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АНАЛІТИЧНА ХІМІЯ. ФІЗИЧНА ТА КОЛОЇДНА ХІМІЯ. НЕОРГАНІЧНА ХІМІЯ. ОРГАНІЧНА ХІМІЯ

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SYNTHESIS OF ZINC SULPHIDE-SELENIDE SOLID SOLUTION FILMS. REVIEW

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A review of the main physical and chemical methods of synthesis of zinc sulfide-selenide (ZnS_xSe_{1-x}) thin films was made. The phase diagram of the ZnS–ZnSe system and the regions of existence of different phases within this diagram have been analyzed. The features and parameters of ZnS_xSe_{1-x} film synthesis by various methods have been considered. The main characteristics of the obtained films are presented, including crystal structure, thickness, and band gap width, depending on the synthesis method. Special attention is given to chemical bath deposition and its prospects for practical use in obtaining ZnS_xSe_{1-x} films.

Keywords: zinc sulfide, zinc selenide, solid solution, semiconductor films, film synthesis, chemical deposition.

Introduction

The synthesis of solid solution films based on A^2B^6 group compounds, particularly zinc sulfide-selenide (ZnS_xSe_{1-x}), is an important topic in materials science research. These materials attract attention due to their unique optical and electronic properties, which can be regulated within certain limits by adjusting the solid solution composition. As a result, ZnS_xSe_{1-x} films are used in the fabrication of photodetectors, light-emitting diodes, solar cells, and other optoelectronic devices [1–3]. Therefore, a review of existing synthesis methods of ZnS_xSe_{1-x} films is a relevant scientific task, as the variety of deposition approaches and their parameters significantly influence the structural, optical, and semiconductor properties of the material.

The aim of this work is to analyse and summarise the current state of the main synthesis methods of ZnS_xSe_{1-x} films and to characterise their properties depending on the synthesis approach.

Analysis of the phase diagram of the ZnS–ZnSe system

To assess the probability of forming ZnS_xSe_{1-x} solid solutions with a certain crystal structure, we consider the phase diagram of the ZnS–ZnSe system, which represents the relationship between the solid solution composition (on the x-axis) and temperature (on the y-axis) (Fig. 1). Since ZnS and ZnSe are isostructural compounds with either a cubic (sphalerite) or hexagonal (wurtzite) crystal structure, they form a continuous series of ZnS_xSe_{1-x} solid solutions across the entire composition range ($0 \leq x \leq 1$). The melting points of the pure components differ: ZnS melts at 1718 °C, while ZnSe melts at 1526 °C [4, 5]. The melting temperatures of the solid solutions vary depending on composition, forming liquidus and solidus lines between these two points. The ZnS–ZnSe phase diagram (Fig. 1) has the following regions:

Liquid phase (*L*). This region corresponds to the existence of the liquid phase at temperatures above the liquidus line.

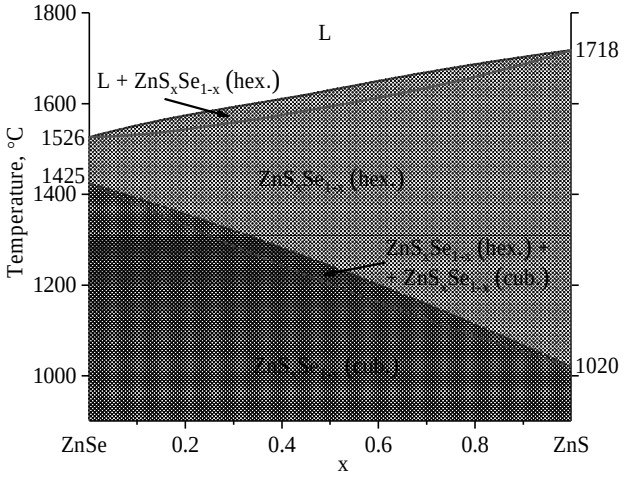
Two-phase region ($L + ZnS_xSe_{1-x}$ (*hex.*)). Located between the liquidus and solidus lines. This region represents the coexistence of liquid and solid phases (according to [6]).

Single-phase region (ZnS_xSe_{1-x} (*hex.*)). This solid-phase region corresponds to the existence of ZnS_xSe_{1-x} solid solutions with a hexagonal structure at temperatures below the solidus line.

