International Journal on
"Technical and Physical Problems of Engineering"
(IJTPE)
Published by International Organization of IOTPE

ISSN 2077-3528
IJTPE Journal
www.iotpe.com
ijtpe@iotpe.com

March 2022	Issue 50	Volume 14	Number 1	Pages 156-160

$Cu_2ZnSnSe_4$ THIN FILMS FOR SOLAR CELL APPLICATIONS

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Abstract- Various technological modes of the magnetron sputtering method are investigated to obtain high-quality thin $Cu_2ZnSnSe_4$ (CZTSe) layers for solar cells. It is shown that this method can be used to obtain homogeneous thin films with a mirror-like morphology of their surface. Thin CZTSe films were obtained on sodium glass substrates and on thin molybdenum films deposited on glass substrates. Pressed powders of crystalline $Cu_2ZnSnSe_4$ were used as a target. The crystallinity of $Cu_2ZnSnSe_4$ was checked by X-ray diffraction and X-ray phase analysis, and the composition was determined by elemental analysis on a scanning electron microscope (SEM). The morphological features of the film surface were studied under a metallurgical optical microscope and an atomic force microscope (AFM). X-ray studies of CZTSe thin films have shown that thin amorphous layers are obtained on glass substrates, but they have a tendency to crystallize. Studies of the absorption spectrum at the intrinsic absorption edge have shown that the intrinsic absorption edge is shifted towards short waves. This is due to the fact that films with a thickness of about 100-120 nm were used.

Keywords: $Cu_2ZnSnSe_4$ Thin Films, Magnetron Sputtering Method, X-ray Diffraction Analysis, SEM Analysis, Raman Spectroscopy, Photoluminescence, High Optical Absorption Coefficients.

1. INTRODUCTION

Thin-layer photovoltaic converters on the basis of $CuInGaSe_2$ [14] Cu_2ZnSnS_4 (CZTS) and $Cu_2ZnSnSe_4$ (CZTSe) are in great demand today. In these materials with a crystal structure of the kesterite type, the structure of the energy band varies from 1.0 to 1.5 eV, depending on their characteristics and the composition of the components, and the absorption coefficient exceeds 10^4 cm^{-1}. It is one of the most promising materials for cheap solar cells. The materials in this 4-component formulation are less toxic and more abundant in nature. No toxic Cd and two expensive composite materials, In and Ga, are used.

Despite its short history, CZT (S, Se) technologies are developing, and now the Coefficient of Performance (Efficiency) of solar cells, which is 10.1%, have been obtained in [1-15]. The theoretical efficiency in the case of using CZT (S, Se) films is 32%.

In addition, the production of these non-toxic elements does not harm the manufacturers, nature and the environment. Surprisingly, the features of CZTSe have not been studied in detail.

At present, $Cu_2ZnSn(SSe)_4$ absorbing layers have been synthesized in a number of laboratories around the world, their electrophysical and optical properties have been studied, and on the basis of this material have been created samples of photocells with an efficiency of 10.1%. However, this is less than the theoretically obtained efficiency (32%). The reasons for this are not completely clear. The most probable reasons are problems with the synthesis of single-phase samples of a given composition or with the production of precursor films during deposition and formation.

The physicochemical mechanism of the preparation of $Cu_2ZnSn(SSe)_4$ compounds is not fully understood, since this system is relatively new and poorly studied. Other researchers obtained thin layers of $Cu_2ZnSn(SSe)_4$ in two ways - one-stage electrochemical deposition and thermal evaporation in vacuum. The influence of the synthesis conditions on the electrophysical and optical properties was also studied. The main experimental results in the study of electrophysical and optical properties were obtained using the following methods: X-ray phase analysis, Raman spectroscopy, X-ray fluorescence analysis, optical spectroscopy, scanning electron microscopy and photoelectrochemical method.

