Crystal growth and characterisation of In-rich phases in Cu-In-Ga-Se system

J.I. FILIPOWICZ*, R. BACEWICZ, and A. WOLSKA

Faculty of Physics, Warsaw University of Technology
75 Koszykowa Str., 00-662 Warsaw, Poland

Technological parameters of crystal growth using Bridgman-Stockbarger method for some materials of Cu-In-Se and Cu-In-Ga-Se systems are presented. Single crystals as large as 1 cm³ have been grown. The composition variation along crystal ingots was determined by the microprobe analysis. A strong segregation effect is observed. Crystals with composition close to the compounds with nominal compositions $Cu_2In_4Se_7$, $CuIn_3Se_5$, $CuIn_5Se_8$, $CuGa_3Se_5$, and $Cu(In_{0.8}Ga_{0.2})_3Se_5$ were identified. Photoluminescence spectra of the crystals from the Cu-In-Se system were measured and analysed in terms of quasi-donor-acceptor transitions.

Keywords: crystal growth, ternary chalcogenides, multinary compounds, photoluminescence.

1. Introduction

Ternary and multinary phases of the Cu-In-Se and Cu-In-Ga-Se systems with high content of the third group element (In and Ga) attracted much attention when In-rich layer with composition corresponding to $CuIn_3Se_5$ compound was identified on the interface of $CdS/CuInSe_2$ solar cells [1]. It seems to play a crucial role in the recombination processes and solar cell performance. In recent years the interest in these materials systematically increases [2,3]. These phases have been proposed to have defected chalcopyrite structure and are called ordered vacancy compounds (OVC). However, this structural assignment has been questioned for $CuIn_3Se_5$ where neither defect chalcopyrite nor ordered vacancy structure was found [4]. According to the phase diagram by Fearheiley [5] and Boehnke&Khn [6], for Cu-In-Se system, in the indium-rich range four ternary phases exist: is the phase for homogeneity region from 47.5 to 55 mol% In_2Se_3 (e.g,. ordered $CuInSe_2$), is the phase between 66.5 and 79 mol% In_2Se_3, is the phase from 82 to 90 mol% In_2Se_3 range and the is the phase extending from 40 to 65 mol% In_2Se_3 (above 900 °C) and representing homogeneity region of disordered $CuInSe_2$. The compounds as $CuInSe_2$, $CuIn_4Se_7$, $CuIn_3Se_5$ and $CuIn_5Se_8$ represent the phases mentioned above. The gallium containing phases which are copper poor are of special interest since the best thin film solar cells are fabricated with $CuIn_{1-x}Ga_xSe_2$ as an absorber. In analogy with $CuInSe_2$ based devices, thin layer of copper poor phase is expected on the interface of the junction. However, there is no data available on the phase relations in the Cu-In-Ga-Se system.

In this paper we present crystal growth procedure and some photoluminescent properties of In-rich phases of Cu-In-Se system and the analogous crystals with about 20 at% of In substituted by gallium.

2. Crystal growth

The Bridgman-Stockbarger method was used. It is known as the vertical gradient freezing method. The crystal growth apparatus consisted with resistance furnace and EUROTHERM controller/programmer 815. Starting elements were closed in quartz ampoule under vacuum. After heating up to 1040°C, (keeping it about 5 hours), material was cooled with the cooling rate 1°C/h down to 750°C, then with the cooling rate 5°C/h down to 500°C. Temperature gradient along an ingot was about 10°C/cm. Figure 1 shows typical ingot [starting charge composition $Cu(In_{0.8}Ga_{0.2})_3Se_5$].

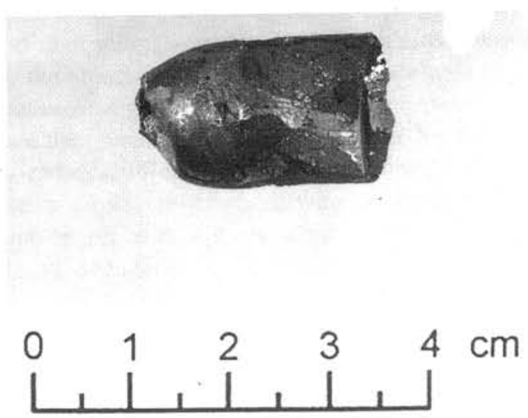

Fig. 1. Picture of typical ingot. Starting charge composition $Cu(In_{0.8}Ga_{0.2})Se_2$.

