

## Monograin layer solar cells

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### Abstract

The paper presents results of studies directed towards the production of monograin powders of  $\text{CuInSe}_2$  for possible use in solar cells preparation. The results concern the tailoring of chemical and defect composition of materials, development of the technology of manufacturing monograin layers (MGL) on the base of developed materials and the cleaning of open surfaces of the grains in the MGL by different mechanical, chemical and electrochemical methods. It is shown that up to now the low efficiency of MGL solar cells is associated with the chemical and defect composition of the monograin powder materials and with difficulties in cleaning the surfaces of the crystals in the MGL before depositing active contacts.

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*Keywords:* Crystallization; Electrical properties and measurements; Solar cells; Copper indium diselenide

### 1. Introduction

The high production cost of conventional solar cells necessitates the search for cheaper materials, methods and devices. Chalcopyrites ( $\text{CuInSe}_2$ ,  $\text{CuInS}_2$ ) are widely used in solar cells because of their high absorption coefficients and direct optical bandgap [1]. In addition to very expensive monocrystals, the above-mentioned compounds can be produced in a cheaper, polycrystalline form. Considerable efforts have been made to reduce grain boundary effects in thin film structures. The optimisation of growth conditions (deposition and annealing conditions) and several types of surface treatments (chemical and photoelectrochemical etchings) serve this purpose and are regularly discussed [2]. At the same time, the manufacture of thin films of  $\text{CuInSe}_2$  with a large surface area and good reproducibility is technically complicated.

Powder technologies are the cheapest technologies for producing materials and are free of the above-mentioned shortcomings. We have shown 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 inherent defects [3,4]. The advantages of the developed powder materials are: (1) single-crystalline structure of every grain; (2) uniform distribution of doping impurities; (3) narrow granulometric composition.

The idea of monograin layers (MGL) for construction of optoelectronic devices was proposed more than 30 years ago by researchers of the Philips company [5,6]. The MGL consists of a thick layer of grains of monograin powder embedded into an organic resin. The MGLs combine the high photoelectronic parameters of monocrystals and the advantages of polycrystalline materials such as: (1) low cost and simple technology of materials and devices; (2) the possibility of making flexible devices; (3) the possibility of using of materials up to 100%.

In spite of these advantages, MGLs have until now not found wide use in industrial production of photoelectronic devices and solar cells. This could be explained by some unsolved technical problems, such as: (1) many designs need powder grains of nearly equal size and perfect monocrystalline structure; (2) there are problems of surface preparation of the grains in the MGL.

The aim of this report is to summarize our recent research results on technological developments in the field of monograin materials and on optoelectronic

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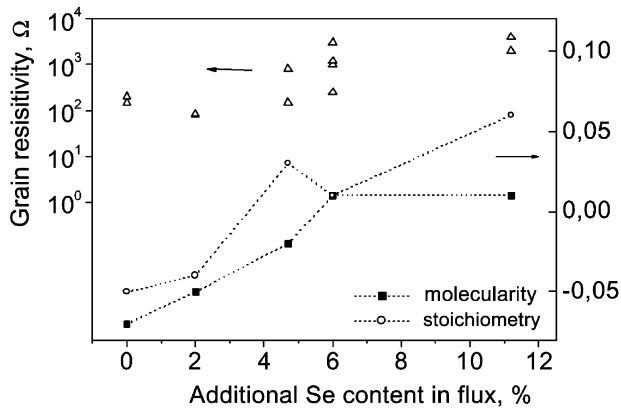


Fig. 1. Influence of flux content on the chemical composition and electroresistivity of monograin  $\text{CuInSe}_2$  powders.

parameters of MGL solar cells. The following topics are addressed in this paper:

1. possibilities for producing  $\text{CuInSe}_2$  monograin powders with composition and structure acceptable for MGLs use;
2. photoelectrical parameters of MGL solar cells.