$Cu_2ZnSn(SeS)_4$ compounds are direct-gap semiconductors, have an optical band gap (0.8-1.7 eV) close to the optimal amount for effective absorption of light, and have p-type electrical conductivity, which allows them to be used in heterostructured solar cells. $Cu_2ZnSnSe_4$ has an almost ideal forward band gap E_g ~ 1.5 eV. Due to the fact that $Cu_2ZnSnSe_4$ has a high absorption coefficient (10^4 cm^{-1}) a layer of this material with a thickness of 1 micron can absorb most of the visible region of the solar spectrum. Thin films based on CZTSe do not contain rare metals, toxic materials, and when combined with a cadmium-free buffer layer, these solar cells can be expected to have a completely non-toxic manufacturing technology. The aim of this work is to obtain a thin $Cu_2ZnSnSe_4$ layer on medical glass substrates by magnetron sputtering. The tasks of performing the work are the following points:

• Determination of the structure of $Cu_2ZnSnSe_4$ thin films by X-ray structural analysis,
• Determination of phonon frequencies by studying the Raman spectrum in thin layers using a confocal Raman microspectrometer Nanofinder ®30 (Tokyo Instr., Japan).
• Nanofinder ®30 (Tokyo Instr., Japan) Study of the photoluminescence spectrum in thin layers using a confocal Raman microspectrometer.

2. SAMPLING AND EXPERIMENTAL METHODOLOGY

Thin Mo layers were used as ohmic contacts. The lower molybdenum contact was deposited on a glass substrate, and the upper contact was applied to a CdS layer. Both the lower and upper molybdenum films were obtained by magnetron sputtering in an argon atmosphere from a molybdenum target 10 cm in diameter.

Thin $Cu_2ZnSnSe_4$ (CZTSe) layers were deposited on a Mo layer in a modified vacuum installation by magnetron sputtering of a target from a pressed powder of crystalline $Cu_2ZnSnSe_4$ material in a gas of Ar at room temperature. Part of which were deposited on a glass substrate for optical measurements. Figure 1 shows a schematic view (top and side) of the resulting Mo/p-$Cu_2ZnSnSe_4$/n-CdS/Mo multilayer structure on a glass substrate.

In this device, thin layers of CdS were deposited on films of $Cu_2ZnSnSe_4$ by thermal evaporation [1-3]. The surface morphology of the obtained thin layers was carried out under a MicroOptix metallurgical optical microscope and a Brucker atomic force microscope (AGM) [1-3]. An X-ray diffraction analysis of thin $Cu_2ZnSnSe_4$ layers has been carried out.

X-ray diffraction analysis (RFA) of CZTSe thin films obtained at room temperature by magnetron sputtering on a 20×20 mm glass substrate was performed on a D2 Paser (Bruker, Germany) X-ray apparatus. The Raman spectrum and photoluminescence spectra of a thin layer of semiconductor kesterite CZTSe deposited on a glass substrate by magnetron sputtering were studied on a Nanofinder 30 confocal Raman microspectrometer (Tokyo Instr., Japan).

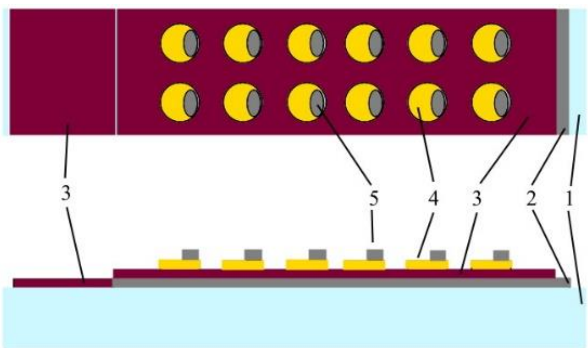

Figure 1. A schematic top and side view of the resulting Mo/p-$Cu_2ZnSnSe_4$/n-CdS/Mo multilayer structure, where, 1- glass substrate, 2- Mo film - bottom contact, 3- $Cu_2ZnSnSe_4$ film, 4- Cds film, 5- Mo film - top contact), Magnetron sputtering occurs in a gas discharge with a voltage of ~ (350-600) V and a current of ~ (3-5) A. Mo)

3. DISCUSSION OF EXPERIMENTAL RESULTS

3.1. X-Ray Diffractions Analysis of a Thin Film Based on $Cu_2ZnSnSe_4$

The XRD analysis of the samples were carried out on a D2 Phaser (Bruker, Germany) X-ray apparatus. The Figure 2 shows the XRD patterns carried out for $Cu_2ZnSnSe_4$ in powder form. The analysis of XRD data shows that synthesized $Cu_2ZnSnSe_4$ powder has a polycrystalline nature.

