

DOI:

UDK 538.911

A. Dedoborz, associate professor, Mathematphysics@gmail.com

A. Kletskov, assistant, alex.k187@i.ua

Department of higher mathematics and physics of the Dnepr state agrarian-economic university

THE METHODS BY CONTROL OF THICKNESS TAPES IN CdSe/ZnTe GOT BY METHOD OF QCV

Considered various methods of measuring lines of semiconductor tapes and comparison with experimental data got the method of receipt in the quasi-closed volume.

Keywords: *time of evaporation; speed of besieging; vaporizer; lining.*

Розглянуті різноманітні методи вимірювання товщин напівпровідникових плівок та зіставленні з експериментальними даними отриманими методом отримання в квазізамкненому об'ємі.

Ключові слова: *час випаровування; швидкість осадження; випарник; підкладка.*

Problem's Formulation

The receipt of semiconductor tapes of different thickness puts the problem of choice of methods for exact determination them thickness. Choice most optimal by means of which it is possible most exactly to measure thickness for different configurations of semiconductor pellicle structures.

Analysis of recent research and publications

Research of methods of measuring of thickness of semiconductor tapes of connections of A2B6 many works are sanctified to, including [12,13,14,15]. For determination of the most optimal method of measuring of thickness of semiconductor tapes and their comparing to experimental data, got in QCV drawn on the results of research of authors [1—15].

Formulation of the study purpose

The purpose of work is determination of the most optimal method of measuring of thickness of semiconductor tapes on the basis of comparison with experimental data by the used method of QCV.

Presenting main material

Semiconductor tapes of CdSe and ZnTe are materials of group AІІВVI for the use in modern electronic devices, such as sunny elements, light-emitting diodes, gas touch-controls et al [1,2].

A synthesis of thin-films of CdSe and ZnTe, receipt and understanding of physical information about their properties is the necessary condition of development of stable devices on their basis.

For the receipt of tapes of selenid of cadmium and telurid of zinc use different methods: high-frequency magnetron nebulized [3], gas-transport method (PVT) [4], chemical gas phase besieging (CVD) [5], molecular-radial epitaxition [6], thermal vacuum evaporation [7] and thermal evaporation in the quasi-closed volume (QCV)[8].

A receipt is enough clean semiconductor tapes of group AІІВVI, in particular CdSe and ZnTe, in the conditions of vacuum becomes complicated by the difference of pressures of the saturated pair of components of connections. Also the important parameter of synthesis of tapes in a vacuum is a level of remaining gases which are able to enter into chemical reactions with the matter of lining and included in the grates of crystals. They, as a rule, out-of-control influence on speed of height of tapes, their structure. Therefore growing of semiconductor tapes from a steam phase it is necessary to conduct in a gas-free vacuum system with remaining pressure chemically active gases not more than 10^{-5} Па.

The choice of method of QCV in this work is conditioned by that he allows to get the homogeneous, structurally perfect thin-films of semiconductor materials, near to the thermodynamics equilibrium which is basic advantage of this method before other vacuum technologies [9,10]. Important advantage of method is high pressure of pair of halhogenide in QCV, pressure of remaining gases in the swept volume [11], that considerably exceeds (on four orders) pressure of remaining gases in the swept volume.

In this research a device was used for the all-epitaxial increase of tapes of VCC-5M, which shows by itself QCV (fig. 1). At thermal evaporation distance of L between a vaporizer and lining folded from a 100 mm a to 500 mm. Radius of ring of vaporizer — $r = 5$ mm. Vaporizer was cutting-in in tungsten thin (\varnothing to the wire a 0,8 mm) with quartz crucible, where hallogenide was loaded. Mass of evaporant folded from 50 mg to 200 mg. A lining area is covered by the layer of tape of $F = 3 \cdot 10^{-4} \text{ m}^2$. Pressure of remaining gas of $P = 10^{-1}$ Step. A closeness of matter of tape is $\rho (\text{CdSe}) = 5,81 \cdot 10^3 \text{ kg/m}^3$, a closeness of matter of tape is $\rho (\text{ZnTe}) = 6,34 \cdot 10^3 \text{ kg/m}^3$.

