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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

ELECTRIC AND PHOTOELECTRIC PROPERTIES OF SOLAR CELLS BASED ON $CuInSe_2$-$GaInSe_2$ THIN FILM HETEROJUNCTİONS

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The work is completed at "Physics and electronics of non-crystalline semiconductors" laboratory of the Institute of Physics of the Ministry of Scicence and Education Republic of Azerbaijan.

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INTRODUCTION

Relevance of the research topic. The presented dissertation is focused on the researches for increasing the efficiency of solar energy converter systems and reducing their production costs. Thin films of $CuInSe_2$, $GaInSe_2$, $CuInS_2$, $GaInS_2$, $CuInGaSe_2$, $Cu(In,Ga)(Se,S)_2$ with semiconductor properties and heterojunctions based on these compounds are used as absorber layers in solar converters, which are considered the most promising type of alternative energy in the modern world. Among $A^1B^3C^2_6$ compounds, triple compounds of Cu ($CuInSe_2$, $CuInS_2$, $CuGaSe_2$, $CuGaS_2$) and solid solutions play a special role in photovoltaic technology. For this reason, interest in their production has increased. It is known that the value of the width of the forbidden zone of the material (E_g) plays an important role in the efficiency of the device. Chalcopyrite-based materials - $CuInSe_2$, $CuInS_2$, $CuGaSe_2$ and their alloys, with a bandgap value ranging from 1.05 to 1.7 eV, are widely used for solar cells. In order to be useful for photogalvanic applications, the device must convert solar energy into electrical energy, the material used should be cheap and the technology used should be harmless, and the manufacturing method of the device should be cheap, fast, simple and environmentally friendly.

Studying the photoelectric and optical properties of the widely studied photosensitive $CuInGaSe_2$ (CIGS) material for the solar cell is an urgent issue of scientific and practical importance. These materials are widely used in the production of third-generation solar inverters, which have a low cost. The width of the band gap (E_g) of the studied $CuIn_{1-x}Ga_xSe_2$ material varies between 1.04 and 1.68 eV, depending on the value of x. It should be noted that the width of the forbidden zone can be changed by adding other group III (for example, Al) or group VI elements (for example, S and Te) to the composition of the material. One of the ways to increase the efficiency of thin-film $CuInGaSe_2$-based solar cells (CIGS) is to determine the optimal value of the band gap width of the material by changing the value of the band gap width, at which the solar cell efficiency (GE) is maximal for this structure of the solar cell.

Until now, various heterostructures have been created based on $Cu(In,Ga)(Se,S)_2$ materials. $Cu(In,Ga)(Se,S)_2$ compounds can be used to increase the conversion efficiency. In addition, it is possible to control the band gap value of these absorbing layers by changing the Ga/(In+Ga) ratio. Controlling this ratio plays an important role in increasing the efficiency of $Cu(In,Ga)(Se,S)_2$-based solar cells. At present, multicomponent compounds of the $Cu(In,Ga)(Se,S)_2$ group, which have the necessary properties to create high-efficiency converters that convert electromagnetic radiation into electrical energy, attract the attention of researchers. The value of the forbidden zone of these compounds varies in a wide range (~ 1.0 - 2.35 eV), and the absorption coefficient is in the range ($\alpha \sim 10^5$ cm^{-1}).

Research purpose and objectives of the research:

Obtaining heterojunctions on the basis of complex composition thin films of the $CuIn_{1-x}Ga_x(Se_{1-y}S_y)_2$ system, determining the possibilities of obtaining charge transport mechanisms and solar cells as a result of a complex study of electrical and photoelectric properties.

In order to achieve the set goal, the following works have been carried out.

1. Triple $CuInSe_2$, $CuInS_2$, $CuGaSe_2$ and $CuGaS_2$; development of synthesis methods of fourfold $CuInGaSe_2$ and $CuInGaS_2$, fivefold $CuIn_{1-x}Ga_x(Se_{1-y}S_y)_2$ compounds. Study of the crystal structure of the obtained compounds by X-ray structure and X-ray phase analysis.
2. Development of methods of obtaining Cu-In precursors obtained on different substrates by the method of magnetron sputtering of Cu+In-containing target of $CuInSe_2$ and $CuInS_2$ thin films obtained by thermal method by thermal treatment method in Se(S) gas environment.
3. Development of the technology of production of $CuInGaSe_2$, $CuInGaS_2$ and $CuInGa(Se,S)_2$ layers according to the

deposition method of Cu-In-Ga precursors obtained on glass and flexible metal foils (titanium, molybdenum, aluminum, stainless steel) by magnetron sputtering in Se, S, and Se+S gas environments.

4. Obtaining of $CuIn_{1-x}Ga_xSe_2$, $CuIn_{1-x}Ga_x(Se_{1-y}S_y)_2$ thin films with complex composition according to the sputtering method of targets consisting of $CuInSe_2$, $CuGaSe_2$, $CuInS_2$ and $CuGaS_2$ and $CuInGaSe_2$ systems from two magnetrons whose magnetic systems are shifted towards each other.

5. Complex investigation of temperature dependence of x-ray, electrical and photelelectric properties of thin layers.

6. Buffer layer of ZnO thin film for solar cell, development of the technology for obtaining ZnO and ZnO:Al thin films for the use of the ZnO:Al top layer as a contact material.

7. Determining the nature of defects formed as a result of impinging different doses of accelerated, high-energy Ar^+ ions on the newly formed layer in different regimes of magnetron sputtering. Main depth profiles, morphology, microstructure and phase analysis of $CuInGaSe_2$ layers fabricated on various flexible metal foils(titanium, molybdenum, aluminum, stainless steel).

8. Preparation of $p\text{-}Cu(In_{1-x}Ga_{x)})(Se_{1-y}S_y)_2/n\text{-}GaAs$ heterojunctions by magnetron sputtering using monocrystalline n-GaAs substrate, study of electrical and photoelectric properties of obtained heterojunctions.

