PHYSICS AND CHEMISTRY OF SOLID STATE
V. 25, No. 1 (2024) pp. 40-44
Section: Physics
DOI: 10.15330/pcss.25.1.40-44

Vasyl Stefanyk Precarpathian National University
ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 25, № 1 (2024) С. 40-44
Фізико-математичні науки

PACS: 68.55.-a, 68.37.-d ISSN 1729-4428

A.I. Kashuba[1], I.V. Semkiv[1], B. Andriyevsky[2], H.A. Ilchuk[1], N.T. Pokladok[1]

Structural and morphological properties of $CdSe_{1-x}S_x$ thin films obtained by the method of high-frequency magnetron sputtering

[1]*Department of General Physics, Lviv Polytechnic National University, Lviv, Ukraine,* andrii.i.kashuba@lpnu.ua
[2]*Faculty of Electronics and Computer Sciences, Koszalin University of Technology, Koszalin, Poland*

$CdSe_{1-x}S_x$ (x= 0.3, 0.4 and 0.6) thin films were deposited on quartz and silicon substrates by the method of high-frequency magnetron sputtering. The chemical composition analysis and crystal structure refinement was examined with using X-ray fluorescence spectroscopy and X-ray diffraction data. $CdSe_{1-x}S_x$ thin films crystallizes in hexagonal structure (structure type – ZnO, space group $P6_3mc$ (No. 186)). The lattice parameters (a, c and V), crystallite size (D), strain (ε), dislocation density (δ) and the texture coefficient $T_C(hkl)$ was estimated from X-ray diffraction analysis. Units-cell parameters decrease with increasing S content in $CdSe_{1-x}S_x$ thin film.

Keywords: thin film, solid-state solution, crystal structure, X-ray fluorescence spectroscopy, X-ray diffraction, crystallite size, texture coefficient.

Received 15 October 2023; Accepted 01 February 2024.

Introduction

Solar cells based on thin films of cadmium chalcogenides are devices that occupy a prominent place in the solar energy market. Such elements allow obtaining high efficiency of photoconversion while being characterized by a lower cost of modules compared to widely used elements based on silicon. CdTe is an excellent light-absorbing layer for solar cells [1, 2]. When forming high-efficiency heterojunctions based on *p*-CdTe used as window layers of solar batteries, cadmium sulfide (CdS) is mainly employed [3, 4]. When used in the heterojunction (CdS/CdTe) CdS as a window layer with a thickness near 150–300 nm, the photogenerated charge carriers almost completely recombine inside the CdS film and do not generate photocurrent. Due to a high absorption of light manifested by the CdS films, no photocurrent appears in the structure.

However, the occurrence of photocurrent is negatively affected by the lattice mismatch between the absorbing (CdTe) and window (CdS) layers. The reduced lattice mismatch between these active layers can be cut by the formation of CdS_xTe_{1-x} (or $CdTe_xS_{1-x}$) solid solutions. However, formation of such a solid solution has a problem of loss of efficiency which connected with high defect density [4–6]. The decreasing lattice mismatch between absorbing (CdTe) and window (CdS) layers can be solved by forming a solid solution CdTe-CdSe and CdS-CdSe. In the first step of studies, the solid solution $CdSe_{1-x}S_x$ thin films were deposited by the chemical method [7]. However, this method does not give films with different composition ratios (only $CdSe_{0.7}S_{0.3}$ films were obtained [7]). Also, the concentration behavior of the electronic and optical properties of the solid solution $CdSe_{1-x}S_x$ thin films was studied using the theoretical and experimental methods only for $CdSe_{0.7}S_{0.3}$ [7, 8]. In the present work, we report on the investigation of the structural and morphological properties of $CdSe_{1-x}S_x$ (x= 0–1) thin films which were produced on quartz and silicon substrate by HF magnetron sputtering.