## 2. Experimental

$\text{CuIn}$  (1:1) alloy,  $\text{CuSe}$  and  $\text{Se}$  were used as the initial materials for the monograin powder growth process.  $\text{CuIn}$  alloy and  $\text{CuSe}$  were synthesized from their elements in evacuated quartz ampoules and were ground in an agate mortar before use in the powder growth process [7]. The growth temperature was varied in the range of 800–1025 K. After growth, the flux ( $\text{CuSe}$  and  $\text{Se}$ ) was removed by dissolving in a 10%  $\text{KCN}$  aqueous solution. The electrical resistivity of the powder crystals

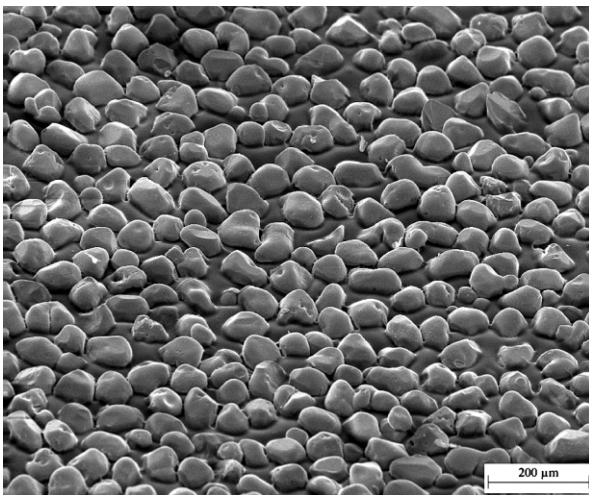


Fig. 2. SEM picture of typical  $\text{CuInSe}_2$  MGL.

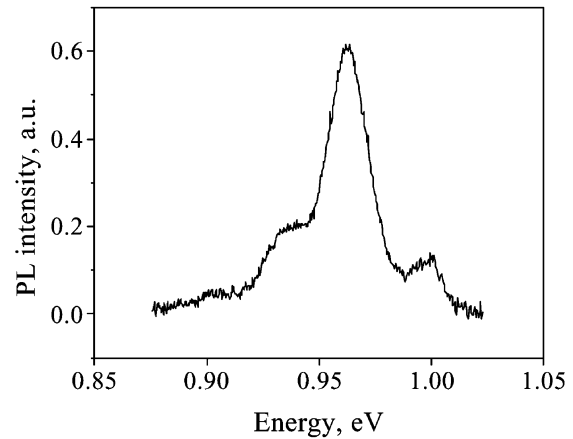


Fig. 3. PL spectrum of typical  $\text{CuInSe}_2$  monograin powder.

was measured by pressing individual grains between two  $\text{In}$  contacts. The type of conductivity was determined by the thermo-probe method. Photoluminescence (PL) measurements were carried out at 8 K using a closed-cycle He cryostat. A He–Cd laser with a wavelength of 441.6 nm for the PL excitation and a computer controlled 0.4 m single grating monochromator were used in the PL measurements. The shape and surface morphology were studied using scanning electron microscopy (SEM) and chemical and phase compositions using polarographics and mass-spectrometric chemical analyses, energy dispersive spectroscopy (EDS) and X-ray diffraction. MGLs were prepared using the technology described by us in Ref. [8].

## 3. Results and discussion

### 3.1. Monograin powders

Melted binary  $\text{Cu–Se}$  phases have been used for the growth of large  $\text{CuInSe}_2$  and  $\text{Cu(InGa)Se}_2$  grains in the process of producing thin films in a stacked elemental

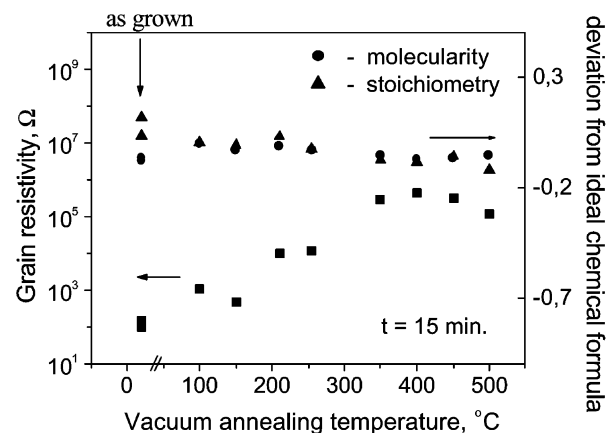


Fig. 4. Influence of vacuum annealing on the chemical composition of powders.

