STRUCTURAL AND OPTICAL PROPERTIES OF THIN FILMS OF Cu(In,Ga)Se$_2$ SEMICONDUCTOR COMPOUNDS

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The chemical composition of Cu(In,Ga)Se$_2$ (CIGS) semiconductor compounds is analyzed by local x-ray spectral microanalysis and scanning Auger electron spectroscopy. X-ray diffraction analysis reveals a difference in the predominant orientation of CIGS films depending on the technological conditions under which they are grown. The chemical composition is found to have a strong effect on the shift in the self-absorption edge of CIGS compounds. It is shown that a change in the relative proportion of Ga and In in CIGS semiconducting compounds leads to a change in the band gap E$_g$ for this material in the 1.05–1.72 eV spectral range at 4.2 K.

Keywords: *chalcopyrite semiconductors, chemical composition, absorption coefficient, x-ray diffraction analysis, structure.*

Introduction. Recent progress in the creation of solar energy converters based on four-component Cu(In,Ga)Se$_2$ (CIGS) semiconductors with a chalcopyrite structure has stimulated research on the further development of technologies for growing ever more perfect and efficient thin film structures [1–4]. A thin-film CIGS solar cell with an area of 0.42 cm^2 with an efficiency of ~19.9% has been created in the laboratory and this is the current record for known semiconductor thin film materials [1]. Numerous studies in recent years have shown that the most appropriate concentration of gallium atoms substituting for indium atoms in the four-component chalcopyrite compound CIGS is in the range of 3–10 at. %. It has been found that energy photoconversion in CIGS solar cells is optimal for a Ga/(Ga+In) ratio of ~0.2–0.4 [1, 2]. Improvements in the technology for fabricating solar cells, which are currently underway at various research centers, have led to ZnO/GdS/CIGS/Mo/glass heterostructures with a stable efficiencies of 14–19%. It is to be expected that further optimization of the chemical structure of CIGS compounds with a chalcopyrite structure and a reduction in the concentration of growth defects owing to deviations of the structure from ideal stoichiometry will facilitate further improvements in the parameters of the solar cells, including their efficiency. Studies of the structure of CIGS compounds and their electronic properties are important for establishing the nature of the growth defects at an atomic level, and are useful, generally, for increasing our knowledge of the actual crystalline structure of complicated multicomponent compounds, which will undoubtedly aid in improving the technology for the manufacture of solar cells based on these compounds. Thus, the basic task of this paper is to establish how the energy band structure in the region of direct allowed transitions behaves as a function of the chemical composition of CIGS compounds, i.e., of the ratio of the primary elements Ga and In over a wide range of concentrations.

Experiment. The process of obtaining structurally perfect films of the required composition was optimized here using standard technologies for growing thin films of semiconducting CIGS compounds on glass substrates based on thermal vaporization of the element Cu, In, Ga, and Se [5–7] or magnetron deposition of metallic layers of Cu, In, and Ga, followed by the two-stage addition of selenium at temperatures of 300–580°C [8]. For this purpose CIGS films were produced under various technological conditions directly on glass substrates as well as on glass substrates

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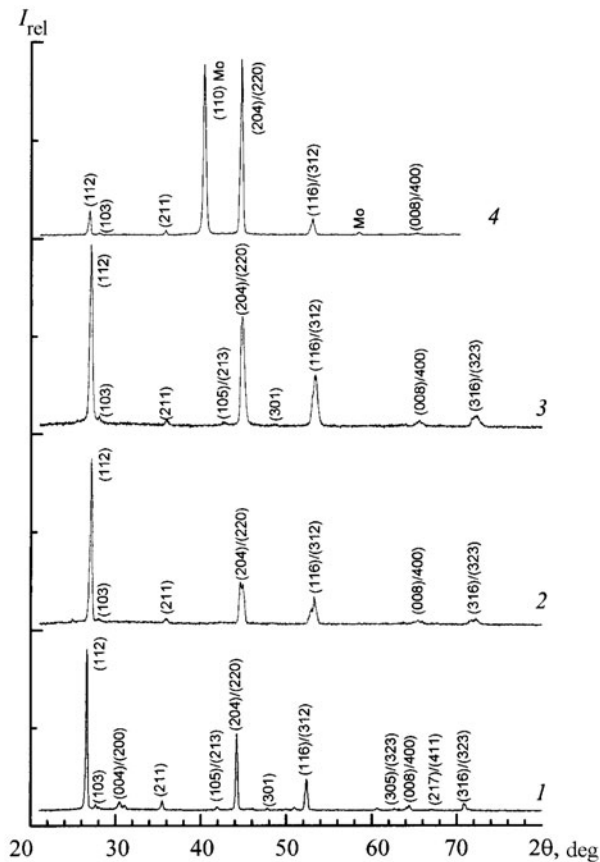
Fig. 1. X-ray diffraction spectra of thin films of semiconducting compounds grown on glass substrates: (1) CuInSe$_2$; (2, 3) Cu(In,Ga)Se$_2$, samples 5 and 6; (4) Cu(In,Ga)Se$_2$/Mo.