Research methods:

The research objects were synthesized under vacuum conditions by the standard method. The crystal structure of the obtained compounds was analyzed by X-ray diffraction using a Siemens D5000 diffractometer with CuKα radiation and a CAMECA SX-100 device. Raman scattering measurements of $CuInSe_2$ thin films, which are the object of research, were performed on a DILOR XY 800 spectrometer using polarized light at room temperature. An argon laser with a wavelength of 514.5 nm was used as a light source.

$CuInGaSe_2$ thin films were obtained by the sputtering method from two magnetrons with shifted magnetic systems at the УВН-71 device.

The surface morphology and microstructure of the studied thin films were analyzed using a JEOL 6400 SEM microscope and AFM. The optical parameters of these layers were determined from the transmission (T) and reflection (R) spectra in the 200-3000 and 190-3300 nm regions of the spectrum at room temperature using a Carry 500 Scan UV-VIS-NIR spectrometer. The resistivity of the layers was measured by the Van der Pauw method.

The Rutherford backscattering technique was used to study the depth concentrations of defects created by different doses of 30 keV Ar ion beam in Cu, In, Se sublattices of $CuInSe_2$ monocrystal with high structural quality.

The main provisions for the defense:

1. Dependence of the forbidden band width value on the In/(In+Ga) ratio in $CuInGaSe_2$ thin films.
2. Dependence of the value of the band gap width of the material from the reflection and transmission spectra of $CuInGaSe_2$ layers obtained on glass substrates.
3. Fabrication of $CuIn_{1-x}Ga_xSe_2$-based varying bandgap thin films.
4. Determination of the variation of the width of the forbidden zone of $Cu(In_{1-x}Ga_x)(Se_{1-y}S_y)_2$ thin films depending on the amount of Ga and S in the material.
5. Investigation of photosensitivity in p-$Cu(In_xGa_{1-x})(Se_{1-y}S_y)_2$/n-GaAs heterojunction.

Scientific novelty of the research:

- For the first time, $Cu(In_xGa_{1-x})(Se_{1-y}S_y)_2$ thin films were obtained by sputtering from two magnetrons with the magnetic systems shifted towards each other. Depending on the technological modes, as a result of layer thickening, the value of the width of the forbidden zone of these layers changes depending on the composition. It was determined that depending on the selection of these regimes, the width of the forbidden zone of the composition increases or decreases depending on the speed and mode of sputtering of the targets in the direction of layer thickness.It was determined that the band gap width of $Cu(In_{1-x}Ga_x)(Se_{1-y}S_y)_2$ thin films increases from 1.04 eV to 1.47 eV depending on the content of Ga and S.

- Single-phase $Cu(In_{1-x}Ga_x)(Se_{1-y}S_y)_2$ thin films were obtained by thermal treatment method in S/Se atmosphere. From the study of the composition and some optical properties of $Cu(In_{1-x}Ga_x)(Se_{1-y}Se_y)_2$ layers, it was determined that the width of the forbidden zone of these thin layers is in the region of 1.27 eV - 1.41 eV, which is important for the solar spectrum, depending on the S/(S+Se) ratio.
- $CuInSe_2$ thin films were implanted with Ar^+ ions and studied using an electron microscope, revealing a high concentration of packing defects and dislocation loops. According to TRIM (a Monte-Carlo simulating ion interaction with matter) calculations, it was determined that each Ar ion with an energy of 30 eV creates 525 defects. After implantation at a dose of $3x10^{15}$ cm^{-3}, the total number of defects is $3x10^{16}$ cm^{-2}. This indicates that only 10 of the 525 defects created by each implanted Ar ion remain unrepaired.
- The resistivity of the ZnO:Al layers was determined from Hall effect measurements. After thermal treatment at a temperature of 500 C for one hour, the electrical resistivity of these layers decreases. In the subsequent thermal treatment, the electrical resistivity gradually decreases with the increase in temperature.
- The possibility of increasing photosensitivity in $p\text{-}Cu(In_{1-x}Ga_x)(Se_{1-y}S_y)_2/n\text{-}GaAs$ heterojunctions was shown by changing the ratio of holes and electrons in $Cu(In_{1-x}Ga_x)(Se_{1-y}S_y)_2$ and GaAs. It was determined that in these heterojunctions, according to the values of x and y, the values of the resistivity and the width of the forbidden zone are different. The photosensitivity of heterojunctions corresponds to the wavelength range of 0.56 -

0.92 μm of the spectrum. It has been shown that the photosensitivity when illuminated from the side of the heterojunction $Cu(In_{1-x}Ga_x)(Se_{1-y}S_y)_2$ layer is higher than the sensitivity obtained when illuminated from the GaAs side.

Theoretical and practical significance of the research:

$CuInSe_2$, $GaInSe_2$, $CuInS_2$, $GaInS_2$, $CuGaInSe_2$, $CuGaIn(Se,S)_2$ thin films and heterostructures based on these compounds play important role in the production of solar cells. The ability to control the forbidden zone depending on the composition of these compounds has created new application opportunities in modern electronics. Therefore, the investigation of the physical properties of these compounds, their application in various fields, and the preparation of new absorbent layers based on them are of significant scientific and practical importance.

The variation of the band gap value of $Cu(In_{1-x}Ga_x)(Se_{1-y}S_y)_2$ thin films from 1.04 to 1.47 eV, depending on the amount of Ga and S, expands their application possibilities. It is known that semiconductor compounds are widely studied in various fields of electronics. The use of Cu-containing semiconducting chalcogenide materials in solar converters, which is considered the most promising type of renewable energy source, is of great practical importance. The production cost of these materials is significantly lower than other Si-containing materials. Low cost is one of the main criteria in the production of solar cells. From this point of view, the study of the properties of the materials we are studying is of scientific and practical importance. Therefore, the obtained results can stimulate the improvement and development of new theoretical knowledge in this field.

Although the obtained results are of applied nature, they are also important in the field of fundamental physics. The transmission, reflection, and absorption coefficients of the studied layers were calculated. In $CuIn_{1-x}Ga_xSe_2$ thin films, it was determined that the width of the forbidden zone changes with the increase of x according to the linear law $E_g(CuIn_{1-x}Ga_xSe_2)=1.08+0.6x$.