I. Details of experiment

$CdSe_{1-x}S_x$ thin films were deposited on quartz and silicon substrates with a size of 16×8×1.1 mm^3 by the method of HF magnetron sputtering (13.6 MHz) using a VUP-5M vacuum station (Selmi, Ukraine). Before the

sputtering process, the chamber was evacuated. The gas pressure inside the chamber was 4×10^{-4} Pa. The sputtering was carried out at a pressure of argon (Ar) in the range of 1.0–1.3 Pa. The power of the HF magnetron was maintained at the level of 50 W. For heating the substrates, a high-temperature tungsten heater with a power of 300 W was used, and the temperature of the substrate was kept at 453 K. The temperature was controlled by means of a proportional–integral–derivative (PID) controller for controlling heating and cooling rates, as well as for ensuring the temperature conditions of deposition. A crystalline target of 99.99 % purity of $CdSe_{0.75}S_{0.25}$, $CdSe_{0.5}S_{0.5}$ and $CdSe_{0.25}S_{0.75}$ (thickness – 1 mm, diameter – 40 mm) was used. The target–substrate distance was 60 mm. The deposition time was 16 min for all samples. The start and end of the process were controlled by means of a movable shutter.

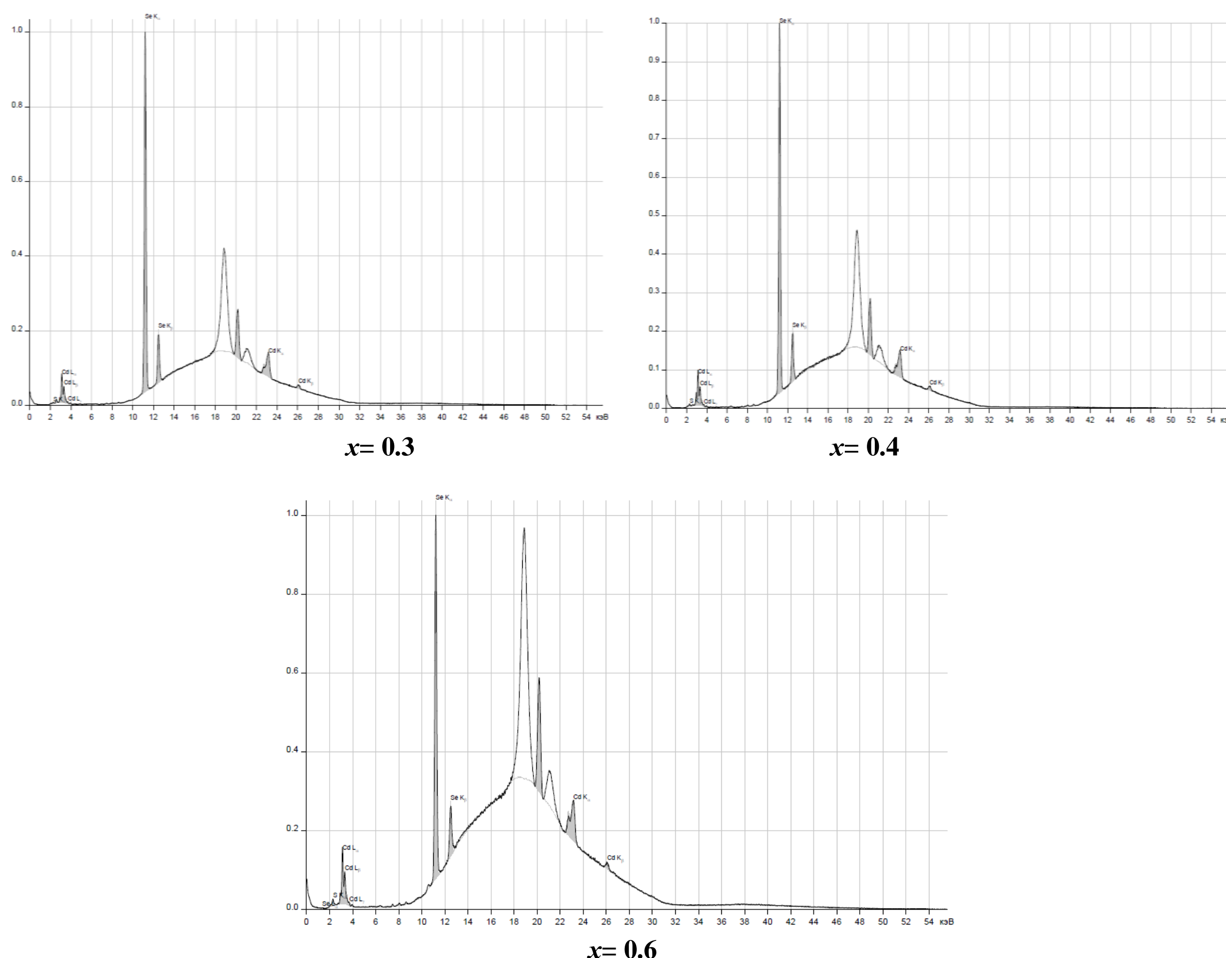
The phase analysis and crystal structure refinement were examined with using X-ray diffraction data at the room temperature. The arrays of the experimental intensities and angles of reflection from the investigated samples were obtained using a DRON-2.0M diffractometer (FeKα1 radiation, λ= 1.936087 Å). The X-ray fluorescence spectroscopy (XRF) studies were used for analyzing the chemical composition of materials [6].