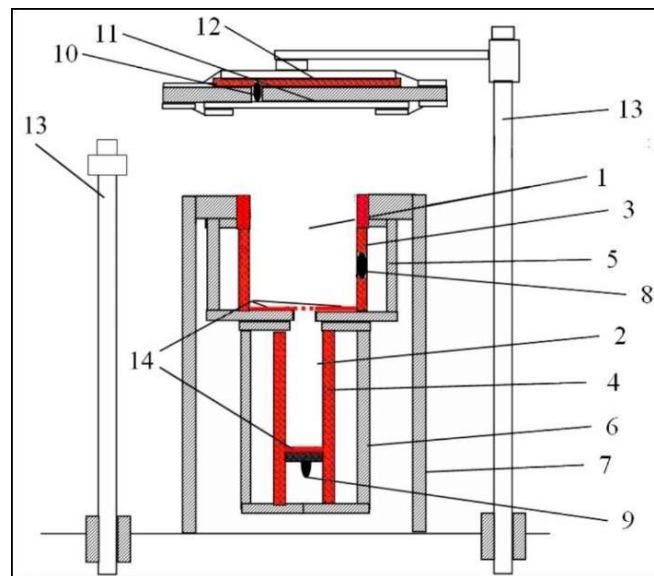


Fig. 1. Chart of device for the synthesis of tapes of CdSe and ZnTe in QCV: 1, 2 are the evaporated compartments; 3, 4 are heaters of walls; 5—7 are afterheaters; 8—10 are thermocouples; 11 is lining; 12 is a lining heater; 13 are stands; 14 are heater elements of vaporizer [12]

During research were is got semiconductor tapes in the wide range of thin.

A necessary condition for the receipt of devices on the basis of semiconductor tapes of group AIIIVI is control of thickness of used standards. Measuring of thickness of tapes possibly both after and in the process of (in situ) their vaporise.

Will consider at first "in situ" methods. These methods are widely enough widespread, and most modern vacuum options of vaporise are equipped by the corresponding supervisory systems. A photometric method and method of quartz resonator behave to them.

The photometric method of control of thickness is used both for opaque and for transparent in the visible range of light of tapes.

Essence of him is taken to measuring of transmissivity (whether reflection) of vaporised tape on the special control standard (witness, companion). For transparent tapes this method is very effective, but requires the use of monochromatic light, as the phenomenon of interference is here used. In this work a device was used for the all-epitaxial increase of tapes of VCC-5M in which control of thickness of tapes was carried out by means of sensors which work exactly on the photometric method of control.

Will consider the method of quartz resonator more more detailed. Frequency of vibrations of quartz crystal of f with mass of M arcwise changes with the change of mass of material of m , that is besieged.

Change of resonance frequency

$$\Delta f = f \cdot m/M. \quad (1)$$

Knowing a closeness ρ and area of S of tape, it is possible to get expression for determination of her thickness:

$$d = \frac{m \cdot \Delta f}{S \cdot \rho \cdot f} \quad (2)$$

The choice of frequency depends on the range of measureable thickness of tapes. For thin-films and large sensitiveness use high-frequencies. The sensitiveness of quartz resonator is estimated as $m/\Delta f = 10^{-10}$ g/Hertz. Application of radiotechnical apparatus at $f = 20$ Mhz allows to define the change Δ of $f = 20$ Hertz, that enables to measure the increase of mass an about 10^{-9} g/sm² or 0,01—0,1 nm thickness. Practically exactness folds 2—20 nm. Will mark, that with high enough exactness it is possible this method to control speed of height of tape.

Farther of will consider a few most widespread methods of verification of thickness of standards after their receipt.

1. Experimental method — if to examine a vaporizer as ring of certain radius which is in QCV, then it is possible on the basis of initial data of receipt of standards to expect the value of thickness of semiconductor tape.

Speed of evaporation v_B inid est the amount of matter which evaporating for one second from unit of area of surface of vaporizer calculates in obedience to the formula of Hertz-Knudsen [13] but looks like:

$$v_B = 0,585 \cdot P_s \sqrt{\frac{m}{T}}, \quad (3)$$

where P_s is pressure of pair of matter.

In times of t evaporation an amount of the evaporated matter is from the vaporizer of radius of r :

$$\sigma = v_B \cdot \pi \cdot r^2 \cdot t. \quad (4)$$

On condition that all atoms of evaporant condense on lining, it is possible to consider that $\sigma = m$, where m is mass of the got tape.