The composition of the target material was determined by elemental analysis of the polycrystalline $Cu_2ZnSnSe_4$ powder on the scanning electron microscope (SEM); the results are shown in Table 1. The results of XRD analysis of $Cu_2ZnSnSe_4$ thin films on the glass substrate are shown in Figure 3.

Table 1. The composition of polycrystalline $Cu_2ZnSnSe_4$

Characteristic X-rays	Weight %	Atomic %
CuK	23.40	28.53
ZnK	12.03	14.26
SeL	45.88	45.01
SnL	18.68	12.20
The results	100	100

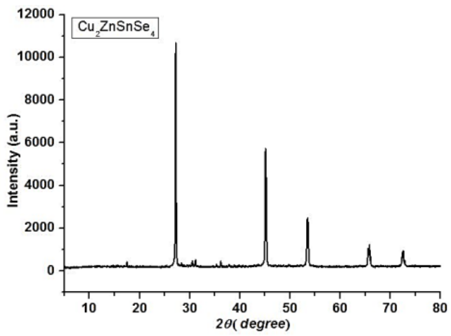

Figure 2. XRD patterns carried out for cristalline Cu2ZnSnSe4 in powder form (wavelength, 1.540060 A)

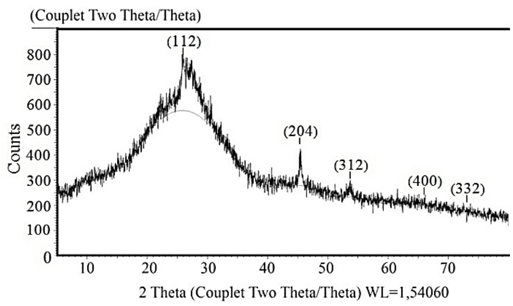

Figure 3. XRD spectrum of a $Cu_2ZnSnSe_4$ thin film obtained by magnetron sputtering in an argon gas atmosphere on a glass substrate at room temperature [15]

The X-ray structural analyzes of the samples suggest that thin $Cu_2ZnSnSe_4$ films obtained by DC magnetron sputtering method in an argon gas atmosphere on a glass substrate at room temperature have wide peaks. Undoubtedly, it is possible to crystallize the layers by heat treatment. The shape of these peaks proves that the resulting sample is amorphous, but tends to crystallize to some extent. Thin $Cu_2ZnSnSe_4$ layers with a thickness of ~ 100 nm obtained by magnetron sputtering are brown.

Raman spectra were measured using a confocal Raman microspectrometer Nanofinder 30 (Tokyo Instr., Japan). Generation of the second harmonic of a Nd: YAG laser with a wavelength $\lambda = 532$ nm and a power of 10 mW was used as an excitation source. The spectral resolution is 0.5 cm^{-1} over the spectrometer grid of 1800 lines/mm. The scattering radiation detector is a CCD camera that operates in the photon counting mode and is cooled down to -70 °C. The spectra were measured perpendicular to the scattering direction.

Figure 4 shows the peaks with a typical Raman spectrum and Lorentzian curves measured in the S_3CZTSe sample. All observed peaks can be interpreted, and no modes associated with possible secondary phases have been identified. In a thin film of $Cu_2ZnSnSe_4$, five modes were recorded, covering the region of the Raman spectrum of 30-500 cm^{-1}. The most intense spectral line was observed at 179 cm^{-1}. Other modes are observed at 197 cm^{-1}, 235 cm^{-1}, 248 cm^{-1} and 385 cm^{-1}. The existence of these modes is associated with the presence of phonons corresponding to these frequencies.