II. Results and Discussion

The chemical composition of materials and the composition ratio in thin films were analysed by the X-ray fluorescence spectroscopy (XRF). The XRF analysis of $CdSe_{1-x}S_x$ thin films is shown in Fig. 1. The spectra show that the thin film is formed from the desired elements (Cd–Se–S). Also, the chemical composition obtained from XRF spectroscopy is listed in Table 1.

We observed a composition change in the composition ratio of the used target and the ratio obtained from XRF. This composition change is also observed when depositing $Cd_{1-x}Zn_xTe$, $CdTe_{1-x}Se_x$ and $Cd_{1-x}Mn_xTe$ thin films, and is caused by the nonequilibrium deposition process [6–7, 9, 10].

Crystal structure of $CdSe_{1-x}S_x$ (x= 0.3, 0.4 and 0.6) has been determined from XRD (see Fig. 2). $CdSe_{1-x}S_x$ thin



x= 0.3 **x= 0.4**

x= 0.6

Fig. 1. XRF of $CdSe_{1-x}S_x$ thin films.

Table 1.

Results of XRF analysis for $CdSe_{1-x}S_x$ thin films.

Composition ratio of used target	Composition ratio obtained from XRF	x
$CdSe_{0.75}S_{0.25}$	$CdSe_{0.7}S_{0.3}$	0.3
$CdSe_{0.5}S_{0.5}$	$CdSe_{0.6}S_{0.4}$	0.4
$CdSe_{0.25}S_{0.75}$	$CdSe_{0.4}S_{0.6}$	0.6

films crystallizes in hexagonal structure (structure type – ZnO, space group $P6_3mc$ (No. 186)). Unit-cell parameters are listed in Table 2. As we can see, from XRD analysis the units-cell parameters decrease with increasing S content in $CdSe_{1-x}S_x$ thin films (see Fig. 3). This effect is caused by the decreasing atomic radius when atoms Se (R_{Se}= 140 pm) substitute by S (R_S= 127 pm). No additional XRD peaks belonging to other compounds can be detected, which indicates the formation of a pure single phase, as well as the fact that S is well integrated into the CdSe lattice.

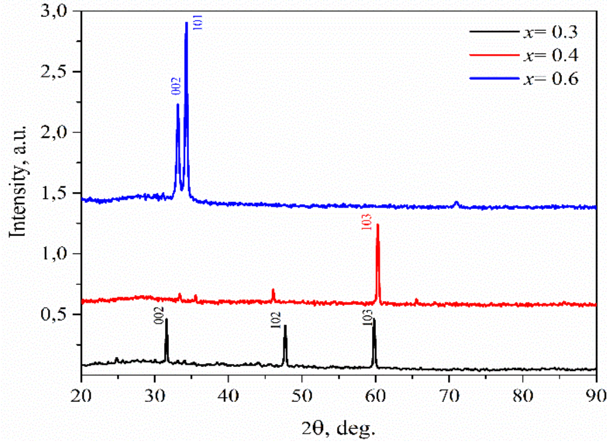


Fig. 2. XRD pattern of $CdSe_{1-x}S_x$ thin films.

Table 2.