Two-phase region (*ZnS_xSe_{1-x} (hex.)* + + *ZnS_xSe_{1-x} (cub.)*). There are no reports in the literature about the existence of this region in the ZnS–ZnSe system. However, a similar region has been investigated and constructed for the related CdSe–ZnSe system [6]. Considering this, along with the ability of ZnS and ZnSe to exist in both hexagonal (high-temperature) and cubic (low-temperature) modifications, it can be assumed that a two-phase coexistence region for ZnS_xSe_{1-x} solid solutions exists within a certain temperature range. According to [4, 7], the phase transition temperatures between sphalerite and wurtzite at normal pressure (1 atm) are 1020 °C for ZnS and 1425 °C for ZnSe. Thus, the two-phase coexistence region of hexagonal and cubic ZnS_xSe_{1-x} solid solutions should be located within this temperature range. This region is marked with dashed lines in Fig.

Single-phase region (*ZnS_xSe_{1-x} (cub.)*). This solid-phase region corresponds to the existence of ZnS_xSe_{1-x} solid solutions with a cubic structure and is located at temperatures below the sphalerite ↔ wurtzite phase transition zone.

Therefore, according to the ZnS–ZnSe phase diagram, synthesising ZnS_xSe_{1-x} samples at temperatures below 1020 °C is most likely to obtain ZnS_xSe_{1-x} in a cubic structure, as it is the most thermodynamically stable form. The formation of hexagonal ZnS_xSe_{1-x} as a metastable phase in the low-temperature region is probably possible under certain specific conditions and synthesis methods.



Phase diagram of the ZnS–ZnSe system

Analysis of literature data on synthesis methods of ZnS_xSe_{1-x} films

The next important step in obtaining film materials based on ZnS_xSe_{1-x} solid solutions is selecting an appropriate deposition method. The literature describes numerous methods for synthesising compounds of A^2B^6 group, which can be divided into three main types: physical, chemical, and combined methods. Since 2010, deposition techniques for ZnS_xSe_{1-x} solid solution films have primarily focused on the following approaches: pulsed laser deposition, molecular beam epitaxy, radio-frequency magnetron sputtering, thermal evaporation, and screen printing with sintering (as physical methods); chemical bath deposition (as a chemical method); and chemical vapour deposition, electrodeposition, and spray pyrolysis (as combined methods). A comparative analysis of these methods is presented in Table 1 and Table 2. Below, we briefly review the essence of each method.

Pulsed laser deposition. The work [8] describes the obtaining ZnS_xSe_{1-x} thin films by pulsed laser deposition in vacuum. For this purpose, an excimer laser with a wavelength of 248 nm (KrF) and pre-prepared targets were used. For each deposition, the laser energy was set to 2 J/cm^2, the repetition rate to 10 Hz, and 2500 pulses were applied. The targets (pressed tablets) were prepared by mixing the appropriate masses of ZnS and ZnSe powders, pressing the mixture, and annealing at 950 °C for 3 days. The films were deposited onto n-type GaAs (100) substrates at a temperature of 400–450 °C. The films thickness ranged from 100 to 220 nm, and the ZnS_xSe_{1-x} composition was controlled by varying the ZnS and ZnSe content during target preparation. As a result of this synthesis, ZnS_xSe_{1-x} films with an epitaxial structure matching that of the GaAs (100) substrate were obtained. However, the authors [8] achieved this characteristic only for a substitution parameter *x* ranging from 0.02 to 0.1. They did not study ZnS_xSe_{1-x} samples with higher *x* values, explaining that their structure was no longer epitaxial but polycrystalline (probably one of the typical – cubic or hexagonal).

Molecular beam epitaxy. In the study [9], ZnS_xSe_{1-x} films were synthesized using the molecular beam epitaxy (MBE) method with an SVT Associates BLT MBE system. High-purity ZnS and ZnSe compounds were used as source materials,

supplied from separate effusion sources. Silicon wafers served as substrates, with their temperature maintained at 200 °C. The film thickness and composition were controlled by adjusting the material flow rate from the effusion sources, allowing for the deposition of high-quality films with specific parameters. The *x* value in the film composition varied from 0 to 1, providing the formation of solid solutions with different S/Se ratios. However, the authors [9] did not investigate the exact thickness, band gap, or crystalline structure of the ZnS_xSe_{1-x} films in their study.