coated with a layer of molybdenum for electrical contact with the solar cells. The thickness of the base layer of CIGS was 1.0–1.5 µm. The chemical composition of the CIGS films was determined by Auger electron scanning spectroscopy with layer-by-layer etching and analysis of the distribution of elements over the depth of the films, as well as by local x-ray spectral microanalysis (XSA). X-ray structural analysis of the thin CIGS films was carried out with a DRON-3M x-ray diffractometer in monochromatized CuK$_\alpha$ radiation. The x-ray scan was taken continuously over angles $2\theta \sim 20$–80°.

Transmission and reflection spectra at wavelengths of 0.2–3.0 µm were recorded on a Carey-500 Scan UV-Vis-NIR (Varian, USA) spectrophotometer, as well with an MDR-3U diffraction grating monochromator with a mirror objective focal distance of $f = 0.6$ m and a 600 lines/mm grating. The optical detectors were liquid nitrogen cooled PbS photoresistive cells or InGaAs p-i-n photodiodes (Hamamatsu, Japan). The signals from the detectors were processed with narrow band amplifiers and converted into dc signals by synchronous detection followed by analog to digital conversion. The light source for measuring the transmission and reflection spectra was a 100 W tungsten halogen incandescent lamp. The optical spectra were corrected for the spectral sensitivity of the detectors, the instrument function of the monochromator, and the spectral characteristics of the tungsten lamp. The transmission spectra at low temperatures were recorded by direct immersion of the samples in the coolant, liquid nitrogen (~78 K), or liquid helium (4.2 K). Other features of the technique have been described elsewhere [9].

Discussion. As an example, Fig. 1 shows x-ray diffraction spectra with the lines of the main identified phases indicated for four films. Spectrum 1 of Fig. 1 is the x-ray diffraction spectrum of a three component chalcopyrite compound CuInSe$_2$ (CIS). The CIS film, grown directly on a glass substrate, was a standard for comparative analysis

of the structural quality of the material with other, more complex, four component films of CIGS created by similar technologies [8]. The major reflections correspond to the chalcopyrite phase of the compound CIS. It is important to note that the intensity ratio of the major reflections, $I_{(112)}/I_{(204,220)}$ is ~2 and is close to the characteristic ratio for randomly oriented CIS powders [10]. We believe that this indicates a high quality of the deposited CIS films; this is also confirmed by the observation, in their luminescence spectra, of luminescence excitation and absorption in narrow lines of free excitons A and B at 4.2 K [11]. The x-ray diffraction spectra 2–4 contain narrow reflections of the CIS phase for CIGS films formed directly on glass substrates (spectra 2 and 3) and, in addition to the CIS phase, reflections from a molybdenum film on glass (spectrum 4). The overall shape of the x-ray diffraction spectra, the high intensity of the reflections, and the absence of reflections from other phases, as well as the small half width of the main reflections, are indications of high quality in the films made of the four component semiconducting compound CIGS and confirm the presence of a crystalline lattice with a chalcopyrite structure in the grown films. Furthermore, as can be seen in Fig. 1, texturing can be seen that depends on the technological conditions under which the CIGS films were grown. Thus, for example, for a film grown on molybdenum a strong predominant texturing occurs for the (204)/(220) reflexes with an intensity ratio $I_{(112)}/I_{(204,220)}$ ~ 0.13 for the main reflections. For the CIGS films grown on glass, the intensity ratio of the reflections is ~1.62 (spectrum 3) and 3.9 (spectrum 2). Thus, we have seen a different degree of predominant texturing in polycrystalline CIGS films grown under different technological conditions, as has been observed in other experiments [7, 12–14].