* e-mail: jfil@mech.pw.edu.pl

Obtained ingots exhibited a segregation effect consisting in the decrease of the Cu to In ratio along the growth direction. The composition of crystals versus the position along the ingots was determined by microprobe. It is presented in Figs. 2 and 3 for the crystals with the starting composition corresponding to the nominal $CuA^{III}{}_3Se_5$ formula, where A^{III} denotes the third group element. The gallium concentration stays almost constant throughout the ingot indicating much weaker segregation effect than for indium.

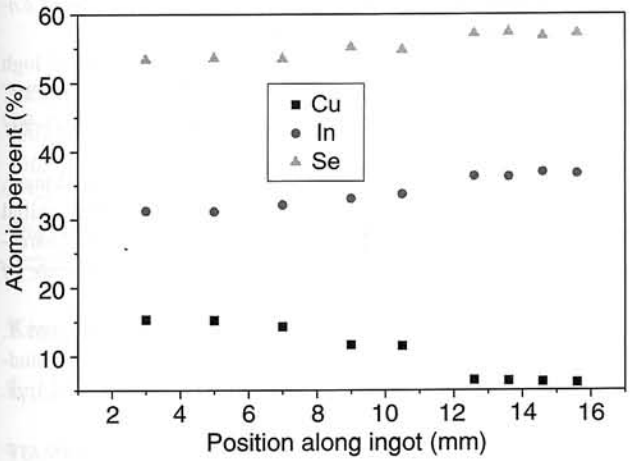

Fig. 2. Concentration of the elements versus position along ingot (from the first to freeze end) for Cu-In-Se system. Starting charge composition $CuIn_3Se_5$.

For Cu-In-Se ingots, the indium-rich side of an ingot was lamellar and soft. Its composition was close to $CuIn_5Se_8$. The X-ray Laue pattern showed the hexagonal ordering with the c-axis perpendicular to the cleavage plane. On the other side of the ingot, crystals belonging to the tetragonal β-phase were found. The lattice constants determined from the powder X-ray diffraction analysis are: a = 5.766 Å, c = 11.5417 Å for $Cu_2In_4Se_7$, and a = 5.754 Å, c = 11.523 Å for $CuIn_3Se_5$.

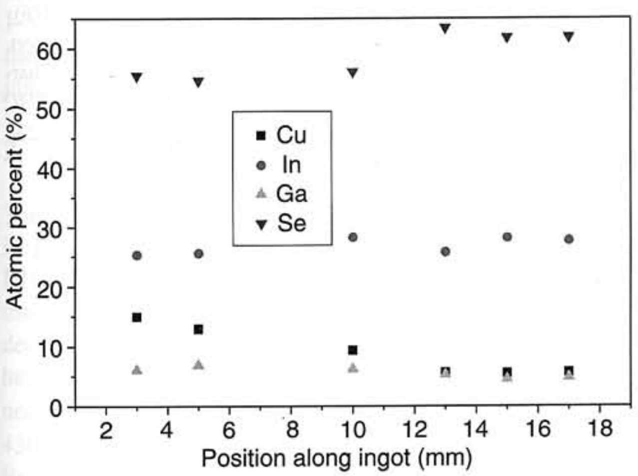

Fig. 3. Concentration of the elements versus position along ingot (from the first to freeze end) for Cu-In-Ga-Se system. Starting charge composition $Cu(In_{0.8}Ga_{0.2})_3Se_5$.

3. Photoluminescence spectra

Photoluminescence (PL) measurements were carried out using 488 nm line of Ar^+ laser as an excitation. Closed cycle refrigerator (working in the range 8–300 K) and germanium detector were employed. The excitation intensity was varied by the use of neutral filters. Samples of the tetragonal β-phase ($Cu_2In_4Se_7$ and $CuIn_3Se_5$) were cut from an ingot and polished, samples of $CuIn_5Se_8$ were cleaved.