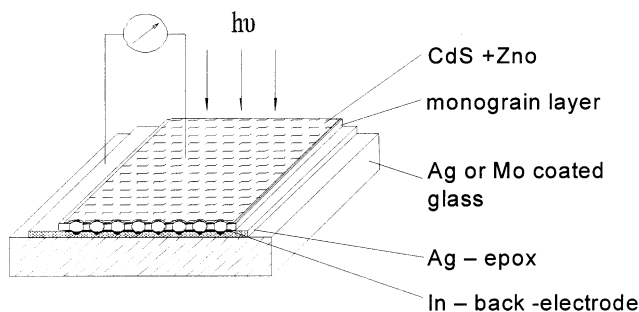


Fig. 5. Structure of MGL solar cell.

layer process [9] and for the solution growth of bulk  $\text{CuInSe}_2$  and  $\text{CuGaSe}_2$  crystals [10–12]. The phase diagram of Cu–Se [13] shows that, at temperatures 530 °C and higher, there should not exist any solid phase in the system used other than  $\text{CuInSe}_2$ . This gives a prerequisite to use melted binary Cu–Se phases for the synthesis and monograin growth process of  $\text{CuInSe}_2$  monograin powders. Molecularicity expressed as  $\Delta m = \text{Cu}/\text{In} - 1$ , stoichiometry expressed as  $\Delta s = 2\text{Se}/(\text{Cu} + 3\text{In}) - 1$  and electrical resistivity of  $\text{CuInSe}_2$  monograin powder material synthesized at a temperature of 800 K are represented in Fig. 1 as a function of additional CuSe selenium content in the flux.

The chemical composition of individual  $\text{CuInSe}_2$  crystals in the powders (determined by EDS) was not notably influenced by the growth temperature. At the same time, the ratio (Cu/In) showed a tendency to increase while the Se content decreased. Crystals of the powder were of a uniform, round shape, with smooth surfaces (Fig. 2).

Crystal size is described by the equation  $d_m = At^{1/n} \exp(-E_d/kT)$ , where  $A$  is the constant,  $d_m$  is the mean diameter of the crystals,  $E_d$  is the activation energy of linear crystal growth and  $n$  is the geometric factor of the growth mechanism. Experimentally determined val-

ues of  $E_d$  and  $n$  were  $n = 3.7(\pm 0.24)$  and  $E_d = 0.28(\pm 0.03)$  eV, respectively [7]. The value of  $n$  and the shape of the crystals indicate that crystal growth proceeds as the recrystallization of material rather than the sintering of crystal nuclei formed in the initial stages of thermal treatment.

A typical PL spectrum of our CIS crystals is dominated by a band at 0.991 eV together with a second band at 0.973 eV followed by phonon replicas as shown in Fig. 3. The 0.991 eV band is usually seen in nearly stoichiometric CIS only [14–16]. The 0.973 eV band is characteristic of Cu-rich CIS [14]. As a result, our PL data indicate that we have a stoichiometric starting material with Cu/In = 1. A typical PL spectrum of our CIS crystals is dominated by a band at 0.991 eV together with a second band at 0.973 eV followed by phonon replicas as shown in Fig. 3. The 0.991 eV band is usually seen only in nearly stoichiometric CIS [14–16].

The 0.973 eV band is characteristic of Cu-rich CIS [14]. As a result our PL data indicate that we have a stoichiometric starting material.

### 3.2. Engineering of $\text{CuInSe}_2$ stoichiometry in vacuum annealing processes

$\text{CuInSe}_2$  powder materials were annealed in dynamic vacuum ( $10^{-2}$  Torr) at different temperatures from 370 to 800 K for a constant time period for the tailoring of the materials' electrical parameters. The annealed materials were characterized by electrical conductivity and by deviations of molecularicity and stoichiometry. The results (Fig. 4) reveal that the molecularicity did not change in the annealing process up to 725 K for 15 min but the selenium already starts to be removed from materials at 370 K. The grain resistivity increases up to 670 K but at higher temperatures has a tendency to decrease.

