Surface Composition of CIS Compound Affected by Xe+ Irradiation

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The paper presents the results of investigation of element composition of $CuInSe_2$ (CIS) compounds obtained by vertical Bridgman technique and on a glass substrate by the thermal deposition of Cu–In thin films with the subsequent annealing in selenium vapour. The depth profile distribution of elements in these samples using the Rutherford backscattering spectrometry/channeling technique in conjunction with the RUMP code simulation is also discussed.

1. Introduction

Among Cu-chalcopyrite semiconductors, the compound $CuInSe_2$ (CIS) is of great interest in photovoltaics as a result of acceptable energy gap width (1–2.4 eV), high optical absorption coefficient ($(3-6) \times 10^5$ cm^{-1}), high efficiency (20.3%) and radiation resistance [1–5]. These features give an opportunity to use CIS compound for production of inexpensive, operation stable and high-performance solar thin-film elements (STE).

As it is known [6–9], atomic concentration of elements in the CIS films depends on element synthesis conditions and so far a common method of absorbent layer production that would give the acceptable reproducible results has not been found. Besides, defect formation in this layer by both deposition and operation can result in degradation as well as solar elements efficiency rise [10–19]. This indicates insufficient investigation of defect creation in the $CuInSe_2$ films system and poor knowledge of these processes that does not allow to realize CIS potential in full.

In this paper the surface composition data of $CuInSe_2$ films produced by thermal deposition on the glass substrate are presented and the influence of irradiation on the elemental composition and the defect creation in CIS absorbing layers are discussed.

2. Experimental technique

The CIS films samples of group A were produced by thermal deposition [20]. The essence of the thermal deposition method is: (1) coating a substrate by Cu–In layers; (2) Cu–In layers are annealed in selenium vapour at different temperatures: (a) 260 °C — selenium saturation of metal layers, (b) 400 °C — synthesis

of $CuInSe_2$ compound, (c) 540 °C — promotion to the recrystallization and formation of single-phase compounds of the layers. After that the samples were cooled down to room temperature.

The Rutherford backscattering spectrometry method (RBS) was used to study the surface composition of our samples. Helium ions with the energy $E_0 = 2.5$ MeV and the 0° entrance angle were scattered. The scattering angle was 165°. The detector resolution was 15 keV, depth resolution ≈21 nm. To determine the surface composition and construct the compounds profile, the programme RUMP was used that helps to model an experimental RBS spectrum.

The group B samples were grown by the vertical Bridgman technique with the following diamond paste polishing in alumina suspension (0.5 μm). After that the samples were etched in 0.1% Br/methanol solution for 1 min and annealed for 30 s in vacuum at 300 °C to remove Se layer on the surface after etching [11].

One of the methods to determine the radiation resistance of products is to study influence of inert gases ions (with the mass equal to that of Xe or more) on the radiation damage accumulation and on the samples surface composition based on the CIS compound [11]. With that aim in view, the Rutherford backscattering/channelling (RBS/C) technique of helium ions with their channelling along $\langle 221 \rangle$ axis which helps to establish the localization of extrinsic and displaced atoms, to get radiation damage profiles, the depth and thickness of the damage layer was applied. In the experiment the incident He+ ion energy was 2 MeV, the angle of incidence was 0°, the scattering angle was 165°. The energy detector resolution was 25 keV, the depth resolution was ≈35 nm. To study the fluence dependence on CIS system composition of the group B, samples were affected by the 40 keV Xe+ ion irradiation with the fluences: 1×10^{13}, 3×10^{13}, 10^{14}, 3×10^{14}, 10^{15}, 3×10^{15} cm^{-2} [11]. To determine the composition of the subsurface layer samples (behind the damage layer, the analyzed depth was ≈65 nm), we used the iteration method [21].

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3. Results and discussion

Figure 1 presents the RBS He$^+$ ions spectra (experimental and model) from the surface of group A samples. According to the presented data within the accuracy of observation, the observed signals corresponded to helium ions scattering on In sublattice (channel ≈838), Se (channel ≈786) and Cu (channel ≈748). From the experimental spectra modelling, the compound depth profiles were obtained, and the deposited film thickness ≈3 μm was determined (Fig. 2).
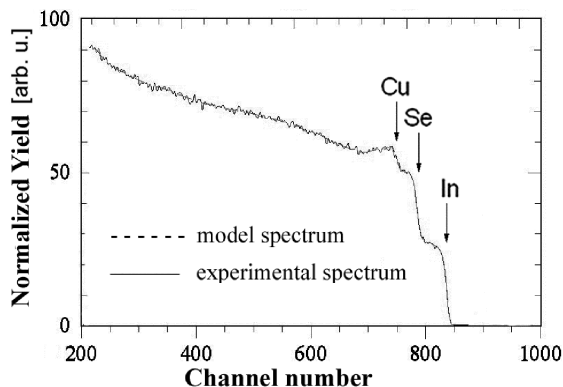