Radio-Frequency (RF) magnetron sputtering with thermal treatment. ZnS_xSe_{1-x} films were synthesized using this method by annealing magnetron-sputtered zinc in sulfur and selenium vapors [10]. First, zinc was deposited onto the substrates by magnetron sputtering for 4 min. The substrates with the zinc coating were then placed in quartz ampoules, along with a controlled amount of sulfur and selenium powders. The ampoules were vacuumed to prevent unwanted reactions with residual gases and heated to 250 °C for 1 h, generating S and Se vapors. Then, thermal treatment was conducted at 700 °C for 6 h, providing the formation of ZnS_xSe_{1-x} films with a specified ratio of chalcogens. The films composition was controlled by adjusting the sulfur-to-selenium ratio in the ampoule, which influenced the *x* parameter, ranging from 0 to 1. The studies conducted by the authors of [10] determined that the film had a hexagonal structure, with a band gap (E_g) ranging from 2.53 to 3.58 eV.

Thermal Evaporation. This method was used to obtain ZnS_xSe_{1-x} films in several works [11–17]. High-purity ZnS and ZnSe mixtures, combined in specific proportions to achieve the desired *x* composition, were used for film deposition. The authors [11] limited *x* value to a narrow range ($x = 0 - 0.1$), whereas others [12–17] covered the entire compositional interval ($x = 0 - 1$). ZnS_xSe_{1-x} films were deposited by thermal evaporation of the prepared mixture onto substrates in a sealed vacuum chamber. Evaporation was conducted at both high temperatures (427–1100 °C) [11–15] and low temperatures (100 °C [16] or room temperature [17]). The obtained ZnS_xSe_{1-x} films had a cubic structure, with a thickness ranging from 200 to 1000 nm and a band gap of 2.56 to 3.50 eV.

Screen printing with sintering. In study [18], ZnS_xSe_{1-x} films were obtained using this method. High-purity ZnS and ZnSe powders were used as starting materials and mixed in stoichiometric ratios to obtain a specific *x* composition. A paste was then prepared by adding to this mixture a few drops of ethylene glycol, which acted as a binding agent, along with anhydrous $ZnCl_2$ as an adhesive. The resulting paste was applied to substrates and held on a hot plate at 120 °C for 4 h to prevent crack formation. Subsequently, the samples were placed in a furnace at 500 °C for 10 min. To minimize temperature gradients between the upper film surface and the substrate, the samples were covered with glass plates of the same size as the substrate during cooling. As a result, the authors [18] obtained ZnS_xSe_{1-x} films with a hexagonal structure, but only with a single substitution parameter *x*, the exact value of which was not provided. The determined E_g value of the ZnS_xSe_{1-x} film was 2.84 eV.

Chemical vapor deposition. The synthesis of ZnS_xSe_{1-x} films by this method is presented in work [19]. A mixture of zinc(II) bis (diethyldiselenocarbamate) $Zn(Se_2CNEt_2)$ and zinc(II) bis (diethyldithiocarbamate) Zn (S_2CNEt_2) was used in molar ratios of 1:1 and 1:0.75. These compounds were dissolved in 15 ml of tetrahydrofuran, and the resulting solution was converted into an aerosol using an ultrasonic humidifier. A flow of argon gas carrying the aerosol was directed onto substrates placed in the hot zone of a reactor at 350 °C. In this hot zone, $Zn(Se_2CNEt_2)$ and $Zn(S_2CNEt_2)$ underwent thermoslysis, forming ZnS_xSe_{1-x} films with a cubic structure. The degree of chalcogen substitution (*x*) in the ZnS_xSe_{1-x} films depended on the molar ratios of $Zn(Se_2CNEt_2)$ and $Zn(S_2CNEt_2)$. The obtained *x* values were from 0.30 to 0.54, while the band gap varied from 2.25 to 2.66 eV. This is the lowest E_g range reported for ZnS_xSe_{1-x} among the studies included in this review. As for the film thickness, the authors [19] did not determine it.

Electrodeposition. The authors [20, 21] synthesized ZnS_xSe_{1-x} films on a conductive substrate (which essentially acted as the electrode) using electrochemical processes at a constant current density of 80 mA/cm^2 in a temperature range of 30–80 °C. The working solution for electrodeposition

contained zinc sulfate, sodium thiosulfate, and sodium selenosulfate. By varying the concentrations of $Na_2S_2O_3$ and Na_2SeSO_3, ZnS_xSe_{1-x} films were obtained with a substitution parameter *x* ranging from 0 to 1 and a bandgap from 2.64 to 3.58 eV. The crystal structure of the synthesized ZnS_xSe_{1-x} was found to be hexagonal, which is less common compared to other synthesis methods, as well as the greatest films thickness – from 1000 to 1500 nm.