It has been shown [14] that the most efficient (with an efficiency of ~19.5%) solar cells on CIGS films have a predominant orientation in the <204/220> direction with an intensity ratio $I_{(204,220)}/I_{(112)}$ ~ 1.94 [15] or 15.4 [14] for the reflections. Here predominant texturing during growth of CIGS films can be attained using an excess (at a level of 3–4 times) pressure of the selenium vapor over that of the metal vapors [7]. Our results show that predominant texturing with an intensity ratio $I_{(204,220)}/I_{(112)}$ ~ 8 for the reflections can be realized during growth of CIGS films with a selenium pressure exceeding that of the metals by only a factor of 2 when high quality adhesion of the molybdenum layer on the glass substrate is attained. Reducing the pressure threshold for the selenium vapor above the pressure for the metal is important from a technological standpoint for further improvement of the techniques for growing structurally perfect CIGS layers and, accordingly, obtaining solar cells based on them which have a higher photoconversion efficiency.

As an example, Fig. 2a shows transmission spectra of the chalcopyrite compound CIGS (see Table 1) recorded with a spectral resolution of ~0.2 meV at temperatures of 4.2, 78, and 300 K. Sample No. 6 has a relatively high transmission, 50–70%, at long wavelengths, and a mildly sloping intrinsic transmission edge at 1.15–1.35 eV with a CIGS film thickness of ~1.5 μm. The reflectivity of the films at 0.8–1.7 μm was R ~ 0.15. As the temperature in the experiment is reduced, the fundamental absorption edge shifts toward higher energies, as is typical for straight band CIGS semiconductors. The optical absorption coefficient $\alpha(h\nu)$ was calculated using the formula [16]

$$\alpha = \frac{1}{d} \ln \frac{\sqrt{(1-R)^4 + 4T^2 R^2} + (1-R)^2}{2T}, \qquad (1)$$

where R is the reflectivity, T is the transmission coefficient, and d is the film thickness. For semiconductors with a straight band structure, the absorption coefficient has the following spectral dependence [17]:

$$\alpha(h\nu) = A(h\nu - E_g)^{1/2}, \qquad (2)$$

where A is a constant and E_g is the band gap. Figure 2b shows the spectral dependence of the square of the transmission coefficient calculated using Eqs. (1) and (2) for sample 6 at different measurement temperatures. The band gap E_g was determined by extrapolating the (steep) slope of the $\alpha^2(h\nu)$ curve to the abscissa; for 4.2, 78, and 300 K it was equal to 1.235, 1.230, and 1.214 eV, respectively. It should be noted that our values for the temperature shift in the edge of the fundamental absorption for CIGS film, ~25 meV, are in good agreement with data on the temperature shift of the exciton absorption and luminescence edge of CuInSe$_2$ [18, 19]. Figure 2a′ shows optical transmission spectra of sample No. 5 at temperatures of 4.2, 78, and 300 K. For this sample, the long wavelength transmission is somewhat lower, 40–50%, and the fundamental absorption edge is steeper than for sample No. 6. The variation in the
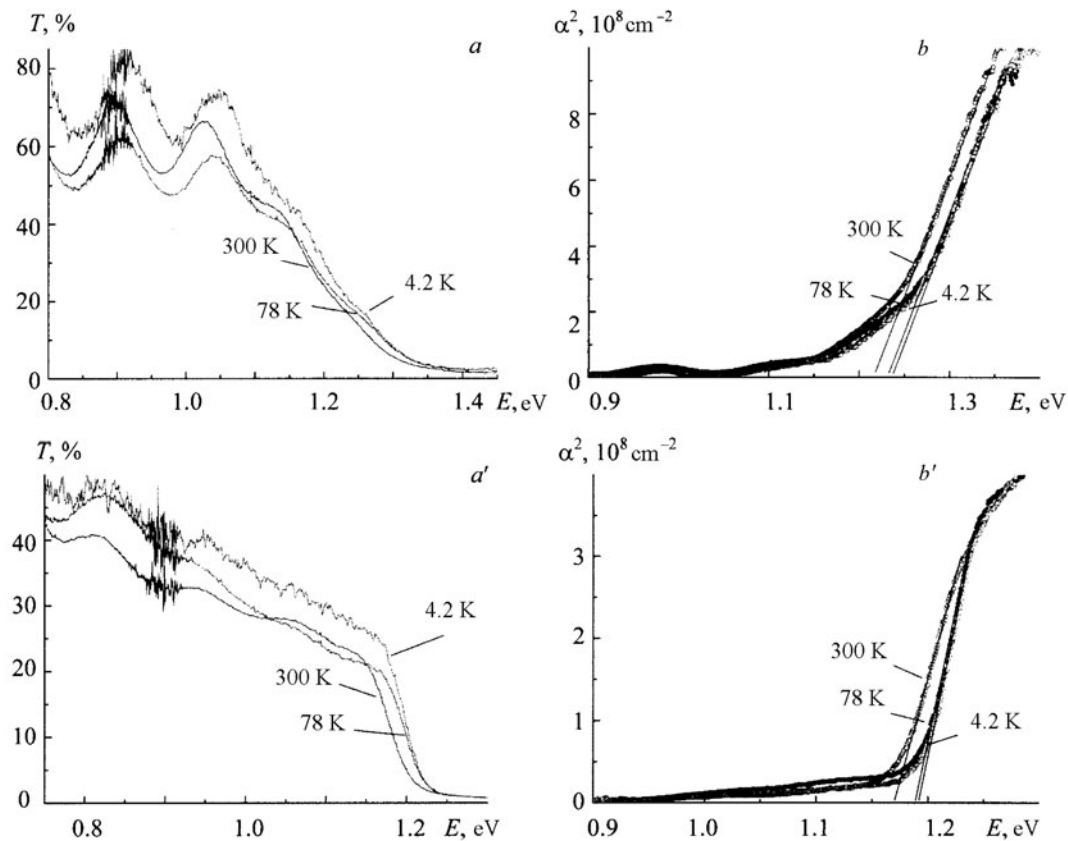
Fig. 2. Transmission (a, a′) spectra and calculated spectral variations of the square of the absorption coefficient (b, b′) at different temperatures for CIGS films: sample 6 (a, b), sample 5 (a′, b′).