The thickness of tape can be certain from correlation:

$$d = \frac{v_B \cdot \pi \cdot r^2 \cdot t}{F \cdot \rho} = \frac{0,585 \cdot P_s \sqrt{\frac{m}{T}}}{F \cdot \rho} \cdot \pi \cdot r^2 \cdot t, \quad (5)$$

where m is mass of evaporant, t is time of evaporation.

2. Theoretical method — if to examine a vaporizer as ring of certain radius which is athwart to the normal to the surface of lining.

The thickness of tape on a flat subspoon which is athwart to the normal to the surface of vaporizer is determined by expression [14]:

$$d = \frac{m \cdot L^2}{\pi \cdot \rho \cdot a^4}, \quad (6)$$

where a is distance from a vaporizer to the viewing point, L is distance from a vaporizer to the center of lining.

For determination of thickness of d it is necessary to examine evaporation from all elements of ring [14]. The angular co-ordinates of element of vaporizer are determined by a corner α , and for the stowage of holding from every element it is necessary to integrate for α from 0 to 2π .

$$a^2 = L^2 + r^2 + h^2 + 2 \cdot h \cdot r \cdot \cos(\alpha), \quad (7)$$

where h is distance from the center of lining to the viewing point, r is a radius of ring of vaporizer.

At calculations for a "constant ring which consists of point or superficial vaporizers". Integration for α equalization (6) taking into account equality (7) gives for a size d expression:

$$d = \frac{m}{\pi \cdot \rho} \cdot \frac{L^2 \cdot (L^2 + h^2 + r^2)}{((L^2 + h^2 + r^2)^2 - 4 \cdot r^2 \cdot h^2)^{3/2}}. \quad (8)$$

3. A spectral method is determination of thickness of tapes by means of spectrums of key-in.

Research of spectral dependence of optical key-in in a visible and near infra-red area is conducted with the use of spectrophotometer of Shimadzu UV-3600. All optical researches were conducted at a room temperature.

For determination of thickness of the investigated tapes it is possible to use equalization:

$$d = \frac{M \cdot \lambda_1 \cdot \lambda_2}{2 \cdot (n(\lambda_1, \lambda_2) - n(\lambda_2, \lambda_1))}, \quad (9)$$

where λ_1 and λ_2 are lengths of waves, corresponding to the nearby extreme points on the spectrum of key-in, $M = 1$ for two nearby extremums one to the type (max - max, min - min) and $M = 1/2$ for two

nearby extremums of opposite type (max - min, min - max). The value of index of refraction is taken from his spectral dependence, resulted in [15].

Farther expect on equalization (9) the mean value of thickness for all combinations of extreme points.

4. A gravimetrical (gravimetric) method is determination of thickness by means of weighing.

A gravimetrical method (whether method of mikro weighing) is based on the exact weighing of lining to and after besieging of tape. Thickness of tape:

$$\text{---}, \quad (10)$$

where m_1 , m_2 is lining mass without tape and with her, accordingly; ρ it is a closeness of tape; S is her area.

This method is simple, but requires, that a lining form was to the outage, and her surface — viewly. In addition, the closeness of the inflicted material which can change depending on the terms of the technological modes (remaining pressure, contaminations by the molecules of gas and other) influences on exactness of measuring. Exactness of determination of thickness of tape depends this method, first of all, from the sensitiveness of scales and weighing exactness, and also from exactness of determination of area of tape and her closeness. Test-sensitivity of weighing folds 1—10 mkm/m².

5. Method of multibeam interferometry — consists in a supervision in the microscope of interference stripes, which arise up at consideration in the monochromatic light of two surfaces, located under a corner to each other.

For that, not to damage the got standards of measuring of thickness conducted on the so-called "alarm" standard which turned out at the same terms and has sizes. Before measuring get on a standard a "step" — sharp lateral limit of tape on lining. For this purpose part of lining at vaporize of tape is chemically deleted. In a microscope look after the change of interference stripes (fig. 2).

Light and dark interference stripes alternate with the step of L on the surface of both tape and lining and moved in relation to each other on a limit tape is lining on the value of l .