Results of XRD analysis for $CdSe_{1-x}S_x$ thin films.

x	**0.3**	**0.4**	**0.6**
Structure type	ZnO		
Space group	$P6_3mc$		
***a*, Å**	4.300(2)	4.231(5)	4.220(1)
***c*, Å**	6.812(4)	6.811(10)	6.801(4)
***V*, Å³**	109.13(7)	105.7(2)	104.93(7)
***D*, nm**	98.1	59.3	108.2
δ, nm⁻²	1.04 10⁻⁴	2.84 10⁻⁴	8.54 10⁻⁵
ε	0.05	0.07	0.04

However, is the dependences of the cell parameters *a*, *c*, and *V* on the content index *x* are not linear but they show the close to parabolic behavior with deviation downwards. Such behavior of structure parameters must have an effect on the optical, electrical and other properties of study samples. This assumption however needs to make additional measurements.

A detailed comparison of the positions and intensities of experimental reflexes with theoretical peaks allowed the determination of the strong preferential orientation of the grains in the deposited $CdSe_{1-x}S_x$ thin films. In the observed diffractograms, the reflexes from all planes with the *hkl* Miller indices are quenched in intensity, and the exception is the observed reflexes from the planes (002), (101), (102) and (103). The observed insignificant noise can be explained by reflexes from the substrate. Also, we can see from Fig. 2 that the largest intensity of the reflex corresponds to the (101) plane with sulfur content x= 0.6. When S content decreases (x= 0.3 and 0.4) in thin films the largest intensity is observed for (103) plane.

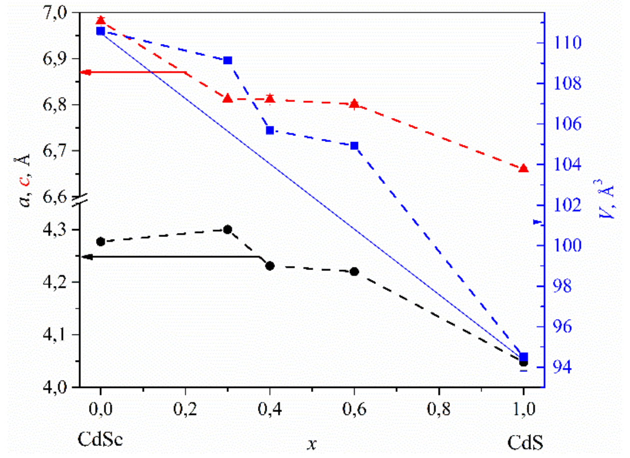


Fig. 3. Concentration dependence of lattice parameters of the $CdSe_{1-x}S_x$ thin films. Data for CdSe and CdS taken from [11].

The crystallite size (D) was estimated from the peaks broadening using Scherrer's equation [7]:

$$D = \frac{0.9\lambda}{B\cos\theta} \quad (1)$$

where λ is the wavelength of X-rays, B is full width at half maximum (FWHM) and θ is the Bragg's angle. The strain (ε) and the dislocation density (δ) were calculated using the following relations [7, 12]:

$$\delta = \frac{1}{D^2} \quad (2)$$

$$\varepsilon = \frac{\Delta(2\theta)\cdot\cos\theta}{4} \quad (3)$$

The parameters (D, δ and ε) obtained from XRD are listed in Table 2. The preferential growth orientation is determined using the texture coefficient $T_C(hkl)$ [13]:

$$T_C = \frac{I(hkl)/I_0(hkl)}{(1/N)\sum_N I(hkl)/I_0(hkl)} \quad (4)$$

where $I(hkl)$ is the measured relative intensity of the plane (hkl), $I_0(hkl)$ is the standard intensity of the plane (hkl) taken from the JCPDS data, and N is the number of diffraction peaks. The texture coefficient shows an allotment for each reflection orientation in comparison to an utterly randomly oriented sample. The random orientation corresponds to $T_C = 1$, while the T_C values above 1 show preferential orientation in the related direction [6, 14]. The parameters obtained from X-ray diffraction are listed in Table 3.

Unification may be obtained by calculating the standard deviation [15]:

$$\sigma = \left[\frac{\sum_N\left(T_C(hkl)-T_{CR}(hkl)\right)^2}{N}\right]^{0.5} \quad (5)$$

where the $T_{CR}(hkl)$ is the value for a randomly oriented sample ($T_{CR}(hkl)$= 1). Values of standard deviation, σ, close to zero indicate the absence of order. This value is listed in Table 3. Analysis of the texture coefficients shows that the preferred orientation for $CdSe_{1-x}S_x$ thin films with x< 0.5 is (103) and it changes to (101) for samples with

Table 3.