Fig. 1.   Experimental and model RBS He$^+$ ions spectra from the CIS sample surface (group A). The dashed line corresponds to the results calculated with a help of the model.
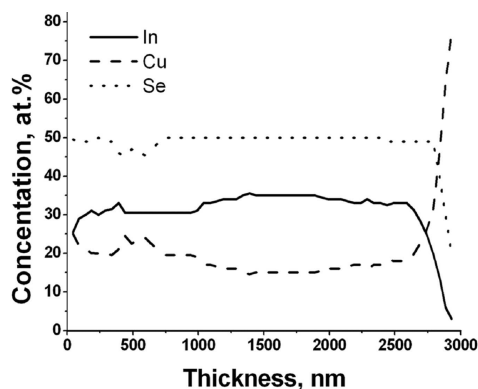

Fig. 2.   Depth profiles of Cu, In, Se concentration in the CIS sample (group A).

In spite of the fact that the elements profiles are irregular (Fig. 2), there are some layers of different thickness, where the concentration of elements remains constant. Indium concentration is constant at the depth range ≈0.44–0.94 μm (≈30.5 at.%) and ≈1.44–1.89 μm (≈35 at.%). The copper concentration does not change at the depth range ≈0.74–0.94 μm (≈19.5 at.%) and ≈1.44–1.89 μm (≈15 at.%). According to the presented data there was determined the layer at the depth from ≈1.44 to 1.89 μm where the concentrations of selenium (≈50 at.%), indium (≈35 at.%) and copper (≈15 at.%) are constant, and the surface composition

is not stoichiometric. Copper deficiency of the samples was determined by the depth increase. It could indicate the highly absorbing layers production [11]. At the depth ≈2.6 μm there could be seen elements redistribution in the surface composition: copper concentration increases, indium and selenium concentration decreases. One can suppose that the non-uniform distribution of elements concentration is primarily determined by the In–Cu layer deposition or the elements concentration redistribution (probably in the selenium saturation stage). During annealing in selenium vapour, copper concentration increases, indium and selenium concentrations decrease.

TABLE I

Elements concentration obtained from RBS and RBS/C spectra on the ≈65 nm depth for group A and B unirradiated (virgin) CIS samples.

	Concentration [at.%]		
	Cu	In	Se
group A	22	29	49
group B	41	16	43

In Fig. 3 the RBS/C spectra from the 40 keV Xe$^+$ implanted CIS group B samples are presented. The peaks indicate copper (channel ≈311), selenium (channel ≈327) and indium (channel ≈348). Surface composition of the samples (Table I) irradiated by xenon ions was computed at the depth ≈65 nm in the area behind the peaks characterized by the most surface damage rate.
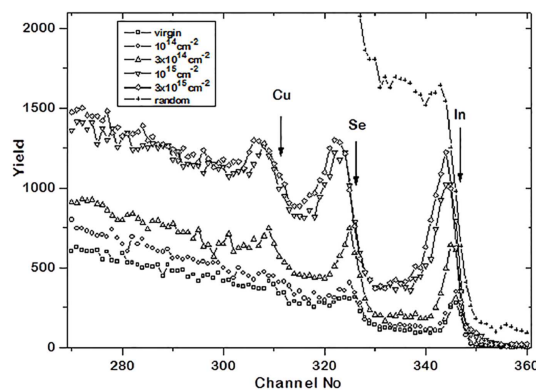

Fig. 3.   RBS/C spectra of He ions from the CIS crystal (group B) irradiated by 40 keV Xe$^+$ ions with different fluences [11].

Based on the iteration method of analysis it was established that the surface composition is characterized at this depth by the other elements content: Cu — 41 at.%, In — 16 at.%, Se — 43 at.%. The indium deficiency is observed. Besides with the fluence increase, In and Se concentrations increase from 15 and 39 at.% at $\Phi = 10^{14}$ cm^{-2} to 19 and 45 at.% at $\Phi = 10^{15}$ cm^{-2}, respectively. Then we can see that the selenium concentration increases to 50 at.% with the fluence increase (3×10^{15} cm^{-2}), and the indium concentration decreases
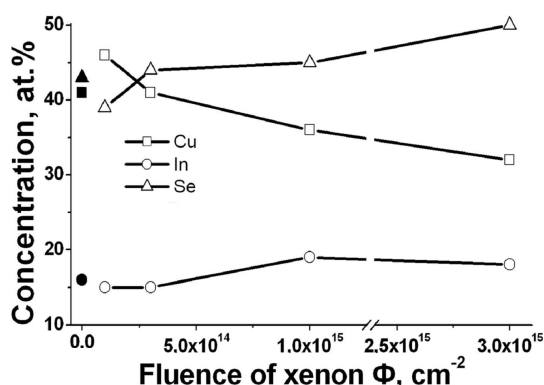
Fig. 4. Cu, In, and Se atomic surface concentration dependence on the Xe$^+$ fluence (full symbols — elements concentration in the unirradiated CIS crystal, group B).