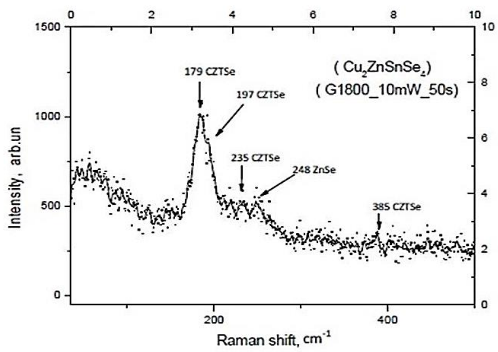

Figure 4. Raman spectrum of $Cu_2ZnSnSe_4$ thin film [15]

On the other hand, according to the Raman spectrum, 5 modes were recorded in a thin $Cu_2ZnSnSe_4$ layer on a Mo layer deposited on a glass substrate (Figure 3). The sharpest of these modes corresponds to frequencies of 180 cm^{-1}, and the remaining peaks are 197 cm^{-1}, 218 cm^{-1}, 247 cm^{-1}, 392 cm^{-1}. This is due to the presence of phonons corresponding to these frequencies. Comparison of the spectra in Figures 4 and 5 show that the frequencies observed in the Raman spectra for both parts of the sample are practically identical.

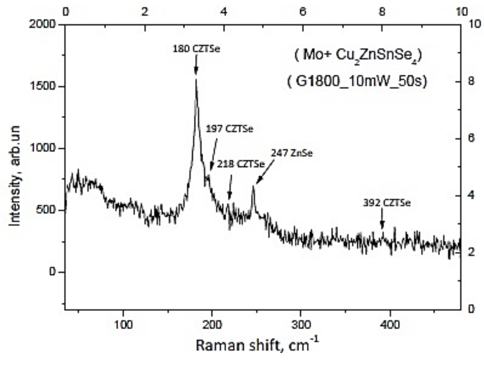

Figure 5. Raman spectrum of a $Cu_2ZnSnSe_4$ film deposited by magnetron sputtering on a Mo thin film [15]

Simultaneously, 8-10 Mo/$Cu_2ZnSnSe_4$/CdS/Mo heterostructures in the form of circles were created on a glass substrate (Figure 1). Separate films of Mo, $Cu_2ZnSnSe_4$, and CdS were obtained on the same glass substrate. This made it possible to study the morphology of the film surfaces, the electrical and photoelectric properties of heterostructures, and the physical properties of each layer independently.

The Raman spectrum of the $Cu_2ZnSnSe_4$ part was obtained and investigated. However, in this case, the Raman spectrum covers the region of 30-500 cm-1 and gives results that sharply differ from the previous Raman spectra of $Cu_2ZnSnSe_4$. The number of modes present in the kesterite semiconductor was 3, and the sharpest peak was observed at 301 cm^{-1}. The rest of the modes corresponded to frequencies of 41 cm^{-1}, 602 cm^{-1}. Comparison of the Raman spectra showed that this difference between the modes is associated with the presence of CdS (Figure 6).

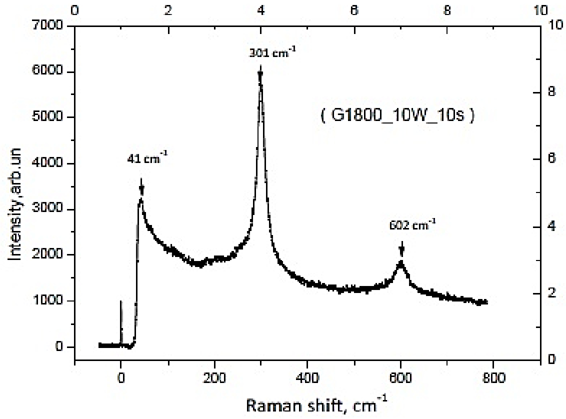

Figure 6. Raman spectrum of a CdS film deposited on a substrate from a $Cu_2ZnSnSe_4$ film by thermal evaporation in a vacuum [15]

Figure 7 shows the Raman spectra obtained in all three cases together. Here are the Raman spectra of:
- thin CdS layer on $Cu_2ZnSnSe_4$ / Mo (1);
- a thin layer of $Cu_2ZnSnSe_4$ on the molybdenum layer (2);
- only a thin $Cu_2ZnSnSe_4$ layer on a glass substrate (3).