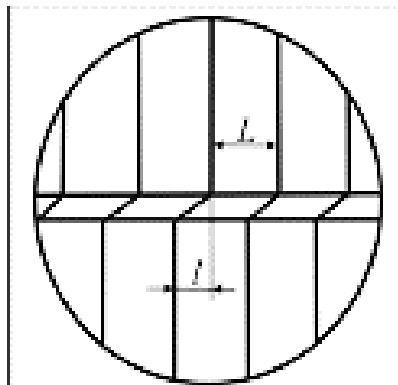


Fig. 2. Changes of interference stripes

Measuring the change of some certain stripe by means of mikro interference microscope, expect the thickness of tape after a formula:

$$\text{---}, \quad (11)$$

where λ_c is a wave-length of monochromatic light; L is a step between nearby interference stripes; l is a change of interference stripe. Exactness of this method of measuring of thickness of tape folds 15—30 nm. If tape is transparent, in the place of "step" on her and on lining besiege opaque metallic tape which well beats back light additionally, a thickness of which, to decrease the brought in error, must be far less thickness of measureable tape.

6. A method of capacitance-resistance sensor is measuring of thickness of tape on the basis of data of resistance of tape.

At measuring preliminary make the special control lining "witness" from an insulant, on which inflict flat blivets from material of high conductivity. Then this lining is a "witness" set in a working chamber the nearest to the working lining. It is necessary in order that both linings at causing of tape were in identical terms. Tape is inflicted on the control and working linings simultaneously.

The thickness of tape in this case can be defined after a formula:

$$\text{---}, \quad (12)$$

where ρ is specific resistance of tape; R is resistance of tape on a "witness" between contacts; L and h is length and width of tape on a "witness". Test-sensitivity folds 1—5 nm, and maximum thickness of measureable tapes — about 1 mkm.

In future will compare data of thickness tapes got photometric sensors with the calculations of thin, expected by different methods.

Table. 1. Thickness of tapes of CdSe/ZnTe

Mass, mg	d , mkm	d_{kv} , mkm	d_{ek} , mkm	d_{teors} , mkm	d_{sp} , mkm	d_{gr} , mkm	d_{int} , mkm	d_{res} , mkm
25	0,135	0,133	0,133	0,137	0,130	0,132	0,129	0,134
50	0,275	0,273	0,270	0,274	0,270	0,272	0,273	0,273
75	0,415	0,413	0,418	0,410	0,410	0,413	0,415	0,413
85	0,470	0,466	0,472	0,466	0,466	0,468	0,468	0,468
100	0,550	0,552	0,555	0,548	0,552	0,552	0,555	0,550

As evidently from a tabl. 1 most near are calculations conducted by the methods of quartz resonator, gravimetric and method of capacitance-resistance sensor. A method of quartz resonator is "in situ" by a method, while gravimetric and a method of capacitance-resistance sensor is measuring methods on receipt. Each of them has as the advantages so defects. Advantages of gravimetric and capacitance-resistance methods is relative simplicity of their implementation, while their defects are rigorisms enough to the cleanness and quality of used tapes. A method of quartz resonator in turn is let in on the ground also and defects. His advantages are high enough exactness of measuring and possibility in the process of receipt operatively to react on speed of besieging of tapes. Defects is complication of establishment of quartz sensors, if they construction are not planned and necessity enough frequent replacement of quartz resonators, as a result of their contamination by materials of tapes.

Summarizing the above-mentioned it is possible to draw conclusion, that for every case the method of measuring of thickness of the got tapes is accepted. For thin-films the most exact measuring will be for method of quartz resonator, while for more thick thin acceptable results will be and for the methods of capacitance-resistance sensor and gravimetric method.

Conclusions

Considered different methods of control of thickness of semiconductor tapes. Within the framework of the considered methods the chosen methods which most acceptable in certain terms.

By means of the brought methods over the measured thickness of semiconductor tapes. Comparison of results of thin of different tapes is conducted, at it data of experiment with high exactness of equal with data by the expected different methods. The most optimal methods of control of thin are chosen.

References

- [1] Zhang Y. & Li P. & Lau W.M. & Gao Y. & Zi J. & Zheng Z. (2014). Electronic devices of semiconductor. Material Chemical Physics, 145, 441. [in English]
- [2] Al-Kotb M.S. & Al-Waheidi J.Z. & Kotkata M.F. (2014). Opto-electronic characterizations of oriented nano-structure CdSe film/Si (001) heterostructure. Superlattices Microstruct., 69, 149. [in English]
- [3] Wang X. & Li R. & Fan D. (2011). Nanostructured Al-ZnO/CdSe/Cu₂O ETA solar cells on Al-ZnO film/quartz glass templates. Nanoscale Research. Letters, 6, 614 [in English]
- [4] Devadason S. & Muhamad M.R. (2007). Structural and optical properties of vapor deposited multi-layer CdSe thin films. Physica B Condensed Matter, 393, 125. [in English]
- [5] Mahawela P. & Jeedigunta S. & Vakkalanka S. & Ferekides C.S. & Morel D.L. (2005). Transparent high-performance CDSE thin-film solar cells. Thin Solid Films., 480–481, 466. [in English]
- [6] Park Y.M. & Andre R. & Kasprzak J. & Dang L.S. & Bellet-Amalric E. (2007). Molecular beam epitaxy of CdSe epilayers and quantum wells on ZnTe substrate. Applied Surface Science, 253, 6946. [in English]