Approbation and application of the work:

The main results obtained in the dissertation were discussed at national and international conferences:

- Azərbaycan Milli Elmlər Akademiyası doktorantlarının elmi konfransının materialları. Bakı, 2010, s.7-9.
- Azərbaycan Milli Elmlər Akademiyası doktorantlarının elmi konfransının materialları. Bakı, 2011, s.12-15
- 17th. International Conference on Ternary and Multinary Compounds Abstrats. Baku, 2010. p. 18.
- Nanotexnologiyalar və onların texnikada tətbiqi. I Beynəlxalq Konsransı materialları 15-16 dekabr 2010. p.132-137;
- 20th Inernational Conference on Ternary Multinary Compounds. Halle, 2016.
- "16th İnternational and Physical Problrms of Electrical Engineering" İstanbul Rumeli University, İstanbul, Turkey 12-13 October 2020 Number 01 . p.1-6.

The results obtained during the dissertation work were published in 18 scientific works, 12 of which are articles (including 2 foreign journals included in the Web of Sciences database) and 6 are conference materials and theses.

The name of the organization in which the dissertation work is completed:

The dissertation work was performed at "Physics and electronics of non-crystalline semiconductors" laboratory of the Institute of Physics of the Ministry of Scicence and Education Republic of Azerbaijan.

Volume, structure and main content of the dissertation:

The dissertation consists of a total of 257748 characters, including an introduction, four chapters, main results, 16 tables, 12 figures, 44 graphs and 138 cited references.

THE CONTENT OF THE WORK

In the introduction, the relevance and perspectives of the topic of the dissertation, the purpose of the work, scientific innovations, scientific and practical importance, the set goal and the main provisions defended are reflected.

The first chapter of the dissertation is devoted to the literature review of optical and photoelectric properties of $CuInSe_2$, $GaInSe_2$, $CuInS_2$, $GaInS_2$, $CuGaInSe_2$, $CuGaIn(Se,S)_2$ thin-film semiconductor compounds, which are research objects. The band gap value of these compounds varies from 1.0 to 2.41 eV. This makes their use as an absorbing layer for solar cells, as well as a buffer layer, relevant. The gap width of triple $CuInSe_2$ layers with p-type conductivity, absorption coefficient (10^4-10^5 cm^{-1}) is ~1 eV, and they are widely used in photovoltaic devices. It is also a very promising material as solar cells. Optical and electrical parameters of $CuInSe_2$ - absorption coefficient, optical absorption coefficient and value of the forbidden zone vary according to the dissolution temperature. The activation energy of $CuInSe_2$ decreases with increasing Cu/In ratio. The optical properties of $CuInSe_2$ thin films are affected by the annealing temperature. As the temperature increases, the value of the width of the forbidden zone decreases. Also, the substrate temperature during deposition affects the properties of $CuInSe_2$. It is especially important to choose the appropriate temperature of the substrate to obtain the necessary properties. The electrical properties of $CuInSe_2$ depend on the annealing technique and conditions. At the same time, electrical conductivity, Hall conductivity, and activation energy in $CuInSe_2$ layers depend on the thickness of the layers.

Experiments were conducted to study the optical and electrical properties of $CuGaSe_2$ layers and it was determined that they are important in the production of solar cells. The gap width of these layers is 1.65 eV. $CuGaSe_2$ layers have a very large anisotropy. The Hall coefficient is negative. In $CuGaSe_2$ thin films, the main carriers are electrons, with n-type conductivity. Annealing of these layers at a substrate temperature below 300^0 C results in amorphous or pure Se-filled crystals.

Optical properties of $CuInS_2$ (value of band gap, absorption coefficient) and low production costs ensure their use as absorbing materials. This compound is more resistant to radiation than $CuInSe_2$ and has a lower degree of damage. One of the most promising methods of obtaining these materials is sulfidation during magnetron sputtering. The quality of $CuInS_2$ obtained by this method is affected by sulphidation temperature and dusting pressure. From the study of the optical and structural properties of the layers, it can be seen that the layers have high optical and structural properties when they are placed in the tray at a temperature above 450^0 C. Above this temperature, the width of the band gap is 1.05 eV. Zn-doped $CuInS_2$ layers were studied by thermal evaporation from two sources. At this time, the CuInS2 layers show p-type conductivity and the width of the forbidden zone increases from 1.467 eV to 1.585 eV, and its specific resistance is $8 \bullet 10^{-1}$ Ohm cm.

Since the bandgap value of $CuGaS_2$ is not suitable for light absorption in solar cells, it can be doped with metal to match this spectrum. When $CuGaS_2$ is doped with Bi, the bandgap width decreases, which makes it possible to use them as an absorber layer in solar cells. $CuGaS_2$ layers are deposited by vacuum thermal evaporation on glass substrates heated to 200^0 C. From the study of optical and electrical properties, it was determined that the value of the width of the optical forbidden zone of these compounds is approximately 2.36 eV, the absorption coefficient is 10^5 cm^{-1} and the conductivity is p-type.

For large-scale applications, it was determined that it is more convenient to grow $CuInGaSe_2$ thin films by means of two-stage selenization of Cu-In-Ga precursors deposited on glass substrates under N2 flow. From the X-ray diffraction analysis, it was determined that single-phase $CuInGaSe_2$ layers with a dominant direction in the (112) plane were obtained.

The second chapter is devoted to experimental methods designed to achieve the goal set in the dissertation work, various analysis methods, software and devices used to analyze the research results. X-ray diffraction, Raman spectroscopy, ion implantation, and magnetron sputtering methods were used during the research.

The methods of the synthesis of the thin films that we have studied are explained, and the methodology of the study of the optical and photoelectric properties is described.

X-ray diffraction spectra were analyzed and information about the structure of the layers was obtained.

In order to determine the differences in the crystal structures of thin films, atomic dynamics studies were carried out using the Raman spectroscopy method.

$CuIn_{1-x}Ga_xSe_2$ thin films were sputtered on metal foils by simultaneous magnetron sputtering of $CuInSe_2$ and $CuGaSe_2$ targets. At this time, ZnO was used as a buffer layer to eliminate the defects caused by the diffraction of Ga.