The texture coefficient (T_C) of $CdSe_{1-x}S_x$ thin films.

hkl / *x*	002	101	102	103	σ
0.3	0.47	–	1.14	1.38	0.39
0.4	–	–	–	1.98	0.98
0.6	0.79	1.21	–	–	0.21

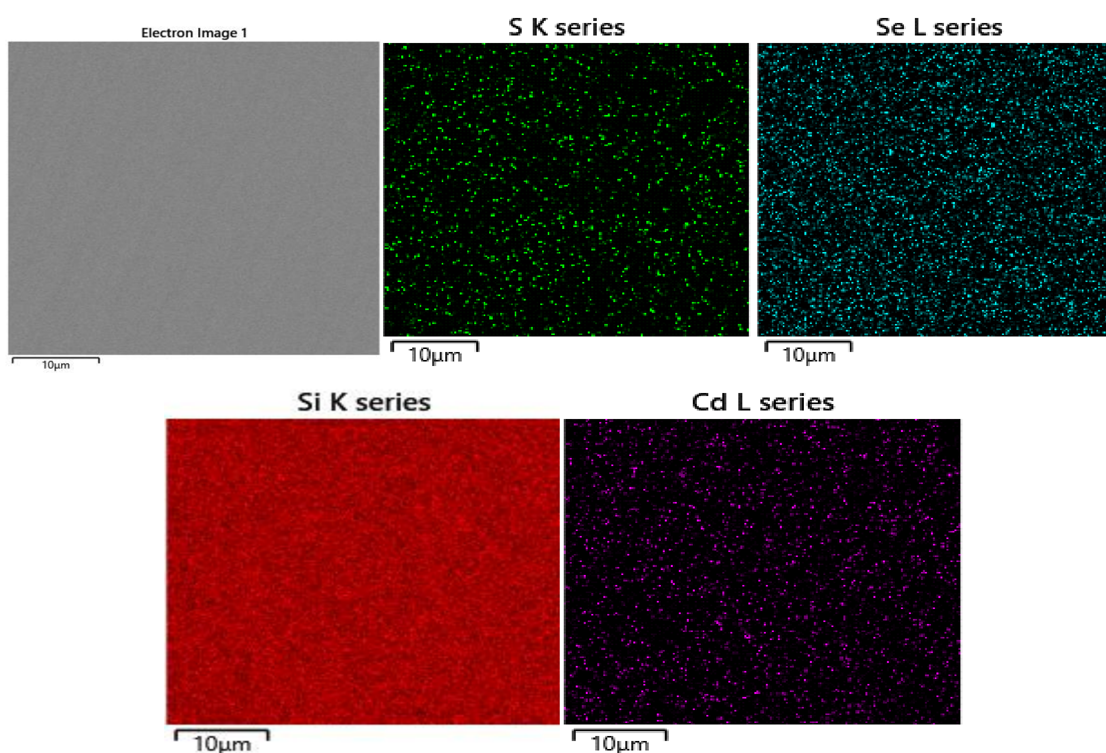


Fig. 4. Surface morphology of the $CdSe_{1-x}S_x$/silicon (x= 0.3) thin film.

x> 0.5. Also, the sample with a composition close to equilibrium shows high ordering ($\sigma_{x=0.4}$=0.98).

The surface morphology of the synthesized $CdSe_{1-x}S_x$/silicon (x= 0.3) thin films is given in Fig. 4. The choice of substrate is determined by the requirements for the experiment (conductivity of studies sample). Therefore, $CdSe_{1-x}S_x$ thin films were deposited on silicon substrates. These measurements are very important for the validation formation of solid solution $CdSe_{1-x}S_x$ thin films with a balanced distribution of chemical elements in samples. The energy dispersive X-ray study (EDX) shows that the thin film is formed from the desired elements and their distribution is umiform. The presence of Si in the sample can be attributed to the substrate.