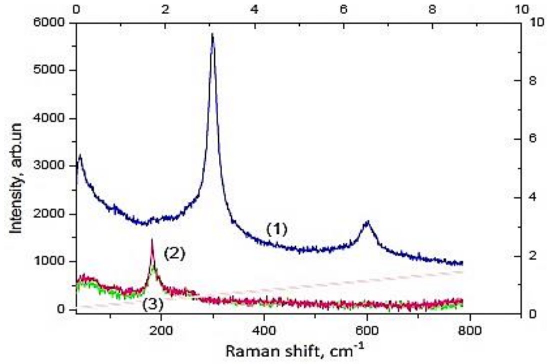

Figure 7. The Raman spectra [15]
- of a thin CdS layer on $Cu_2ZnSnSe_4$ / Mo (1);
- of a thin layer of $Cu_2ZnSnSe_4$ on the molybdenum layer (2);
- of only a thin $Cu_2ZnSnSe_4$ layer on a glass substrate (3)

The luminescence spectra of a semiconductor thin film (~100 nm) with a kesterite structure $Cu_2ZnSnSe_4$ were measured on a 3D confocal Raman microspectrometer Nanofinder 30 (Tokyo Instr., Japan). An Nd: YAG laser with a wavelength λ = 532 nm and a power of 5 mW was used as an excitation source. The scattering radiation detector was a CCD camera operating in the photon counting mode and cooled to -100 °C. The spectra were taken with the backward scattering direction. The cell spectrometer is 10 lines/mm. The wavelength corresponding to the maximum intensity in the photoluminescence spectrum of a thin layer of $Cu_2ZnSnSe_4$ semiconductor deposited on a glass substrate by magnetron sputtering is 850 nm as Figure 8.

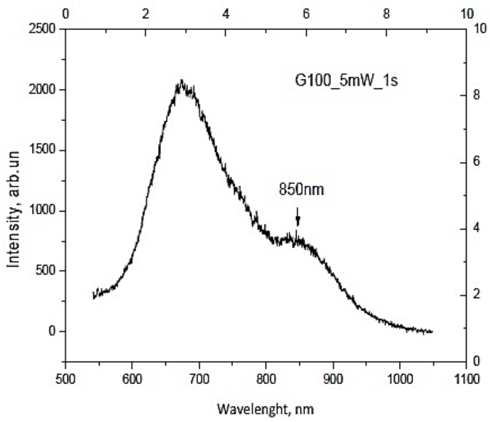

Figure 8. Photoluminescence spectra of a thin $Cu_2ZnSnSe_4$ film with a thickness (~ 100 nm) [15]

Studies of the absorption spectrum (Figure 9) of thin $Cu_2ZnSnSe_4$ film with a thickness (~ 100 nm) at the edge of intrinsic absorption have shown that the edge is shifted towards short waves. Apparently, this is due to the fact that the films are about 100-120 nm thick. For these measurements, we used a two-beam Specord-250+.

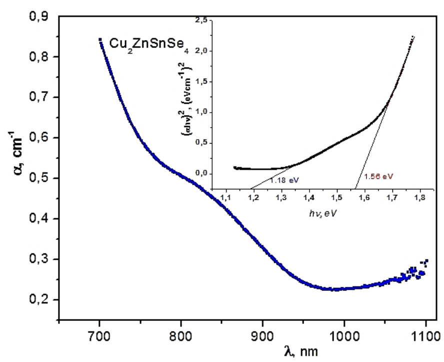

Figure 9. Adsorption spectra of thin $Cu_2ZnSnSe_4$ films obtained by magnetron sputtering method on the glass substrates

4. CONCLUSIONS

X-ray structure analysis revealed that the $Cu_2ZnSnSe_4$-based thin films deposited by magnetron sputtering method on glass substrates are an amorphous substance, but has non-sharp peaks and is prone to crystallization.

Raman spectroscopy was used to obtain Raman spectra from different parts of sample, and based on these spectra, it was determined that 179 cm^{-1}, 197 cm^{-1}, 235 cm^{-1} and 385 cm^{-1} frequency phonons correspond to CZTSe, and 248 cm^{-1} frequency phonons correspond to ZnSe.

From the photoluminescence spectrum of $Cu_2ZnSnSe_4$ thin films deposited by magnetron sputtering on glass substrates of $Cu_2ZnSnSe_4$ powder targets, it was determined that the maximum photoluminescence intensity corresponds to a wavelength of 850 nm.

