X-ray photoelectron spectroscopy method for obtaining a CuIn$_{0.95}$Ga$_{0.05}$Se$_2$ thin film: development of technology and a phase composition studying

Kh Kh Kalazhokov$^1$, Z Kh Kalazhokov$^1$, T M Gadjiev$^2$, M A Aliev$^2$, A M Ismailov$^2$, R M Gadjieva$^2$, A Sh Asvarov$^2$, R K Arslanov$^2$, E N Kozyrev$^3$, V I Filonenko$^3$ and R O Askerov$^3$

$^1$Kabardino-Balkarian State University (KBSU), 360000, KBR, Nalchik, ul. Gorky, 5, Russia
$^2$Amirkhanov Institute of Physics, Dagestan Scientific Center, Russian Academy of Sciences (RAS), 367003 Makhachkala, Russia
$^3$North Caucasian Institute of Mining and Metallurgy (State Technological University), NCIMM (STU), 362021, North Ossetia-Alania, Vladikavkaz, ul. Nikolaeva 44, Russia

E-mail: asker2005@rambler.ru

Abstract. A technology of two stage selenezation method in the carrier gas (nitrogen) stream of the reaction component (selenium) has been suggested for the CuIn$_{0.95}$Ga$_{0.05}$Se$_2$ thin film growing. Morphology and structure of the CuIn$_{0.95}$Ga$_{0.05}$Se$_2$ film have been studied by SEM and XRD methods. Phase compound of film material for the CuIn$_{0.95}$Ga$_{0.05}$Se$_2$ semiconductor solution has been studied by X-ray photoelectron spectroscopy method.

Thin films of CuInGaSe$_2$ with chalcopyrite structure are promising materials from the viewpoint of their application as absorbing layer in solar cells. However, depending on the technology method for obtaining these thin films, there is a dispersion of the electrophysical and photoelectric parameters of the photoconverters [1]. This is due to the phase composition and the structure of these films. A selenization method is a promising route in production of not only CuInGaSe$_2$ thin films, but also many semiconductor materials containing a volatile component in their composition [2, 3].

The aim of this work is a development of technology for obtaining and studying the phase composition of a CuIn$_{0.95}$Ga$_{0.05}$Se$_2$ semiconducting solution film using X-ray photoelectron spectroscopy.

For deposition of preliminary intermetallic CuIn$_{0.95}$Ga$_{0.05}$ films on the glass substrates a dc magnetron sputtering method was employed by using the “Watt AMK-MI” sputtering setup. The vacuum system of the sputtering setup consists from oil-free pumping tools (Anest Iwata ISP-500C dry spiral pre-vacuum pump, cryogenic high-vacuum pump – Cryogenics CryoTorr 8). For vacuum measurement a wide-range SS-100 vacuum gauge was used. An ion source is placed in the vacuum chamber that allows to carry out the final cleaning of the substrate before deposition and ionic assisting of the deposited layers. The target was a conductive disc of 40 mm in diameter and 4 mm in thickness. The target was synthesized by melting of initial elements placed in a quasi-hermetic container with using a high-vacuum furnace of SNVE 1.3-1/16. The process of the target synthesis was carried out at a pressure of 10 Pa and a temperature $T = 1100$ °C for 0.5 h.
Thin films of CuIn$_{0.95}$Ga$_{0.05}$Se$_2$ were obtained by two-step method of controlled selenization of copper-indium gallium layers, in a two-zone thermal diffusion device with the participation of the carrier gas (nitrogen) of the reaction component (selenium).

The surface morphology and the chemical composition of the film CuIn$_{0.95}$Ga$_{0.05}$Se$_2$ were studied using a scanning electron microscope LEO-1450 equipped with EDX. Chemical analysis of thin films showed that the film composition is quasi-stoichiometric and the inhomogeneity of the distribution of the components along the film surface exceed 3%. Figure 1 shows a micrograph of the film surface with a thickness of 1.3 μm. It is established that the film consists from micrograins, with the merging of micrograins into conglomerates.