The possibility of increasing or decreasing the width of their forbidden zones in the direction of the thickness of the layers was investigated. The optical and photoelectric properties of the obtained layers were studied.

$Cu(In_{1-x}Ga_x)(Se_{1-y}S_y)_2$ solid solutions were obtained by placing in the table in a chalcogen atmosphere. Also, $CuInSe_2$ layers were deposited on Mo coated with soda-lime glass using sequential non-vacuum processes. The technological regimes for changing the width of the forbidden zone of the material in the direction of the growth of $CuIn_{1-x}Ga_xSe_2$ thin films were investigated. It was determined that the value of the width of the forbidden zone E_g of the $CuIn_{1-x}Ga_xSe_2$ material varies between 1.04 and 1.68 eV depending on the value of x. Also, the surface morphology and microstructure of the layers were analyzed using scanning electron microscopy (SEM) and atomic force microscopy (AFM). The optical parameters of $CuInGaSe_2$ thin films were determined from emission and return measurements in the spectral range of 200-3000 nm at room temperature using a Carry 500 Scan UV-VIS-NIR spectrometer.

The electrical resistance of the obtained thin films was determined from Hall effect measurements using the Van der Pauw method. It was determined that the thickness of the layers affects their electrical properties.

The structure and morphological properties of the thin layers were investigated **in the third chapter.**

X-ray diffraction studies of CuInGa(Se,S)$_2$ thin films revealed that the obtained peaks strongly depend on the processing mode and chemical composition of the films. Main diffraction peaks were detected for CuInGa(SeS)$_2$ thin films annealed at 400^{0}C - 450^{0}C. At the same time, characteristic (101), (103) peaks and doubly split peaks (116/312), (008/400), (228/424) were also observed. From our studies, it was determined that the strong peak for CIGSS chalcopyrite compounds was obtained from the (112) plane (Figure 1). The degree of superior orientation in the crystal $I_{112}/I_{200/220}$ depends on the temperature. When increasing the selenization temperature from 400^0 C to 520^0 C, this value increases from 1.1 to 1.4. X-ray diffraction spectra of ZnO:Al thin films deposited by magnetron sputtering method showed (002) and (004) diffraction peaks at $2\theta = 34.34$ and $2\theta = 72.41$. The c-axis of these layers has a dominant orientation in the [002] direction perpendicular to the substrate, with a strong peak for this layer obtained from the (002) plane. The peaks corresponding to the reflections of the (112), (103), (220/204) and (312/116) atomic planes of CuInSe$_2$ and CuInS$_2$ layers were determined by comparison with JCPPS 40-1487 and 89-6095 data cards. At this time, it was found that the received layers do not contain two-, three-, and four-phase (Cu-S, Cu-Se, or In-Se) compounds.

Oje electron spectroscopy measurements were used to study the main distribution of elements in the volume of CuInGaSe$_2$ layers. In this case, additional phases do not appear in the material. Table-1 shows the average percentage values of Cu, In, Ga and Se determined by this method for layers obtained on different substrates. Also, the chapter shows images of Oje electron spectra of CuInGaSe$_2$ layers. The elemental composition on the surface of CuInGaSe2 layers was calculated from the relative intensity of the peak in the Oje electron spectrum. According to these calculations, the chemical composition is Cu 30%, In 21%, Ga 3% and Se 46%.

Figure 2 shows a typical depth profile obtained for sample 2X118 under optimal conditions (T~5200 C, t = 20 min.).

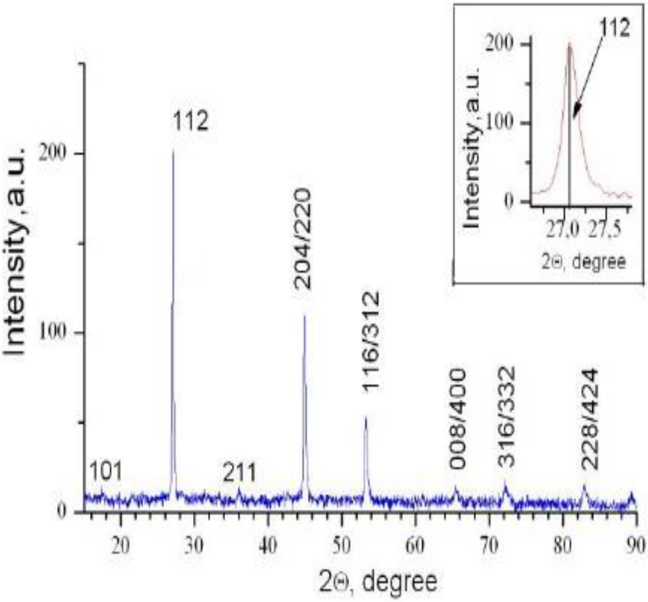

Figure 1. XRD pattern of $Cu_{0,73}In_{1,18}Ga_{0,09}S_{0,87}Se_{1,13}$ thin film grown under 520 ^{0}C

Scanning Electron Microscope (SEM) studies were conducted to study the surface structure of $CuInGaSe_2$ layers. SEM studies revealed that the surface morphology of $CuInGaSe_2$ thin films strongly depends on selenization temperature and deposition conditions. It was determined that the size of the grains on the plate surface is ~1 - 2.5 μm. The chapter shows images of the surface structure of the $CuInGaSe_2$ layer obtained under optimal conditions by means of SEM.

From the SEM images, it was determined that when the selenization temperature is increased from 400^0 C to 520^0 C, the adhesion and homogeneity of the coated layers on different metal foils improves.

ZnO:Al thin films were also investigated by SEM. As a result of these studies, it was determined that the degree of roughness in the layer depends on the amount of Al.

Table 1.Chemical composition of $CuInGaSe_2$ thin layers deposited on different substrates (selenization temperature kept at 520^0 C for 20 minutes).

