CrossMark

Solid-state solutions of copper indium disulfide and zinc indium tetrasulfide: Growth, crystallography and opto-electronic properties

V.V. Bozhko [a,*], A.V. Novosad [a], G.E. Davidyuk [a], V.R. Kozer [a], O.V. Parasyuk [a], N. Vainorius [b], A. Sakavičius [b], V. Janonis [b], V. Kažukauskas [b,**]

[a] Lesya Ukrainka Eastern European National University, Avenue Voli 13, Lutsk 43025, Ukraine
[b] Semiconductor Physics Department and Institute of Applied Research of Vilnius University, Avenue Saulėtekio 9/3, LT-10222 Vilnius, Lithuania

ARTICLE INFO

ABSTRACT

Copper indium disulfide–zinc indium tetrasulfide solid solutions with different contents of zinc indium tetrasulfide, ranging from 4 to 16 mol% were grown by the horizontal modification of the Bridgman–Stockbarger method. Their structural properties were investigated by the X-ray analysis. Spectral dependences of their photoconductivity were analyzed at $T \approx 30$ K. In the single crystals with 8–12 mol% of zinc indium tetrasulfide the induced photoconduction phenomenon was observed. It could be explained by the model of three recombination and trapping centers with different capture cross sections. Indium vacancies V_{In} or substitutional defects Cu_{In} are possibly the fast recombination centers; meanwhile copper vacancies V_{Cu} act as the slow recombination centers. The presence of electrically active shallow defects was confirmed by the measurements of the temperature dependences of electrical conductivity and thermally stimulated currents of these samples with n-type conductivity.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The ternary $CuInS_2$ compound has the chalcopyrite structure and is promising for optoelectronic applications, e.g., for the fabrication of high efficiency thin film solar cells [1–3]. Its direct optical gap of about 1.55 eV is optimally placed relative to the maximum in the solar spectrum. It has high chemical and thermal stability that makes $CuInS_2$ a very attractive material for fabricating cheap and efficient solar elements [4,5]. Advancement of modern electronics requires development of semiconducting materials with precisely controllable properties. The promising way is, for instance, a purposeful combination of traditional materials

with similar structure in the solid alloys. The accurate control of material compositions enables the smooth variation of their optical and electrical properties. In this work solid alloys $CuInS_2$–$ZnIn_2S_4$ with 4, 8, 12, and 16 mol% $ZnIn_2S_4$ were investigated. They had n-type electrical conductivity. Unfortunately, the samples with as much as 16 mol% of $ZnIn_2S_4$ were the two-component ones, i.e., the crystallites of $ZnIn_2S_4$ were formed in the grown samples. The X-ray structural analysis was used to reveal the microscopic structure of the samples.

2. Experimental results and discussion

2.1. Growth and X-ray analysis of solid solutions based on $CuInS_2$

To find the regions of solid-phase solubility in the system $CuInS_2$–$ZnIn_2S_4$ five series of samples with

different contents of $ZnIn_2S_4$ were prepared. High-purity elements (with a purity grade not less than 99.99 wt%) were used for synthesis. The evacuated quartz ampules with the blends were placed into the furnace and heated up to 720 K. They were kept at this temperature for 48 h in order to assure the maximum binding of elemental Sulfur. Afterwards the ampules were heated up to 1470 K, and were kept at this temperature for 1 h. Later on they were cooled with a rate of 10–15 K/h down to the annealing temperature of 870 K. The annealing lasted for 500 h and was followed by the quenching in cold water. The obtained samples were analyzed by the powder X-ray diffraction (XRD), using the Cu Kα radiation diffractometer ДРОН 4-13.

The elementary cell parameters were calculated using the CSD software [6]. The solid-solution ranges were determined by analyzing variation of the elementary cell parameters (Fig. 1). It can be seen that solid solubility of $ZnIn_2S_4$ in the low temperature modification of $CuInS_2$ with chalcopyrite structure can be achieved in the ranges of 0–12 mol% $ZnIn_2S_4$ at the annealing temperature.