Conclusion

$CdSe_{1-x}S_x$ thin films were deposited onto quartz and silicon substrates by the method of HF magnetron sputtering. The composition ratios of the thin films obtained by using XRF method were found to be $CdSe_{0.7}S_{0.3}$, $CdSe_{0.6}S_{0.4}$ and $CdSe_{0.4}S_{0.6}$. XRD analysis has revealed that all deposition thin films are crystallized in a hexagonal structure. The tendency to decreasing of the unit-cell parameters with increasing S content was observed in $CdSe_{1-x}S_x$ thin films. The anomaly reflexes from the planes with Miller indices (002), (101), (102) and (103) are observed. Crystallite size (D), strain (ε), dislocation density (δ) and the texture coefficient T_C(hkl) were estimated from X-ray diffraction analysis for all samples. Based on the analysis of the texture coefficients the obtained preferred orientations are (103) for $CdSe_{1-x}S_x$ thin films with x< 0.5 and (101) for the sample with x> 0.5. It was found that that the composition close to the equilibrium, $CdSe_{0.6}S_{0.4}$, shows the high ordering ($\sigma_{x=0.4}$=0.98). Based on the surface morphology and EDX analysis it was found that the thin film is formed from the desired elements and their distribution is uniorm.

Acknowledgement

This research was supported by the National research foundation of Ukraine (project No 2022.01/0163).

Kashuba A.I. – Ph.D, Doctoral Student at the Department of General Physics;
Semkiv I.V. – Ph.D., Head of the Department of General Physics;
Andriyevsky B. – Sc.D., Profesor at the Department and Electronics and Computer Sciences;
Ilchuk H.A. – Sc.D, Profesor at the Department of General Physics;
Pokladok N.T. – Ph.D, Associate Professor at the Department of General Physics.