The sign of sample	Type of substrate	Cu, %	In, %	Ga, %	Se,%
2X118	Glass	26,2	24,8	1.9	46,7
1MX	Mo	29,1	22,2	3,3	45,4
2TX	Ti	24,1	26,1	2,2	47,6
1TMX	Mo layered Ti	25,0	23,4	2,0	49,6
1HCMX	Mo layered stainless steel	26,7	21,9	2,5	48,9
1AlDX	Al	21,7	26,0	2,2	50,1
1AlMX	Mo layered Al	35,4	22,8	2,1	39,7

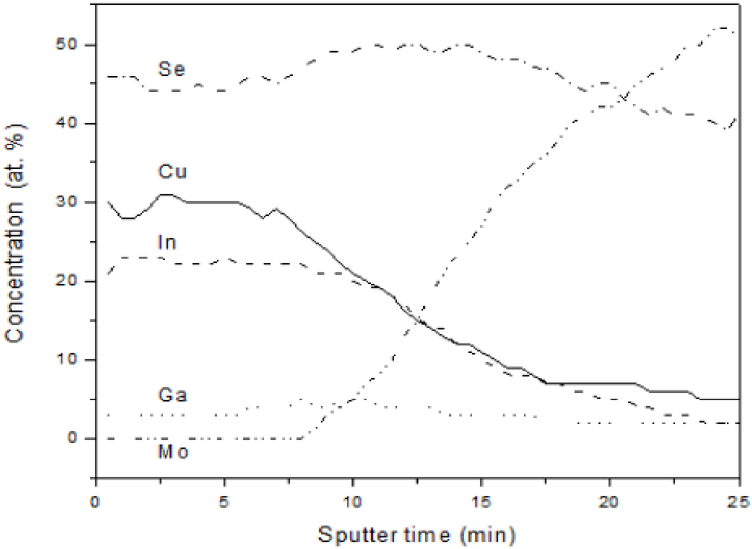

Figure 2. Image of depth profile determined by AES of $CuInGaSe_2$ layer on Mo foil (sample 2X118)

At the same time, statistical parameters were evaluated for all images in both large (10 x 10 μm2) and small (2 x 2 μm2) scale dimensions of roughness.

In the fourth chapter, the optical and photoelectric properties of the thin films we studied were studied. It is shown that the value of the band gap varies in a wide range (from 1.0 eV to 2.4 eV) depending on the composition.

CuIn1-xGax(Se1-ySy)2 (CIGSS) materials are used as absorber layers in solar cells.

In the absorber layers we use in solar cells, Mo forms an ohmic contact with both the bottom CuInGa(Se,S)2 and the top ZnO:Al layer. This contact was obtained from a Mo target by magnetron sputtering. As an alternative to toxic CdS and ZnCdS, ZnO was used as a buffer layer. In this layer, Zn was obtained from the target by magnetron sputtering in Ar + O2 environment.

The optical properties of $CuInGa(Se,S)_2$ layers sputtered on a glass substrate were determined from transmission (T) and reflection (R) spectra measurements. In $CuInGa(Se,S)_2$ thin films obtained by magnetron sputtering, the width of the forbidden zone varies from 1.27 eV to 1.47 eV depending on the S/(S+Se) ratio. The value of the forbidden zone width was determined from the extrapolation of the linear part of the spectral dependence $\alpha \sim f(h\nu)$ and from the release measurements. It was determined that the width of the forbidden zone determined by the emission spectrum for layers with composition x=0 is ~1.08 Ev. The dependence of $(\alpha(h\nu))^2$ quantities on $CuIn_{1-x}Ga_xSe_2$ layers for different values of x on hν is shown in Fig. 3. . It can be seen from the figure that with the increase in the value of x, the value of the width of the forbidden zone increases linearly ($E_g = 1.08+0.6x$). Photoluminescence spectra of CuInGaSe2 thin film at 4.2 K, 78 K and 300 K are given in Fig. 4. It is clear from the graph that by increasing the excitation intensity, a high energy transition (blue transition) occurs in the bands. This transition has different values and strongly depends on the structural quality and chemical composition of the CuInGaSeS2 thin film.

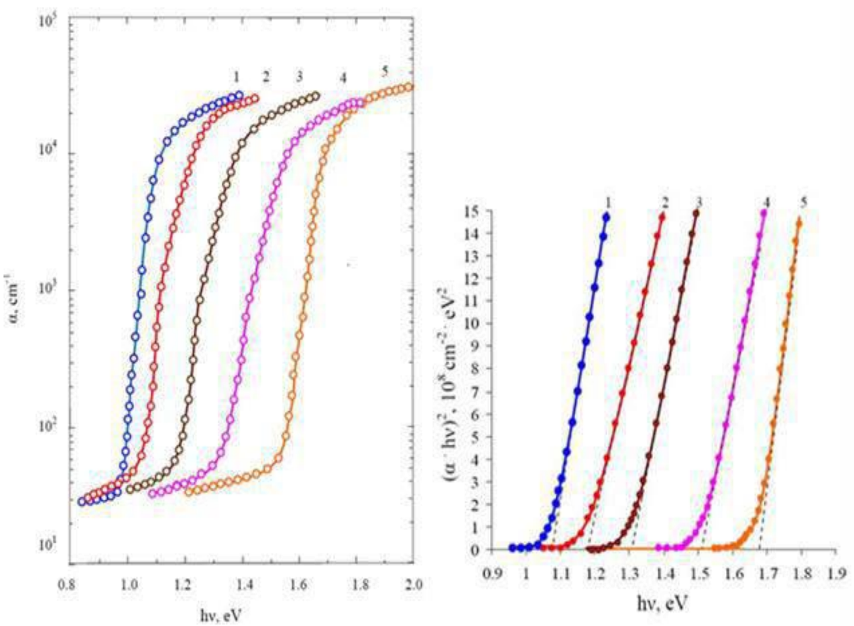

Figure 3. Dependences of absorption coefficient (a) and (α.hν)2 (b) on photon energy hν in thin $CuIn_{1-x}Ga_xSe_2$ films obtained on glass seats. Here, the ratio of components in the layer is: Ga/(Ga+In)=0 (1), 0.2 (2), 0.4 (3), 0.7 (4) and 1.0 (5).