Spray Pyrolysis. In works [22–26], the synthesis of ZnS_xSe_{1-x} films by chemical pyrolytic deposition (spray pyrolysis) is described. For this purpose, a working solution was pre-prepared using either an aqueous solution [22, 25, 26] or an alcoholic solution [23, 24]. As starting reagents, which served as sources of Zn, S, and Se, a zinc salt ($ZnSO_4$ or $ZnCl_2$), thiourea, and selenourea (or, in study [22], Se vapors in place of the latter) were used. The sputtering process was carried out on substrates at temperatures ranging from 275 to 550 °C. The total sputtering duration varied from 0.5 to 48 h. Air [23, 24] or nitrogen [22] was used as the carrier gas. Structural analysis revealed that the ZnS_xSe_{1-x} films obtained by spray pyrolysis in all studies [22–26] had a cubic structure. However, the substitution parameter *x* was in the range of 0.55 to 1 in [22], while in [23–26] it ranged from 0 to 1. The ZnS_xSe_{1-x} film thicknesses varied from 243 nm [23] to 1000 nm [22].

Chemical Bath Deposition. The synthesis of ZnS_xSe_{1-x} films using this method has become the most common in the literature of recent years [27–34] (Table 2). This is primarily due to its advanta ges – simplicity and accessibility compared to the other methods described above. In chemical bath deposition, ZnS_xSe_{1-x} films were synthesized in a bath filled with a reaction mixture (working solution) into which the substrates were immersed. The process was carried out for a predetermined period at a temperature below the boiling point of water (100 °C). After the deposition process was completed, the substrates with the deposited ZnS_xSe_{1-x} films were removed from the solution, washed with distilled water and dried in air.

The reaction mixture for the chemical deposition of ZnS_xSe_{1-x} films contained the following main components: zinc salt, complexing agent for Zn^{2+} ions, and chalcogenizing agents – that is, sulfur-containing and selenium-containing reagents. As sources of zinc ions, solutions of the following salts were used: zinc acetate [27, 28], zinc sulfate [29–32], or zinc chloride [33, 34]. Thiourea and sodium selenosulfate served as the sources of sulfur and selenium, respectively [28–32]. In one study, Se vapors were used instead of sodium selenosulfate to treat the ZnS films after chemical deposition [27]. To prevent the rapid precipitation of the target product ZnS_xSe_{1-x}, one or more complexing agents (such as trisodium citrate [27, 29, 30], triethanolamine [30–32], sodium hydroxide [31–34], ammonium hydroxide [27, 29, 30], or hydrazine hydrate [28–34]) were added to the solution. In addition to the role of complex formation, these reagents could also perform the function of pH regulators for the reaction medium, which is crucial for ensuring the stability of the deposition process.

Studies of chemically deposited ZnS_xSe_{1-x} films have shown that they predominantly had a cubic structure [27, 29–34], except for the study [28], where a mixture of cubic and hexagonal phases was formed. The authors of [28, 31, 32] obtained ZnS_xSe_{1-x} films in the entire compositional interval (x = 0 – 1), whereas others limited their research to partial chalcogen substitution ranges (x = 0.6 – – 1 [27]; 0 – 0.3 [29]; 0.25 – 0.36 [30]; 0.11–0.85 [34]). The band gap values of the deposited ZnS_xSe_{1-x} films varied from 2.61 eV [34] to 3.77 eV [27]. As for the film thickness, among the works where this parameter was determined, it ranged from 70 nm [27] to 486 nm [30].

The authors of this review have also carried out chemical bath deposition of ZnS_xSe_{1-x} films [33, 34]. Unlike other works [28–32], where sodium selenosulfate was used as the selenium source, we used elemental powdered selenium. It was successfully dissolved directly in the working solution. This is due to the fact that the latter contained a high concentration of sodium hydroxide and hydrazine hydrate in its composition. The other synthesis parameters for the ZnS_xSe_{1-x} films and their determined characteristics were similar to those in the other works, listed in Table 2. In summary, it can be argued that the chemical bath deposition method, due to its advantages, is promising for use in the manufacture of materials based on ZnS_xSe_{1-x} films.