To study the mechanism of formation of the investigated solid solutions, we used the X-ray diffraction analysis. As an example, the experimental diffraction patterns in the solid compound $Cu_{3.14}Zn_{0.43}In_4S_8$ (12 mol% $ZnIn_2S_4$) are shown in Fig. 2. In $4a$ (0,0,0) crystallographic position the heterovalent substitution of Cu atoms by Zn atoms was found. In this case one divalent Zn atom replaces two monovalent Cu atoms. As the tetrahedral radii of Cu^+ and Zn^{2+} ions are very similar ($\sim$0.074 nm [7]), the substitution reaction can be written as $2Cu \leftrightarrow Zn + \square$, here $\square$ denotes the tetrahedral cavity. So, the vacancy type cationic defects within the chalcopyrite structure are formed, the density of which is proportional to the density of Zn atoms. Hence, one can expect that properties of the material would be affected by cation vacancies, which are not observed in the chalcopyrite $CuInS_2$ structure, as, e.g., in Ref. [8]. This leads to the reduction of the elementary cell dimensions with growing content of $ZnIn_2S_4$ (Fig. 1), i.e., compression of the tetrahedral cavities because
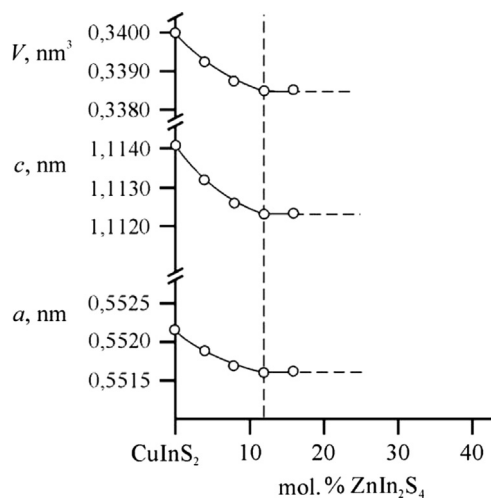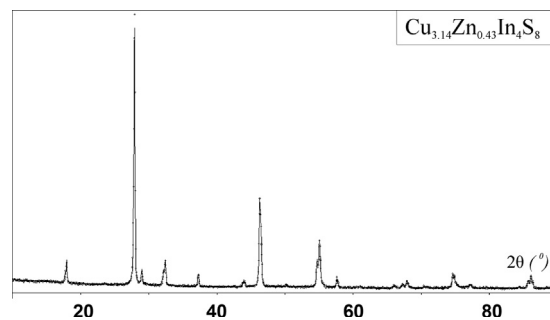

Fig. 2. Experimental diffraction patterns in the solid compound $Cu_{3.14}Zn_{0.43}In_4S_8$ (12 mol% $ZnIn_2S_4$).

Table 1
Crystallographic positions (CP), crystallographic occupation factors and the isotropic parameters of the atoms in the solid compound $Cu_{3.14}Zn_{0.43}In_4S_8$ (12 mol% $ZnIn_2S_4$).

Atom	CP	x	y	z	Crystallographic occupation factors	Isotropic parameters $B_{iso} \times 10^2$ (nm²)
M1	$4a$	0	0	0	0.79Cu + 0.11Zn + 0.11□	1.16(9)
In	$4b$	0	0	1/2	1	1.24(5)
S	$8d$	0.2228(9)	1/4	1/8	1	0.99(10)

Elementary cell parameters: $A = 0.55164(2)$ nm; $c = 1.11229(7)$ nm; $V = 0.33848(5)$ nm³.

of the lack of metal atoms in them. Crystallographic positions of the atoms and the interatomic distances in the solid compound $Cu_{3.14}Zn_{0.43}In_4S_8$ (12 mol% $ZnIn_2S_4$) are presented in Tables 1 and 2.

A horizontal version of the Bridgman–Stockbarger method [9] was chosen for the solid solution crystal growth. Initial compositions were selected within the homogeneity range of the solid solutions at 870 K (Fig. 1). The polycrystalline ingots preliminary synthesized from high-purity elements (better than 99.99 wt%) and weighting 8 g were sealed in evacuated quartz ampoules with conic ends and placed in a two-zone furnace inclined at an angle of 15°.

The technological data and equipment structure are described in detail in Refs. [9,10]. Both zones have independent temperature control and can be translated along the growth axis via a lead screw connected to a motor. The ampoule was fixed on a quartz rod and centered in the furnace tube. The longitudinal temperature profile was measured with an external thermocouple.

After heating to 1470 K, the melts were homogenized for 4 h by rotating the ampules with the attached quartz rod. Afterwards translation of the furnace started at a rate of 1 cm/day, by keeping the ampule stable. The temperature gradient at the crystallization front did not exceed 14 K/cm, assuming that the gradient at the interface is similar to the temperature profile of the furnace. After reaching the isothermal zone at 870 K, the crystals were annealed for 250 h and then cooled down to room

Fig. 1. Parameters of the elementary cells of the $CuInS_2$–$ZnIn_2S_4$ solid solutions depending on $ZnIn_2S_4$ content.