The band gap value of the $CuInGaSeS_2$ thin film was determined from photoluminescence excitation measurements at 78 K. It is determined from this spectrum that the emission slowly reaches a maximum near the forbidden zone. In most cases, photoluminescence and photoluminescence excitation spectra overlap due to absorption. This experimental result shows that the width of the band gap in compensated and highly doped semiconductors can be approximated from the photoluminescence excitation spectrum. As can be seen from the photoluminescence spectrum, only one broad recombination band was observed at 4.2 K. The broad band has an asymmetric spectral shape with a longer tail toward lower energies. The FL band energy varies with temperature. Spectral shape and intensity vary from sample to sample. When the temperature is increased from 4.2 K to 300 K, all the bands shift to higher energy. The FL band energy varies with temperature. Spectral shape and intensity vary from sample to sample.

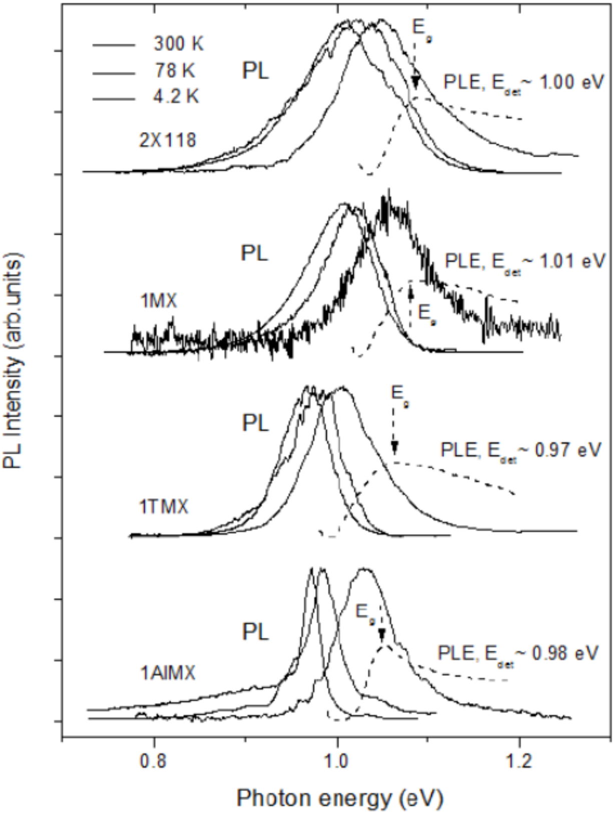

Figure 4. FL spectrum of CuInGaSe2 layers at 4.2 K, 78 K and 300 K temperatures and FL excitation spectrum at 78 K.

When the temperature is increased from 4.2 K to 300 K, all the bands shift to higher energy. For example, the energy for sample 02-26 (Cu - 16.75%, In - 28.26%, Se - 55.10, Cu/In - 0.59, Se/M (metal) - 1.22) varies from 0.933 eV to 1.001 eV. Depending on the sample, the energy changes as the temperature increases. It was determined that when the Se/M ratio decreases in the samples, a large change from higher energies to lower energies is observed. This effect is also shown in the figure for temperatures of 4.2 K and 78 K.

In this chapter, the photoelectric properties of the obtained $CuInGaSe_2$ thin films were also studied. The resistivity of $CuInGaSe_2$ was measured by the Van de Pauw method at room temperature. One of the main quality criteria of $CuInGaSe_2$ thin films used as absorber layer in solar cells is $Cu/(In+Ga) < 1$ ratio.

In the measurement of resistivity, special attention was paid to the layers that satisfy this ratio. The activation energies of the specific defect levels formed during the synthesis were determined by measuring the temperature dependence of the specific resistance in the range of 80 - 400 K. During the research, it was found that the ratio of Cu/(In+Ga) of the studied layers is quite close to the required stoichiometric value (from 1.00 to 1.15) and does not have a noticeable effect on the electrical parameters. Here we mean electrical parameters i.e.h.q. and resistivity is assumed. Accordingly, the chapter shows that the Se↔S substitution does not affect the resistivity. It was determined that the resistivity depends on the substrate temperature, deposition time and thickness. Also, electrical resistance of ZnO:Al layers was determined from Hall measurements. It is shown in the chapter that the ratio of S/(S+Se) for the study of defects in the studied $CuInGa(SeS)_2$ layers is A_1 (Cu – 18.34 %, In – 29.44 %, Ga – 2.19 %, S – 19.89 %, Se – 30.21 %, E_g – 1.27 Ev, ρ – 1.5 x 10^2 Ohm•cm, thermopower – 96 mV/K) for - 0.39, A_2 (Cu – 20.50 %, In – 30.46 %, Ga – 0.95 %, S – 32.27 %, Se – 15.83 %, E_g – 1.29 Ev, ρ – 8.8 x 10^1 Ohm•cm, thermopower – 15 mV/K) for - 0.67, A3 (Cu – 20.15 %. In – 30.29, Ga – 1.57 %, S – 42.05 %, Se - 5.94 %, E_g - 1.41 Ev, ρ - 9.9 x 10^1

Ohm•cm, thermopower - 9 mV/K) samples with 0.88 were used. The area of the samples is 10x10 mm^2 and the thickness is 2 μm.