square of the absorption coefficient with photon energy, calculated using Eqs. (1) and (2), is shown in Fig. 2b′. Extrapolation of the slope of $\alpha^2(h\nu)$ to the energy axis for sample 5 yields E_g = 1.191, 1.187, and 1.169 eV at temperatures of 4.2, 78, and 300 K. Here the relative shift in the fundamental absorption edge for the CIGS films over temperatures of 4.2–300 K is ~21 meV, which also agrees with the relative shift in the fundamental absorption and exciton luminescence edge of the base semiconductor compound $CuInSe_2$. Transmission spectra were also measured for a number of other samples with different proportions of the elements Cu, In, Ga, and Se. The basic results of these measurements are shown in Table 1. The concentrations of Cu, In, and Ga were determined by scanning Auger electron spectroscopy (SAES) followed by averaging over all stages of layer-by-layer etching (~20 layers), as well as by XSA at three points on the sample surface, which values were also averaged. Note that the results of the XSA measurements and those by SAES were approximately the same.

As Fig. 2 and Table 1 show, varying the relative percent content of the impurity atoms In and Ga in CIGS thin films causes a significant change in the band gap, the numerical value of which determines the efficiency of solar cells produced using this semiconductor compound with an optimum composition Ga/Ga+In ~ 0.3 [1]. The experiments showed that, even under essentially identical conditions for creating the base layers of CIGS for solar cells (rates of deposition of the metallic precursors Cu, In, and Ga, and of Se atoms, substrate temperature, selenium vapor pressure, etc.), under actual conditions a significant change in the band gap E_g of the material can result, with a change in the steepness of the intrinsic absorption edge, as well as in the absorption and transmission coefficients. This requires appropriate monitoring of E_g in test structures, both to ensure stability of the technological deposition process, and to provide a systematic estimate of the steepness of the absorption edge, which determines the spectral dependence of the photocurrent response of solar cells in the IR.
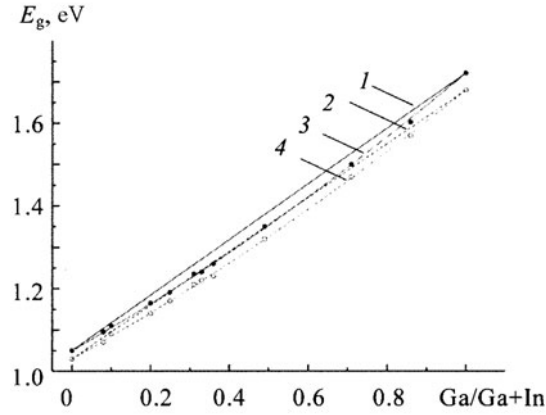
Fig. 3. The band gap E_g as a function of the composition of CIGS compounds (the ratio Ga/Ga+In) at 4.2 K (1, 3) and 300 K (2, 4). The points are experimental data; 1 and 2, linear approximations $E_g^{CIGS} = E_g^{CIS} + ax$; 3 and 4, quadratic approximations $E_g^{CIGS} = E_g^{CGS}x + E_g^{CIS}(1-x) - bx(1-x)$.