a little (18 at.%) by the same fluence. Fluence increase leads to the copper concentration decrease from 46 at.% ($\Phi = 10^{14}$ cm^{-2}) to 32 at.% ($\Phi = 3 \times 10^{15}$ cm^{-2}) (Table II, Fig. 4).

TABLE II

Surface composition of CIS samples (group B) for different 40 keV Xe$^+$ ion fluences.

Xe$^+$ fluence [cm^{-2}]	Concentration [at.%]		
	Cu	In	Se
virgin	41 ± 4	16 ± 2	43 ± 4
1×10^{14}	46 ± 4	15 ± 1	39 ± 3
3×10^{14}	41 ± 3	15 ± 1	44 ± 3
1×10^{15}	36 ± 2	19 ± 1	45 ± 2
3×10^{15}	32 ± 2	18 ± 1	50 ± 2

Thereby by fluence 10^{13} cm^{-2} Cu concentration in the CIS-system composition increases, indium and selenium — decreases obviously as a result of Se evaporation at the time of sample irradiation beginning. Due to the fluence increase, the copper deficiency of the CIS-system near-surface layer takes place, In and Se concentration increases. This phenomenon can be explained by copper atoms sputtered out of the crystal lattice by the xenon ions irradiation or primordial defect formation by the samples growth (Cu atoms leave the interstitial position).

Comparing the data of CIS group A and B sample films, surface compositions of Cu, In and Se concentration misfit were established. According to the data in Table I, Se concentration differs by 12%, In concentration — 45%, Cu concentration — 46%.

Such difference results from what follows. By the absorbing layer formation (both during film growth and by etching or surface annealing) [11] structure damage of sample near-surface, as can be seen in Fig. 3, there is a 65 nm thick layer with the structure defects which shade the true value of the elements concentration behind the damage layer. During ion channeling experiment the ions experience the strong scattering on these defects. As it is shown in Refs. [17, 19], the defects in

CIS films are related with In and Se vacancy or with the In substitution by Cu atoms that leads to the copper concentration increase. As a result of the films irradiation with the 40 keV Xe$^+$ ions (fluence 1×10^{14} cm^{-2}) a defect formation enhancement occurs with the copper concentration increase to 46 at.% (Table II). Following further fluence increase the Cu concentration decreases (32 at.% at 3×10^{15} cm^{-2}), which indicates a damage self-healing effect [11].

4. Conclusions

In the paper the Cu–In layers thermally deposited on glass and subsequently annealed in selenium vapour were studied by RBS. Using the iteration method depth profiles of Cu, In, and Se atoms were calculated. It was established that the elements in the films are distributed irregularly. But there is a layer at the depth $\approx$1.44–1.89 μm from the film surface with the constant Cu, In and Se distributions (15 at.%, 35 at.%, and 50 at.%, respectively). Copper deficiency of films was found up to the depth $\approx$2.6 μm, after that the redistribution of elements concentration takes place. This is related with the method of films formation.

The surface composition of the CIS crystals grown by the Bridgman technique was studied by means of the RBS/C method. It was found that because of defect formation during the sample preparation the elements concentration was as follows: Cu — 41 at.%, In — 16 at.%, and Se — 43 at.%. After ion irradiation, the surface composition change is observed at the fluence 10^{14} cm^{-2} (Cu — 46 at.%, In — 15 at.%, and Se — 39 at.%). The noticeable copper concentration increase is associated with the atoms leaving the interstitial position, and the selenium concentration decrease is determined by its evaporation at the initial moment of irradiation. With the further fluence increase, the elements concentration changes, too — copper decreases, selenium — increases. This can be explained by little damage self-healing.

The values mismatch of elements concentration for the RBS and RBS/C spectra obtained for the samples produced by different methods is explained by the structure defects in the form of copper atoms sputtered out of the crystal lattice nodes, the defects layer which shades the true value of the elements concentration behind the damage layer.

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