This chapter also deals with the preparation of GaAs/$Cu(In_{1-x}Ga_x)(Se_{1-y}S_y)_2$ heterojunctions and the study of electrical and photoelectric properties. Heterojunctions were obtained by depositing thin layers of $Cu(In_{1-x}Ga_x)(Se_{1-y}S_y)_2$ on the surface of GaAs substrates with (100) and (111) dominant planes with n- and p-type conductivity, carrier concentration of 10^{16} cm^{-3}, by magnetron sputtering method. . The lattice parameters of GaAs and the lattice parameters of $Cu(In_{1-x}Ga_x)(Se_{1-y}S_y)_2$ thin films are close to each other, and the band gap value of this material varies between 1.34 and 2.2 eV. Figure 5 shows the absorption spectrum of $Cu(In_{1-x}Ga_x)(Se_{1-y}S_y)_2$ thin films obtained by magnetron sputtering on a glass substrate in $(\alpha h\nu)^2$ and hν coordinates (1) x=0, y=0.49; 2) x=0.67, y=0.6; 3) x=0.4, y=0.65; 4) x=0, y=0.62 – at 300 K). According to the measurements of the optical emission spectrum, it was found that the gap width of the synthesized layers is in the range of 1.34 - 2.2 eV due to the change of x from 1 to 0 and y from 0 to 1. By changing the Ga/(In+Ga) ratio from 0 to 1 and the Se/(S+Se) ratio from 1 to 0, the value of the band gap can be controlled. The band gap value of $CuIn_{1-x}Ga_x(Se_{1-y}S_y)_2$ thin films increases with increasing Ga and S. Therefore, with their growth, the edge of sensitivity shifts towards short waves. The spectral composition of $CuIn_{1-x}Ga_x(Se_{1-y}S_y)_2$-based heterojunctions makes it possible to use them as a buffer layer in multi-cascade heterojunction solar cells. Figure 6 shows the volt-ampere characteristics of n-GaAs/p-$CuIn_{0.86}Ga_{0.14}(Se_{0.8}S_{0.2})_2$ heterojunctions. The right direction of the current was obtained by connecting the $CuIn_{0.86}Ga_{0.14}(Se_{0.8}S_{0.2})_2$ layer of the heterostructure to the positive pole of the current source. As can be seen, at low values of the current ($U < 0.7$ V at $T = 288$ K), the current increases exponentially, and the trends of the exponential parts do not depend on the temperature. This indicates that the current flow is characterized by a tunneling mechanism. The reverse and saturation current of the heterojunction varies according to the law $J \sim \exp(-Ea/kT)$.

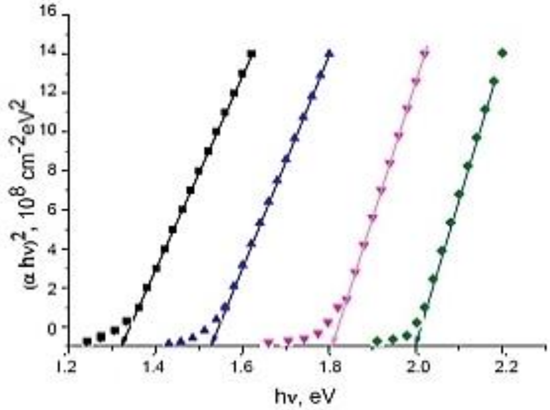

Figure 5. Absorption spectrum of $Cu(In_{1-x}Ga_x)(Se_{1-y}S_y)_2$ thin films obtained on a glass substrate by magnetron sputtering in $(\alpha h\nu)^2$ and (hν) coordinates: 1)x=0, y=0.49; 2) x=0.67, y=0.6; 3) x=0.4, y=0.65; 4) x=0, y=0.62; At 300 K.

Ea is the activation energy of 0.80 eV. This corresponds to the height of the energy barriers in the heterojunction. The short circuit current density and open circuit voltage are Jsc = 30mV/cm2, Uoc = 0.7 eV for the heterostructure, respectively. The GaAs/CuIn0.86Ga0.14(Se0.8S0.2)2 heterojunction obtained is always negatively charged when illuminated by white light with a power density of 100 mA/cm2 from the side of the CuIn0.86Ga0.14(Se0.8S0.2)2 layer. The large values of rectification coefficient, short-circuit current and open-circuit voltage of the thus obtained GaAs/CuIn1-xGax(Se1-ySy)2 heterostructures indicate that a sharp heteroboundary is obtained, and the role of boundary states is insignificant here. The energy diagram of p-CuIn0.86Ga0.14(Se0.8S0.2)2/n-GaAs heterostructures was constructed based on the measurement of electrical and photoelectric properties (Fig. 7). It can be seen from the energy zone diagram that the photosensitivity can be increased by changing the ratio of hole and electron concentrations in CuIn0.86Ga0.14(Se0.8S0.2)2 and GaAs. Figure 8 shows the dark volt-ampere characteristic of p - CuIn0.7Ga0.3(Se0.9S0.1)2/n - GaAs heterojunctions.

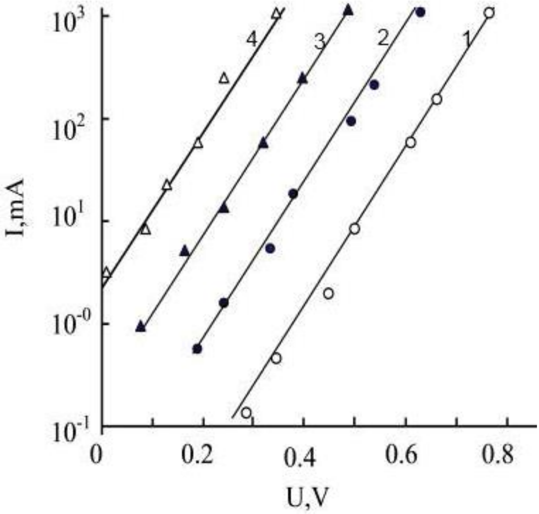

Figure 6. Temperature dependence of the branches in the right direction of the volt-ampere characteristic on a semi-logarithmic scale of the p-$CuIn_{0.86}Ga_{0.14}(Se_{0.8}S_{0.2})_2$/n-GaAs heterojunction. Here T=300K (1), 340K (2), 380K (3), T=420K (4).

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. Heterojunctions (k > 6•105, at U = 1V) have diode characteristics. The breakdown voltage at 300 K is 0.85 V, and the reverse branch of the volt-ampere characteristic has a saturation tendency. The obtained GaAs/$CuIn_{0.7}Ga_{0.3}(Se_{0.9}S_{0.1})_2$ heterojunctions have large values of rectification coefficient, short-circuit current and open-circuit voltage, indicating that a sharp heteroboundary is obtained, and here the role of boundary states is also insignificant.