- [7] Shyju T.S. & Anandhi S. & Indirajith R. & Gopalakrishnan R. (2011). Solvothermal synthesis, deposition and characterization of cadmium selenide (CdSe) thin films by thermal evaporation technique. *Journal of Crystal Growth*, 337, 38. [in English]
- [8] Larramendi E.M. & Karla Gutierrez Z.-B. & O. de Melo & Woggon U. & Schikora D. & Lischka K. (2010). Growth of $ZnSe_{1-x}Te_x$ epilayers by isothermal closed space sublimation. *Journal of Applied Physics*, 312, 1807. [in English]
- [9] Bubnov. Yu.Z, Lerie, M.S., Staros, F.H, Filaretov, G.A (1975) Vakuumnoe nanesenie plenok v kvazizamknutom obeme [A vacuum causing of tapes is in the quasi-closed volume] Moskva: Soveight radio. [in Russian]
- [10] Boiko, B.T, Marunko, S.V, Pancheha, P.A, Polotskii, V.A (1984) Fizika [Physics] Izvestia vuzov. [in Russian]
- [11] Kalinkin, I.P Epitaksialnie plenki soedinenii A2B6 [Epifilms of connections A2B6] Luhansk.: LGU. [in Russian]
- [12] Opanasiuk, A.S. (2011). Strukturni, elektrophizichni ta optichni vlastivosti plivok spoluk A2B6 ta heteroperekhodiv na ikh osnovi [Structural, electro-physical and optical properties of tapes of connections of A2B6 and hetero transitions are on their basis]. Doctor's thesis. Sumy: SumDU [in Ukrainian].
- [13] Maisell, L., Gleng, R. (1977). Tekhnolohiia tonkikh plienok: spravochnik [Technology of thin-films : reference book] (Vols.1). Moskva: Soveight radio. [in Russian].
- [14] Hass G. & Thun R. (1986). Physics of thin films. New York, Academic Press, 3,38-44. [in English]
- [15] Ninomiya S. & Adachi S. (1995). Optical properties of cubic and hexagonal CdSe. *Journal of Applied Physics*, 78, 4681. [in English]

МЕТОДИ КОНТРОЛЮ ТОВЩИНИ ПЛІВОК CdSe/ZnTe ОТРИМАНИХ МЕТОДОМ КЗО

Дідоборець О.Й., Клєцков О.М.

Реферат

Метою роботи є визначення найбільш оптимального методу виміру товщини напівпровідникових плівок на основі зіставлення з експериментальними даними отриманими методом КЗО.

Напівпровідникові плівки CdSe і ZnTe є матеріалами групи АІІВVI для використання в сучасних електронних пристроях, таких як сонячні елементи, світлодіоди, газові сенсори і інше [1,2].

Синтез тонких плівок CdSe і ZnTe, отримання і розуміння фізичної інформації про їх властивості є необхідною умовою розробки стабільних пристроїв на їх основі.

Для отримання плівок селеніду кадмію і теллурида цинку використовують різні методи: високочастотне магнетронне розпиляло [3], газотранспортний метод (PVT) [4], хімічне парофазне осадження (CVD)[5], молекулярно-променева епітаксія [6], термічний вакуумний випар [7] і термічний випар в квазізамкнутому об'ємі (КЗО)[8].

Отримання досить чистих напівпровідникових плівок групи АІІВVI, зокрема CdSe і ZnTe, в умовах вакууму ускладнюється відмінністю тисків насиченої пари компонентів з'єднань. Також важливим параметром синтезу плівок у вакуумі є рівень залишкових газів, які здатні вступати в хімічні реакції з речовиною підкладки і входити в ґрати кристалітів. Вони, як правило, неконтрольовано впливають на швидкість росту плівок, їх структуру. Тому вирощування напівпровідникових плівок з парової фази необхідно проводити в дегазованій вакуумній системі із залишковим тиском хімічно активних газів не більше 10^{-5} Па.