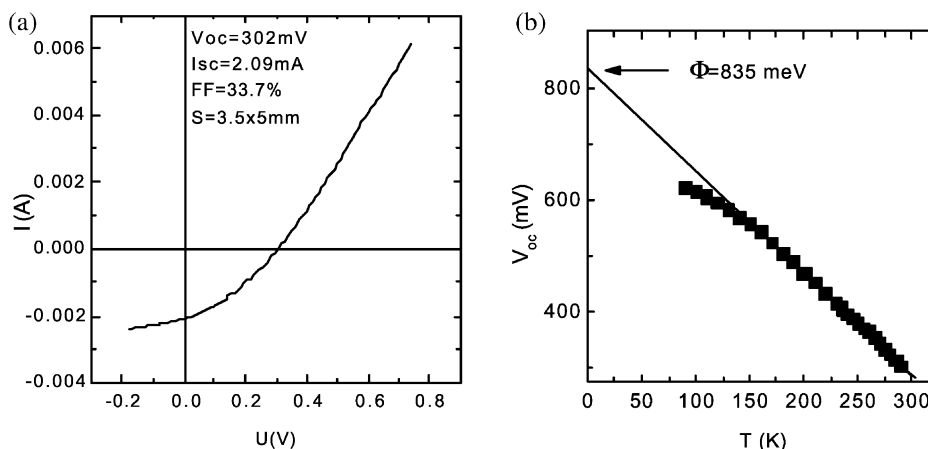


Fig. 6.  $I$ – $V$  curve under standard  $100 \text{ mW}/\text{cm}^2$  illumination (a) and  $V_{oc}$  vs.  $T$  curve for CIS MGL solar cell (b).

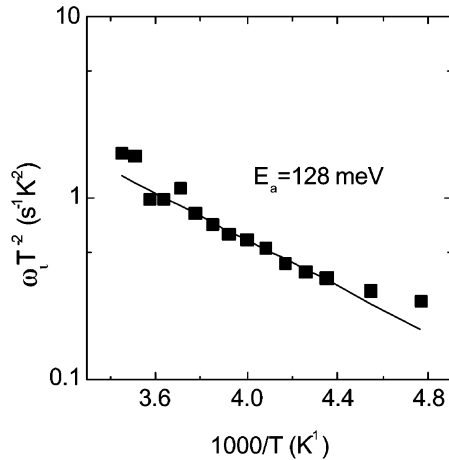


Fig. 7. An Arrhenius plot of the angular frequency of the inflection point  $\omega_i = 2\pi f_i$ , determined from the derivative  $f \times dC/df$  from temperature and frequency dependent admittance measurements.

Treatment of powders under Se atmosphere has no remarkable effect on the volume composition of powder crystals. At the same time, the electrical conductivity of the powders changes by more than 3 orders of magnitude.

### 3.3. Monograin membranes

MGL solar cells were prepared using developed powders (Fig. 5).

The surfaces of MGLs were cleaned before formation of the solar cell structure (before deposition of the barrier layer and electrodes) by mechanical polishing and chemical etching. Contact problems between the grains and contacts were investigated by comparing scanning electron microscope and the electron beam induced current pictures of MGL with those of Schottky barrier [17]. The results confirm that the main problem of MGL technology is the cleaning of the surfaces of grains in the MGL.

A typical current–voltage ( $I$ – $V$ ) curve of our MGL solar cell is shown in Fig. 6. Low values of fill factor and  $V_{oc}$  and quite high  $I_{sc}$  are typical features for MGL solar cells at the present time.

The temperature dependence of the open circuit voltage ( $V_{oc}$ ) (Fig. 6b) gives a barrier height for the junction  $\Phi^p = 835$  meV. This is close to the typical value for Cu-rich CuInSe<sub>2</sub> [18]. We also used admittance spectroscopy to find the activation energy of the dominant defects, see Fig. 7. Only one deep level was detected with  $E_a = 128$  meV. This level seems to be the N1 level ordinarily found in CIGS cells [19].

## 4. Conclusion

In this report the results of studies of the formation of different CIS powders in different molten fluxes with qualities acceptable for MGL design solar cells are given. It is shown that the low efficiency of currently developed MGL solar cells is connected with the materials' defects and chemical composition and also with insufficient cleaning of the surfaces of the crystals in the MGL.

## Acknowledgments

The financial support for this research in the field of solar energy materials and solar cells by different Estonian Scientific Foundation grants is gratefully acknowledged.

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