Table 1

Comparative characteristics of physical and combined methods of ZnS_xSe_{1-x} films deposition

No.	Method	Deposition conditions on substrates	Crystal structure of films	Substitution degree (x)	Band gap (E_g), eV	Thickness, nm	Ref.
1	Pulsed laser deposition	Films were deposited from a prepared target under vacuum at t = 400–450 °C. The targets were obtained by mixing ZnS and ZnSe powders, pressing the mixture, and annealing at 950 °C for 3 days	Epitaxial structure on GaAs (100) substrate	0.02–0.1	Not studied	100–220	[8]
2	Molecular beam epitaxy	Films were deposited from effusion sources (cells with ZnS and ZnSe compounds) at t = 200 °C in a closed system	Not studied	0–1	Not studied	Not studied	[9]
3	RF magnetron sputtering with thermal treatment	Films were deposited by Zn sputtering for 4 min, followed by exposure to S and Se vapors at t = 250 °C for 1 h and subsequent thermal treatment at t = 700 °C for 6 h	Hexagonal	0–1	2.53—3.58	Not studied	[10]
4	Thermal evaporation	ZnS and ZnSe were fused and then evaporated under vacuum at t = 500–1100 °C for 20 min – 3 h	Cubic	0–0.1	Not studied	300–700	[11]
		Thermal evaporation of ZnS and ZnSe powder mixture under vacuum at t = 427–1227 °C	Cubic	0–1	2.65–3.50	200–1000	[12–15]
		Thermal evaporation of ZnS and ZnSe powder mixture under vacuum at t = 100 °C	Cubic	0–1	2.59–3.38	350	[16]
		Thermal evaporation of ZnS and ZnSe powder mixture under vacuum at room temperature	Cubic	0–1	2.56–3.50	250	[17]
5	Screen printing with sintering	Printing a mixture of ZnS, ZnSe, $ZnCl_2$, and ethylene glycol onto substrates at t = 120 °C for 4 h, then at t = 500 °C for 10 min.	Hexagonal	Not studied	2.84	Not studied	[18]
6	Chemical vapor deposition	Working mixture: 5–7 mmol $Zn(Se_2CNEt_2)$ and 7 mmol $Zn(S_2CNEt_2)$ in 15 ml tetrahydrofuran. Deposition occurred from the aerosol of the working mixture onto substrates at t = 350 °C	Cubic	0.30–0.54	2.25–2.66	Not studied	[19]
7	Electrodeposition	Working mixture: 0.2 M $ZnSO_4$, 0–0.05 M $Na_2S_2O_3$, 0–0.05 M Na_2SeSO_3 at t = 30–80 °C, current density 80 mA/cm^2	Hexagonal	0–1	2.64–3.58	1000–1500	[20, 21]
8	Spray pyrolysis	Spraying an aqueous solution of 0.1 M $ZnSO_4$ and 0.1 M $(NH_2)_2CS$ into a vacuum tube with Se vapors at t = 450–550 °C for 0.5–48 h.	Cubic	0.55–1	3.11–3.63	1000	[22]
		Spraying an aqueous solution of 0.05 M $ZnCl_2$ and 0.05 M mixture of $(NH_2)_2CS$ + $(NH_2)_2CSe$ with isopropanol under low pressure at t = 275 °C for 13–14 h	Cubic	0–1	2.76–3.57	243–280	[23, 24]
		Spraying an aqueous solution of 0.05 M $ZnCl_2$ and 0.05 M mixture of $(NH_2)_2CS$ + $(NH_2)_2CSe$ at t = 400 °C	Cubic	0–1	2.73–3.42	550–600	[25, 26]

Table 2

Comparison of the chemical method of ZnS_xSe_{1-x} films deposition from various literature sources

