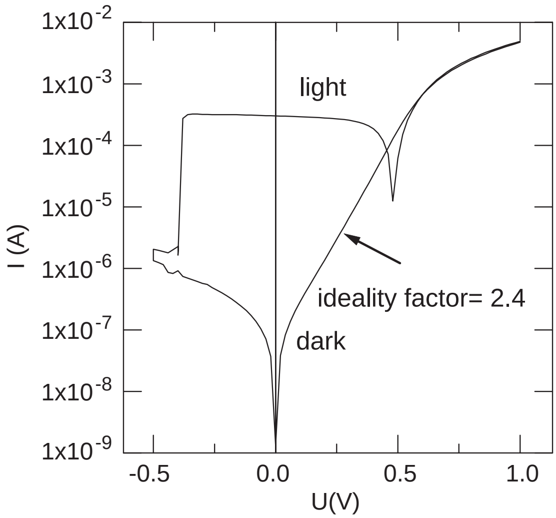

Fig. 5. I–V curve of our cell showing ideality factor $n = 2.4$ and V_{oc}~500 mV.

the increase of value of barrier height after sulphur treatment. At the same time, the I–V curves show reduced current values.

Spectral response measurements show (see Fig. 6) that the optically active absorber region indeed has a higher bandgap, but the overall shape of the curve points to a bad current collection from the absorber layer. We also used various reverse bias voltages to modify spectral response curves. Increasing the reverse bias improved the overall current collection and at higher voltages, the bandgap of

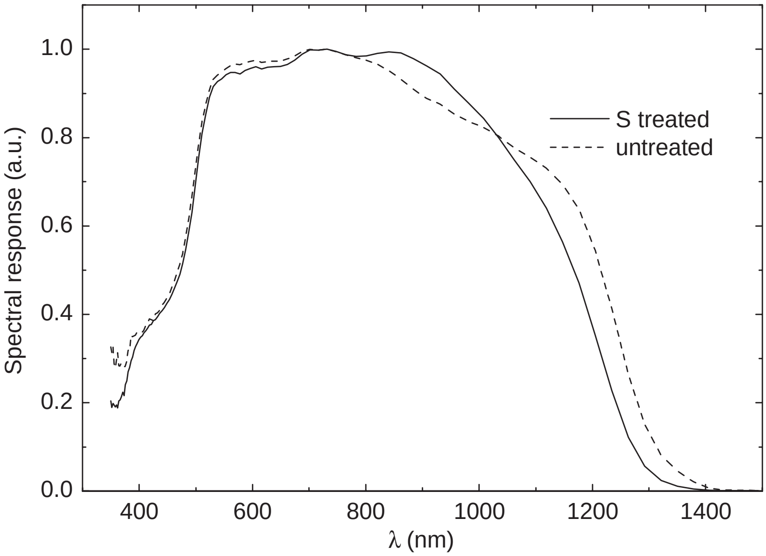

Fig. 6. Normalized spectral response curves for S-treated and untreated solar cells.

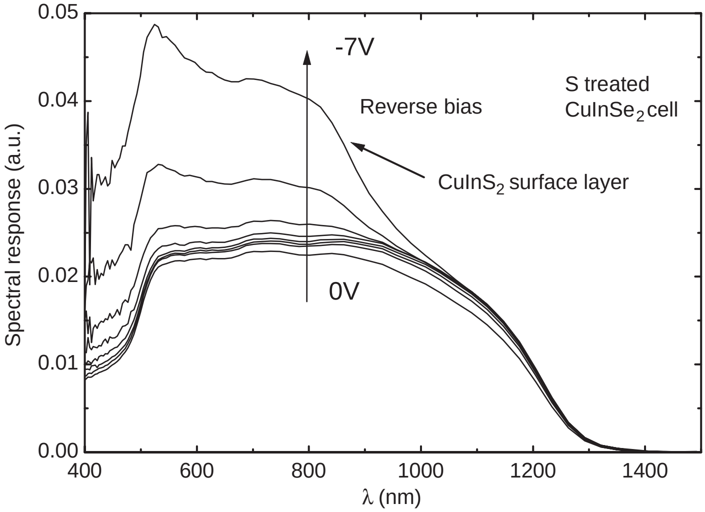

Fig. 7. Spectral response curves of our S-treated $CuInSe_2$ cells measured at different reverse bias voltages.

$CuInS_2$ appears as a step on the spectral response curve (see Fig. 7). This is an indication that the thin surface layer of CIS is completely converted to $CuInS_2$. However, this thin layer has a very high resistance.

Our recent results indicate that the conclusions made in [4] about the shortcuts of monograin layer technology are correct. At the same time period, improvements in the parameters of monograin layer solar cells made during the last period (Table 1) confirm that the technology has good prospects.

4. Conclusions

CIS solar cells in monograin layer design were prepared. Different methods to modify the composition of the adsorber layer by thermal and chemical treatments were investigated by chemical analyses, EDS and SEM. The results show that in spite of the improvement in parameters of monograin layer solar cells, during the last period, additional studies in the field of CIS–CdS interface modification are needed to optimize the parameters of the solar cell structures developed.

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