Figure 4 presents the representative spectra for three different phases of Cu-In-Se system taken at the same excitation level at 8 K. The emission band shifts to lower energies for increasing In content in the crystals. The band gaps of these phases were estimated from the absorption measurements [7]. They were found to have quite similar values close to 1.3 eV at 10 K. This means that for the increasing In content in our phases the observed emission is due to deeper defect states. To determine the recombination mechanism responsible for the observed emission, the excitation dependence of the emission band has been measured. Figure 5 shows variation of the band maximum position with the excitation intensity. The dependence can be described as

$$I = I_0 10^{h\nu_{max}/\beta}$$

where I is the excitation intensity, $h\nu_{max}$ is the energy of the emission band maximum, β is the shift of the band maximum per decade of excitation.

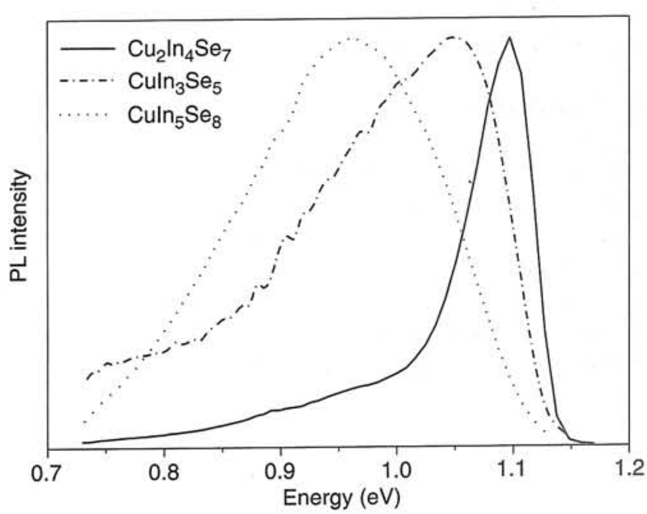

Fig. 4. Comparison of photoluminescence spectra of Cu-In-Se compounds taken at 8 K.

For all crystals studied we have found the values of β: 14.5 meV for $Cu_2In_4Se_7$, 16.5 meV for $CuIn_3Se_5$, and 33 meV for $CuIn_5Se_8$. Those values are much higher than those usually found for donor–acceptor transitions in semiconductors (typically 1–5 meV, Ref. 8). High values correspond to the, so-called, quasi- donor-acceptor transitions [8,9]. The

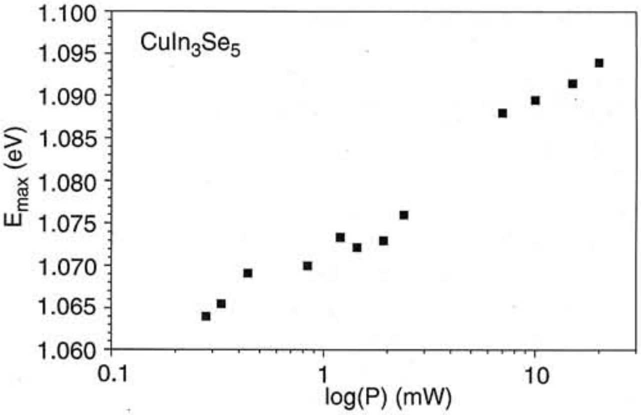

Fig. 5. Excitation intensity dependence of the emission band position.

transitions of this type are observed in highly compensated semiconductors where strong potential fluctuations due to electrical fields of defects are present. They have been observed in both $CuInSe_2$ [10] and $CuIn(Ga)Se_2$ [11]. According to Yu [8], their energy is given by

$$h\nu = E_g - (E_D + E_A) - 2\Gamma$$

where Γ is the average magnitude of the potential fluctuations. The parameter β parameter is proportional to Γ [8]. Since β is the measure of the average depth of potential fluctuations due to charged defects, the high values of β indicate significant degree of compensation of our crystals. The total concentration of ionised defects is the highest in layered $CuIn_5Se_8$ crystals.

4. Conclusions

For both Cu-In-Se and Cu-In-Ga-Se systems crystals of different compositions could be identified and separated in a Bridgman-Stockbarger grown ingots due to the segregation effect. Radiative recombination in the crystals of Cu-In-Se system of different compositions is governed by the quasi-donor-acceptor transitions. This indicates high degree of compensation of the studied materials.

Acknowledgements

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