Вибір методу КЗО в цій роботі обумовлений тим, що він дозволяє отримувати однорідні, структурно досконалі тонкі плівки напівпровідникових матеріалів, близьких до термодина-

мічної рівноваги, що є основною перевагою цього методу перед іншими вакуумними технологіями [9,10]. Важливою перевагою методу є високий тиск пари халькогенідів в КЗО, тиск залишкових газів в робочому об'ємі [11], що значно перевищує (на чотири порядки) тиск залишкових газів в робочому об'ємі.

Необхідною умовою для отримання пристроїв на основі напівпровідникових плівок групи АІІВVI є контроль товщини отримуваних зразків. Вимір товщини плівок можливо як після, так і в процесі (in situ) їх напылення.

Розглянуті різні методи контролю товщини напівпровідникових плівок. В рамках розглянутих методів вибрані методи, які найбільш прийнятні в певних умовах.

За допомогою наведених методів виміряна товщина напівпровідникових плівок. Проведено порівняння результатів товщин різних плівок, при цьому дані експерименту з високою точністю співпадають з даними розрахованими різними методами. Вибрані найбільш оптимальні методи контролю товщин.

Література

1. Zhang Y., Li P., Lau W.M., Gao Y., Zi J., Zheng Z. Electronic devices of semiconductor. Material Chemical Physics. 2014. V. 145. P. 441.
2. Al-Kotb M.S., Al-Waheidi J.Z., Kotkata M.F. Opto-electronic characterizations of oriented nanostructure CdSe film/Si (001) heterostructure. Superlattices Microstruct. 2014. V. 69. P. 149.
3. Wang X., Li R., Fan D. Nanostructured Al-ZnO/CdSe/Cu₂O ETA solar cells on Al-ZnO film/quartz glass templates. Nanoscale Research. Letters. 2011. V. 6. P. 614.
4. Devadason S., Muhamad M.R. Structural and optical properties of vapor deposited multi-layer CdSe thin films. Physica B Condensed Matter. 2007. V. 393. P. 125.
5. Mahawela P., Jeedigunta S., Vakkalanka S., Ferekides C.S., Morel D.L. Transparent high-performance CDSE thin-film solar cells. Thin Solid Films. 2005. V. 480–481. P. 466.
6. Park Y.M., Andre R., Kasprzak J., Dang L.S., Bellet-Amalric E. Molecular beam epitaxy of CdSe epilayers and quantum wells on ZnTe substrate. Applied Surface Science. 2007. V. 253. P. 6946.
7. Shyju T.S., Anandhi S., Indirajith R., Gopalakrishnan R. Solvothermal synthesis, deposition and characterization of cadmium selenide (CdSe) thin films by thermal evaporation technique. Journal of Crystal Growth. 2011. V. 337. P. 38.
8. Larramendi E.M., Karla Gutierrez Z.-B., O. de Melo, Woggon U., Schikora D., Lischka K. Growth of ZnSe_{1-x}Te_xZnSe_{1-x}Te_x epilayers by isothermal closed space sublimation. Journal of Applied Physics. 2010. V. 312. P. 1807.
9. Бубнов Ю.З., Лерье М.С., Старос Ф.Г., Филаретов Г.А. Вакуумное нанесение пленок в квазизамкнутом объеме. Москва: Советское Радио, 1975.
10. Бойко Б.Т., Марунько С.В., Панчева П.А., Полоцкий В.А. Физика. Москва: Известия вузов. 1984.
11. Калинин И.П. Эпитаксиальные пленки соединений А2В6. Луганск: ЛГУ, 1978.
12. Опанасюк А.С. Структурні, електрофізичні та оптичні властивості плівок сполук А2В6 та гетеропереходів на їх основі: дис. докт. фіз.-мат. наук: 01.04.01 / Опанасюк Анатолій Сергійович. Суми, 2011. 378 с.
13. Технология тонких пленок: справочник / Под ред. Л. Майселла, Р. Глэнга. Москва.: Сов. радио, 1977. Т.1. 662 с.
14. Hass G., Thun R. Physics of thin films. New York, Academic Press. 1986. V.3. P. 38-44.
15. Ninomiya S., Adachi S. Optical properties of cubic and hexagonal CdSe. Journal of Applied Physics. 1995. V. 78. P. 4681.