![Figure 1. Microphotographs of CuIn$_{0.95}$Ga$_{0.05}$Se$_2$ films.](image)

X-ray diffraction studies were performed on the Empyrean Series 2 diffractometer (PANalytical, Netherlands) using Cu-K$_\alpha$ radiation (1.5405 Å) within scanning angles of 10–140 deg, using β-filter. Photography scheme was performed by Bregg-Brentano, geometry – 2θ. The phase identification was carried out by comparing experimentally obtained values of interplanar spacings ($d$) with the data of Joint Committee on Powder Diffraction Standard (JCPDS) and calculation methods.

Typical X-ray patterns for CuIn$_{0.95}$Ga$_{0.05}$Se$_2$ thin-films are presented in figure 2. There are replicable diffraction lines characteristic of chalcopyrite: (112), (013), (121) (220/024) (116/132) (040/008) (136/332) (224/228), and the line (112) has a maximum of intensity. According to data for interplanar distances a unit cell parameters for the synthesized films are calculated, in good agreement with JCPDS card.

![Figure 2. The X-ray diffraction pattern of CuIn$_{0.95}$Ga$_{0.05}$Se$_2$ films.](image)

The chemical composition was studied by XPS method on the X-ray photoelectron spectrometer of the K-Alpha system at the Center for Surface Physics, Nanosystems and Nanostructure Technology of the Kabardino-Balkar State University. During the experiments, a vacuum in the analyzer chamber was maintained at least of $4.5 \times 10^{-9}$ mbar. To compensate the charge displacement of the photoelectron
peak positions, a low-energy electron gun was used and the spectra were calibrated by the position of the C1s carbon line with a binding energy of 284.7 eV.

Before studying the composition, the surface was etched with argon ions until completely purified from atoms of chemisorbed oxygen and carbonaceous contaminants. Figure 3 shows overview spectrum for synthesized sample of CuIn0.95Ga0.05Se2, which mainly indicates next elements lines: doublet of copper Cu2p, indium In3d, selenium Se3d and peak of Ga2p, as well as intense peaks of carbon C1s and oxygen O1s.

The atomic concentrations of components obtained from analysis of the overview spectrum and high-resolution spectra are correlated with the chemical analysis data. To analyze the chemical states of elements forming the film material, the chemical shifts of the peaks Se3d, Cu2p, In3d and Ga3d were considered. Significant changes in the positions of the peaks that are not related to their surroundings can be observed due to the effect of charging the surface under X-rays. Therefore, Auger parameters have been calculated for these components, which are the sum of the kinetic energy of the Auger peak and the binding energy of an electron for given line. The Auger parameters obtained from the analysis are given in Table 1.

Table 1. The values of the binding energies of electrons and Auger parameters for material components of the Cu(In, Ga)Se2 film.

| Elements | PE-peak (eV) | Auger peak (eV) | \(\alpha'\) (eV) from [1] | Auger parameter \(\alpha'\) (eV) | Compounds       |
|----------|--------------|----------------|--------------------------|---------------------------------|-----------------|
| Se       | 3d: 54.1     | LMM: 1307.4    | 1361.5                   | 1361.5                          | CuSe2           |
| Cu       | 2p: 932.7    | LMM: 917.18    | 1849.8                   | 1849.8                          | CuSe2           |
| In       | 3d: 444.65   | MNN: 407.46    | 852.1                    | 852.4                           | In2Se3          |
| Ga       | 3d: 19.2     | LMM: 1063      | 1082.2                   | 1082.8                          | Ga2O3           |

The Auger parameters for Se and Cu elements are exactly the same as given in the [4] for CuSe2 phase. For indium, the Auger parameter practically coincides with the values recommended in the [4] and presumably, indium can form the In2Se3 compound.

In the case of gallium a partial overlap of Ga3d and In4d peaks occurs. Thus, the resulting photoelectron peak becomes asymmetrical. This problem is resolved by expanding the Gaussian function for this peak and obtaining the binding energy for Ga3d line that is necessary to determine the Auger parameter (figure 4). Apparently, all gallium is connected to oxygen lattice in the form of Ga2O3 [5].

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Figure 4. The high-resolution spectrum of the Ga3d line and the Auger line Ga LMM.

Morphology and structure of the CuIn$_{0.95}$Ga$_{0.05}$Se$_2$ film have been studied by SEM and XRD methods. Phase compound of film material for the CuIn$_{0.95}$Ga$_{0.05}$Se$_2$ semiconductor solution has been studied by X-ray photoelectron spectroscopy method.

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