Method	Deposition conditions on substrates	Crystal structure of films	Substitution degree (x)	Band gap (E_g), eV	Thickness, nm	Ref.
Chemical bath deposition	Deposition from an aqueous solution prepared by mixing 0.2 M $Zn(CH_3COO)_2$, 0.4 M $(NH_2)_2CS$, 0.2 M $Na_3C_6H_5O_7$, 25 % NH_4OH. Duration: 1 h at t = 80 °C, pH = 10. The deposited samples were annealed in an N_2 atmosphere with Se vapors for 1 h at t = 200–500 °C	Cubic	0.6–1	3.12–3.77	70–235	[27]
	Deposition from an aqueous solution of 0.1 M $Zn(CH_3COO)_2$, 80 % $N_2H_4{\cdot}H_2O$, 0.59 M Na_2SeSO_3, 98 % $(NH_2)_2CS$. Duration: 2 h at t = 80 °C, pH = 10.8	Mix of cubic and hexagonal	0–1	2.68–3.50	Not studied	[28]
	Deposition from an aqueous solution of 0.5 M $ZnSO_4$, 0.4 M Na_2SeSO_3, 25 % NH_4OH, 80 % $N_2H_4{\cdot}H_2O$ followed by the addition of $(NH_2)_2CS$. Duration: 2 h at t = 60 °C, pH = 12	Cubic	0–0.3	2.63–3.17	Not studied	[29]
	Deposition from an aqueous solution prepared by mixing: 0.5 M $ZnSO_4$, 98 % $N(CH_2CH_2OH)_2$, 80 % $N_2H_4{\cdot}H_2O$, 25 % NH_4OH, 0.4 M $(NH_2)_2CS$, 0.6 M Na_2SeSO_3. Duration: 4 h at t = 60 °C, pH = 9.3–10.6	Cubic	0.25–0.36	3.27–3.41	244–486	[30]
	Deposition from an aqueous solution of 0.25 M $ZnSO_4$, 0.25 M Na_2SeSO_3, 0.25 M $(NH_2)_2CS$, 0.2 M $Na_3C_6H_5O_7$, 0.2 M $N(CH_2CH_2OH)_2$, 80 % $N_2H_4{\cdot}H_2O$, 4 M NaOH. Duration: 2 h at t = 80 °C, pH = 10.8	Cubic	0–1	2.70–3.71	260	[31, 32]
	Deposition from an aqueous solution with: .08 M $ZnCl_2$, 5 M NaOH, 0.15 M $N_2H_4{\cdot}H_2O$, 0.01-0.09 M $(NH_2)_2CS$, 0.01-0.09 M of dissolved Se. Duration: 40 min at t = 70–80 °C, pH = 14	Cubic	0.11–0.85	2.61–3.28	Not studied	[33, 34]*

** Synthesis performed by the authors of this review and described in the corresponding references.*

Conclusions

A review of the main physical and chemical methods for synthesizing ZnS_xSe_{1-x} semiconductor films has been conducted. The phase diagram of the ZnS–ZnSe system and the regions of existence of different phases within this diagram have been analyzed. It has been established that the formation of films of ZnS_xSe_{1-x} cubic (sphalerite) structure is the most probable, as it is the most thermosdynamically favourable, which has been confirmed in practice. The features and parameters of ZnS_xSe_{1-x} films synthesis by various methods have been considered. The main characteristics of the obtained ZnS_xSe_{1-x} films, including their crystal structure, substitutional degree (x), thickness, and band gap, depending on the synthesis method, have been presented. Physical methods of film deposition typically require the use of complex or expensive equipment, high temperatures or low pressures, or pre-melting or pressing the initial film components. Considering this, chemical bath deposition has become the most widely used synthesis method for ZnS_xSe_{1-x} films in the literature of recent years. This is primarily due to its advantages – simplicity and accessibility compared to physical

methods. In summary, it can be argued that the chemical bath deposition method is a promising approach for use in the manufacture of materials based on ZnS_xSe_{1-x} films.

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Synthesis of zinc sulphide-selenide solid solution films. Review

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СИНТЕЗ ПЛІВОК ТВЕРДОГО РОЗЧИНУ СУЛЬФІДУ-СЕЛЕНІДУ ЦИНКУ. ОГЛЯД

Проведено огляд основних фізичних і хімічних методів синтезу плівок твердого розчину заміщення сульфіду-селеніду цинку (ZnS_xSe_{1-x}). Проаналізовано фазову діаграму стану системи ZnS–ZnSe та області існування різних фаз у межах цієї діаграми. Розглянуто особливості та параметри синтезу плівок ZnS_xSe_{1-x} різними методами. Представлено основні характеристики отриманих плівок: кристалічну структуру, товщину, ширину забороненої зони залежно від методу синтезу. Окрему увагу приділено хімічному осадженню у ванні та перспективам його практичного використання для отримання плівок ZnS_xSe_{1-x}.

Ключові слова: цинк сульфід, цинк селенід, твердий розчин, напівпровідникові плівки, синтез плівок, хімічне осадження.