[1] R. Petrus, H. Ilchuk, A. Kashuba, I. Semkiv, E. Zmiiovska, *Optical properties of* CdTe *thin films obtained by the method of high-frequency magnetron sputtering*, Functional Materials, 27(2), 342 (2020); https://doi.org/10.15407/fm27.02.342.
[2] H.A. Ilchuk, L.I. Nykyruy, A.I. Kashuba, I.V. Semkiv, M.V. Solovyov, B.P. Naidych, V.M. Kordan, L.R. Deva, M.S. Karkulovska, R.Y. Petrus, *Electron, phonon, optical and thermodynamic properties of* CdTe *crystal calculated by DFT*, Physics and Chemistry of Solid State., 23(2), 261 (2022); https://doi.org/10.15330/pcss.23.2.261-269.
[3] N. Romeo, A. Bosio, V. Canevari, A. Podestà, *Recent progress on* CdTe/CdS *thin film solar cells*, Sol. Energy, 77(6), 795 (2014); https://doi.org/10.1016/j.solener.2004.07.011.
[4] A. Kashuba, H. Ilchuk, I. Semkiv, I. Kuno, N. Pokladok, N. Ukrainets, *Refractive index and optical dielectric function of* $CdTe_{0.9}Se_{0.1}$ *thin film obtained by quasi close-space sublimation method*, Functional Materials, 30(3), 332 (2023); https://doi.org/10.15407/fm30.03.332.
[5] B.B. Dumre, N.J. Szymanski, V. Adhikari, I. Khatri, D. Gall, S.V. Khare, *Improved optoelectronic properties in* $CdSe_xTe_{1-x}$ *through controlled composition and short-range order*, Sol. Energy, 194, 742 (2019); https://doi.org/10.1016/j.solener.2019.10.091.
[6] A.I. Kashuba, B. Andriyevsky, *Growth and crystal structure of* $CdTe_{1-x}Se_x$ ($x \geq 0.75$) *thin films prepared by the method of high-frequency magnetron sputtering*, Low. Temp. Phys., 50(1), 29 (2024); https://doi.org/10.1063/10.0023888.
[7] H.A. Ilchuk, E.O. Zmiiovska, R.Y. Petrus, I.V. Petrovich, I.V. Semkiv, A.I. Kashuba, *Dynamics of change of electronic and optical properties of substitutional solid* $CdSe_{1-x}S_x$ *solutions*, Nanosistemi, Nanomateriali, Nanotehnologii, 18(1), 59 (2020).
[8] A.I. Kashuba, B. Andriyevsky, O.S. Kushnir, I.V. Semkiv, T.S. Malyi, R.Yu.Petrus, *Concentration dependences of electronic band structure of* $CdSe_{1-x}S_x$ *thin films*, Appl. Nanosci., 13(7), 4761 (2023); https://doi.org/10.1007/s13204-022-02613-4.
[9] J. Lai, J. Wang, L. Wang, H. Ji, R. Xu, J. Zhang, J. Huang, Y. Shen, J. Min, L. Wang, Y. Xia, *Characterization of* CdMnTe *films deposited from polycrystalline powder source using closed-space sublimation method*, Journal of Vacuum Science & Technology A, 33(5), 05E125 (2015); https://doi.org/10.1116/1.4927820.
[10] V. Kosyak, A. Opanasyuk, P.M. Bukivskij, Yu.P. Gnatenko, *Study of the structural and photoluminescence properties of* CdTe *polycrystalline films deposited by close-spaced vacuum sublimation*, J. Cryst. Growth. 312(10), 1726 (2010); https://doi.org/10.1016/j.jcrysgro.2010.02.034.
[11] H. Ilchuk, R. Petrus, I. Semkiv, A. Kashuba, *Directional synthesis of* CdX (X= S, Se, *and* Te) *thin films for solar cell application*, Springer Proceedings in Physics, 247, 117 (2020); https://doi.org/10.1007/978-3-030-52268-1_9.
[12] S. Prabahar, M. Dhanam, CdS *thin films from two different chemical baths-structural and optical analysis*, J. Cryst. Growth. 285(1-2), 41 (2005); https://doi.org/10.1016/j.jcrysgro.2005.08.008.
[13] S.N. Alamri, *The growth of* CdTe *thin film by close space sublimation system*, phys. stat. sol. (a), 200(2), 352 (2003); https://doi.org/10.1002/pssa.200306691.
[14] H.R. Moutinho, F.S. Hasoon, F. Abulfotuh, L.L. Kazmerski, *Investigation of polycrystalline* CdTe *thin films deposited by physical vapor deposition, close-spaced sublimation, and sputtering*, Journal of Vacuum Science and Technology, A, 13(6), 2877 (1995); https://doi.org/10.1116/1.579607.
[15] K.H. Kim, J.S. Chun, *X-ray studies of* SnO_2 *prepared by chemical vapour deposition*, Thin Solid Films. 141(2), 287 (1986); https://doi.org/10.1016/0040-6090(86)90356-1.

А.І. Кашуба[1], І.В. Семків[1], Б. Андрієвський[2], Г.А. Ільчук[1], Н.Т. Покладок[1]

Структурно-морфологічні властивості тонких плівок $CdSe_{1-x}S_x$, отриманих методом високочастотного магнетронного розпилення

[1]*Кафедра загальної фізики, Національний університет "Львівська політехніка", Львів, Україна,*
andrii.i.kashuba@lpnu.ua
[2]*Факультет електроніки та комп'ютерних наук, Кошалінський університет технологій, Кошалін, Польща*

Тонкі плівки $CdSe_{1-x}S_x$ (x= 0.3, 0.4 та 0.6) осаджено на кварцові та кремнієві підкладки методом високочастотного магнетронного напилення. Аналіз хімічного складу та уточнення кристалічної структури досліджено за допомогою рентгенівської флуоресцентної спектроскопії та рентгенівської дифракції. Тонкі плівки $CdSe_{1-x}S_x$ кристалізуються в гексагональну структуру (тип структури – ZnO, просторова група $P6_3mc$ (№ 186)). Параметри кристалічної решітки (a, c і V), розмір кристалітів (D), деформація (ε), щільність дислокацій (δ) і текстурний коефіцієнт $T_C(hkl)$ оцінювали за результатами рентгенівського дифракційного аналізу. Параметри елементарної комірки зменшуються зі збільшенням вмісту сеpу в тонкій плівці $CdSe_{1-x}S_x$.

Ключові слова: тонка плівка, твердий розчин, кристалічна структура, рентгенівська флуоресцентна спектроскопія, рентгенівська дифракція, розмір кристалітів, текстурний коефіцієнт.