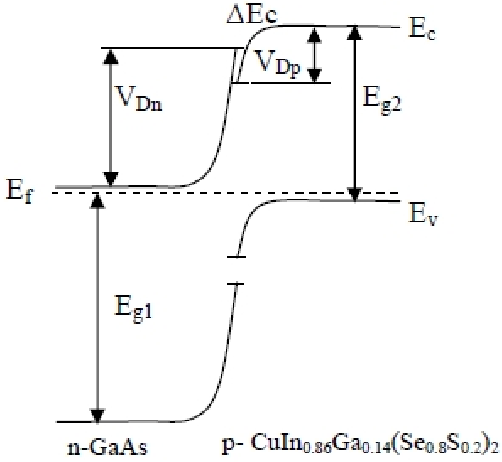

Figure 7. Energy zone diagram of p-$CuIn_{0.86}Ga_{0.14}(Se_{0.8}S_{0.2})_2$/n-GaAs heterojunction

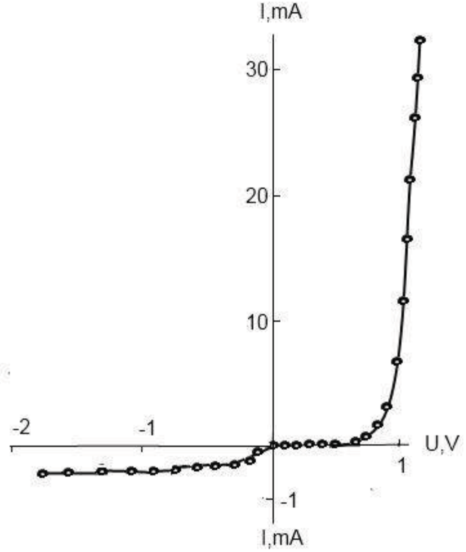

Figure 8. Dark volt-ampere characteristic of p-$CuIn_{0.7}Ga_{0.3}(Se_{0.9}S_{0.1})_2$/n-GaAs heterojunction

CONCLUSİONS

1. The technologies of producing layers with single-phase triple $CuInSe_2$ and $CuInS_2$, quadruple $CuInGaSe_2$ and $CuInGaS_2$, and quintuple $CuInGa(Se,S)_2$ mirror surface morphology were developed in accordance with the deposition method of Cu-In-Ga precursors obtained on glass and flexible metal foils (titanium, molybdenum, aluminum, stainless steel) by magnetron sputtering method in Se, S and Se+S gas environments.
2. Threefold $CuInSe_2$, $CuInS_2$, $CuGaSe_2$, and $CuGaS_2$ and fourfold $CuInGaSe_2$ and $CuInGaS_2$ polycrystalline compounds were synthesized for the target material in magnetron sputtering. Targets with a diameter of 10 cm were prepared from their powder, and the regimes of magnetron sputtering were determined to obtain thin layers of these materials with a mirror surface.
3. Using two magnetrons whose magnetic systems are shifted toward each other, the technology of obtaining single-phase $CuIn_{1-x}Ga_xSe_2$ thin layers by magnetron sputtering from targets obtained by pressing under 16 T pressure from the powder of polycrystalline $CuInSe_2$ and $CuGaSe_2$ materials obtained by synthesis; $CuInGaS_2$ thin films by simultaneous sputtering of powdered $CuInS_2$ and $CuGaS_2$ targets; five-element $Cu(In_{1-x}Ga_x)(Se_{1-y}S_y)_2$ thin films by the method of simultaneous sputtering of targets consisting of powdered four-element $CuInGaSe_2$ and $CuInGaS_2$ materials has been developed. It is shown that it is possible to grow or shrink the forbidden zone in the direction of the growth of the layers, that is, to obtain a variable structure.
4. Technologies for obtaining ZnO:Al thin films doped with ZnO and aluminum have been developed. It has been shown that it is possible to obtain thin films of ZnO and ZnO:Al with a satisfactory surface morphology by the method of magnetron sputtering.
5. X-ray structural analysis of all $CuIn_{1-x}Ga_xSe_2$ layers obtained on various metal foils (titanium, nickel, aluminum, stainless

steel), glass, and GaAs substrates showed that they have a predominant orientation in the (112) direction. As a result of the optical absorption and photoluminescence measurements of the $CuIn_{1-x}Ga_xSe_2$ layers obtained on glass substrates, the regularity of the increase of the forbidden zone of the layers from the value of 0.92 eV ($x = 0$) in the solid solution to the value of 1.63 eV ($x = 0$) with the increase of gallium was determined. It was determined that the optical and structural properties of these layers strongly depend on the coating conditions, the type of substrate and the chemical composition of the layer.

6. Single-phase $Cu(In,Ga)(Se,S)_2$ thin films with a homogeneous distribution of elements throughout the layer depth and a superior [112] orientation were grown by two-stage annealing of sequentially deposited Cu, Ga, and In precursors in S/Se medium. Defects in the $CuInGaSe_2$ layer are reloaded in the temperature ranges of 150-220 K and 260-320 K, and this is determined by the PICTS method. The change in activation energy of the defects depending on the temperature can be explained by the metastable nature of the defects during the reloading process. Comparability and compatibility of photosensitivity of layers and temperatures of recharging defects, as well as changes in the rate of recharging of defects in layers and the presence of inflection points in the temperature dependence, determine the nature of recharging.
7. Implantation of 30 keV Ar^+ ions into a $CuInSe_2$ single crystal creates two defect layers on the surface, due to sputtering dominated by Se and Cu atoms, and in the implanted Ar layer, probably due to packing defects and dislocation loops. It was found that the way to reduce the implantation of Ar^+ ions into $CuInGa(Se,S)_2$ layers during magnetron sputtering is to make the gas discharge voltage and the seat temperature as small as possible.
8. Preparation of $GaAs/Cu(In_{1-x}Ga_x)(Se_{1-y}S_y)_2$ heterostructures and investigation of their electrical and photoelectric properties showed that magnetic systems, sputtering from two

shifted magnetrons can be used to grow epitaxial thin films of complex composition chalcopyrite compounds with good surface morphology. The high photosensitivity of the obtained GaAs/Cu($In_{1-x}Ga_x$)($Se_{1-y}Sy$)$_2$ heterostructures showed that the heterostructures obtained in the described growth modes of the epitaxial layers were sharp and the role of boundary conditions was insignificant.

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