Various technological modes of the magnetron sputtering method have been investigated to obtain high-quality thin layers of $Cu_2ZnSnSe_4$ for solar cells. It is shown that this method can be used to obtain homogeneous thin films with a mirror-like morphology of their surface.

5. ACKNOWLEDGEMENTS

The authors, express our sincere gratitude to Prof. Imir Aliyev, Prof. Imameddin Amiraslanov and Assoc. Prof. Irada Mammadova for their help in the synthesis of bulk crystals, for X-ray measurements for X-ray diffraction analysis and Raman spectroscopy, respectively.

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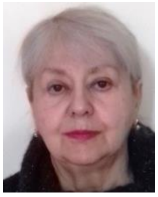
BIOGRAPHIES

Niyazi N. Mursakulov was born in Marneuli, Georgia on May 29, 1948. He is a leading researcher, associate professor in the "Physics of hetero-structures" laboratory of Institute of Physics, Azerbaijan Academy of Sciences, Baku, Azerbaijan. He received his postgraduate education in laboratory of Nobel Prize laureate Zh.I. Alferov, A.F. Ioffe Institute, St. Petersburg, Russia. His scientific research covered the topics of obtaining and researching semiconductor optoelectronic devices based on three and multicomponent solid solutions based on A^3B^5 operating in the medium-wave region of electromagnetic radiation. His research fields include development of technology for producing thin-film layers from chalcopyrite materials and layers from materials with a kesterite crystal structure. His publications are more than 150 articles and patents and 1 monograph. Over the years, at Baku State University, Baku, Azerbaijan and Baku Technical University, Baku, Azerbaijan. He gave lectures on technological methods of obtaining semiconductor devices based on heterojunctions, lectures on optoelectronics and nanotechnology. In recent years, he has lectured to undergraduates of Azerbaijan National Academy of Sciences, Baku, Azerbaijan.

Saida G. Nurieva was born in Saatli, Azerbaijan in 1996. In 2017 she graduated from Faculty of Physics, Baku State University, Baku, Azerbaijan with a bachelor's degree, and in 2019 with a master's degree. The topic of her master's thesis was "Ab-initio study of the electronic spectrum of a $TlFeSe_2$ crystal". She continues her scientific research on this topic. She currently works as a researcher (scientist) at Institute of Physics, Azerbaijan Academy of Sciences, Baku, Azerbaijan. At the moment she is a scientific researcher in the "Physics of nanocrystals" laboratory at the same institute. The topic of her new scientific research is "Obtaining thin-layer heteroconductors based on $Cu_2ZnSn\ (SeS)_4$, investigation their electrical, optical and photoelectric properties".



Nigar Nagi Abdulzade was born in Baku, Azerbaijan on October 13, 1947. She graduated from Faculty of Physics, Baku State University, Baku, Azerbaijan. She is a candidate of physics and mathematics, completed her Ph.D. thesis on "Electrical, optical properties and band energy structure of silver sulfide" in laboratories of A.A. Andreev, L.S. Stilbans and A.R. Regel, A.F. Ioffe Institute, St. Petersburg, Russia. From 1968 to the present, she has been working at Institute of Physics, Azerbaijan National Academy of Sciences, Baku, Azerbaijan. At the moment she is a leading researcher in the "Physics of nonequilibrium processes in semiconductors" laboratory and Associate Professor at the same institute. She continues researching semiconductors of the $A_2^1B^6$ group, and also participates in the development of technology for producing thin-films of chalcopyrite's and materials with a kesterite crystal structure.

Khayala Mazahir Guliyeva was born in Baku, Azerbaijan in 1984. In 2005 she graduated from Faculty of Physics, Baku State University, Baku, Azerbaijan with a bachelor's degree, and in 2007 with a master's degree. The topic of her master's thesis was "Electrical and photoelectric properties of oligo-beta naphthol-based heteroconductors". She have published the articles on this topic in scientific journals. She continues her scientific research on this topic. She currently works as a researcher (scientist) at Institute of Physics, Azerbaijan National Academy of Sciences, Baku, Azerbaijan. At the moment she is a scientific researcher in the laboratory of "Physics of heterostructures" at the same institute.