TABLE 1. Elemental Composition (at. %) According to Scanning Auger Electron Spectroscopy Data and the Band Gap E_g (eV) of CIGS Films on Glass Substrates at Different Temperatures

Sample No.	Cu	In	Ga	Se	Ratio Ga/Ga + In	E_g	
						300 K	4.2 K
1	25.2	24.9	0	49.9	0	1.03	1.050
2	24.8	23.8	2.1	49.4	0.08	1.07	1.095
3	25.3	22.1	2.4	50.2	0.10	1.09	1.110
4	25.0	19.9	5.1	50.0	0.20	1.14	1.165
5	25.5	18.1	6.2	50.2	0.25	1.17	1.191
6	25.2	16.4	7.4	51.0	0.31	1.21	1.235
7	23.9	16.1	7.9	52.1	0.33	1.22	1.240
8	25.7	16.1	9.1	49.1	0.36	1.23	1.260
9	24.8	12.8	12.3	50.1	0.49	1.32	1.350
10	25.3	7.8	19.1	47.8	0.71	1.47	1.500
11	24.9	3.7	23.2	48.2	0.86	1.57	1.602
12	25.1	0	24.8	50.1	1.00	1.68	1.722

Figure 3 illustrates the dependence of the variation in the band gap for CIGS films on the ratio of the concentration of the main elements Ga and In obtained from optical absorption data at 4.2 and 300 K. The experimental data can be fitted by the parabolic function

$$E_g^{CIGS} = E_g^{CGS}x + E_g^{CIS}(1-x) - bx(1-x),\qquad(3)$$

where $E_g^{CIS} \approx 1.050$ eV, $E_g^{CGS} \approx 1.722$ eV, and $b \approx 0.13$ eV (b is the deflection coefficient) for 4.2 K and $E_g^{CIS} \approx 1.03$ eV, $E_g^{CGS} \approx 1.68$ eV, and $b \approx 0.12$ eV for 300 K. As a comparison, Fig. 3 includes linear approximations for the band gap of CIGS compounds corresponding to the formulas $E_g^{CIGS} = E_g^{CIS} + 0.672x$ at 4.2 K and $E_g^{CIGS} = E_g^{CIS} + 0.65x$ at 300 K. The nonlinear dependence of E_g on the Ga and In contents in CIGS may be caused by a statistically disordered distribution of the components of the compounds over the points of the corresponding sublattice. It

should be noted that our deflection coefficient $b \approx 0.13$ eV at 4.2 K is the lowest of the known values for films and monocrystals of CIGS; this indicates growth of relatively high quality films in which the effects of a chaotic distribution of the components of the compound shows up no more strongly than in the earlier papers [20–23].

Conclusion. Local x-ray spectral microanalysis and scanning Auger electron spectroscopy have been used to analyze the chemical composition of grown $Cu(In,Ga)Se_2$ films. X-ray diffraction analysis has shown that the $Cu(In,Ga)Se_2$ films have a chalcopyrite structure and a single phase composition. When the films of $Cu(In,Ga)Se_2$ were deposited on a molybdenum film, the diffraction spectra contained reflections from a molybdenum phase. The intensity ratio of the main reflections for standard films of $CuInSe_2$ grown a glass substrate was $I_{(112)}/I_{(204,220)} \sim 2.0$, chose to the ratio characteristic of polycrystalline $CuInSe_2$ powders. The degree of texturing of $Cu(In,Ga)Se_2$ films was found to depend on the technological conditions under which they were grown.

The absorption coefficient in the region of the fundamental absorption band of semiconducting $Cu(In,Ga)Se_2$ compounds grown on glass substrates was determined from measurements of the optical transmission and reflection. The chemical composition (the ratio Ga/Ga+In) was found to have a strong effect on the shape of the spectral dependence of the absorption coefficient in the region of the fundamental absorption edge. The experimental data on the shift in the edge of the fundamental absorption edge with changes in the composition of the $Cu(In,Ga)Se_2$ compounds can be described by a parabolic dependences with a deflection coefficient $b \sim 0.13$ eV at 4.2 K; this is indicative of a low degree of randomness in the distribution of the components of the compound.

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