Nanostructured ZnO, Cu$_2$ZnSnS$_4$, Cd$_{1-x}$Zn$_x$Te Thin Films Obtained by Spray Pyrolysis Method

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http://dx.doi.org/10.5772/intechopen.72988

Abstract

The paper presents the investigation on the influence of substrate temperature $T_s$ and the sprayed initial solution volume $V_s$ on structural, substructural, optical properties, and elemental composition of ZnO and Cu$_2$ZnSnS$_4$ (CZTS) films as well as state-of-the-art of studying the Cd$_{1-x}$Zn$_x$Te (CZT) films obtained by spray pyrolysis technique. The single-phase nanocrystalline ZnO films with average crystallite size of $D_c = 25$–$270$ nm and thickness of $d = 0.8$–$1.2$ μm can be deposited at substrate temperatures of $T_s > 473$ K. The continuous CZTS films with optimal thickness ($d = 1.3$ μm) for application as absorber layers in solar cells were deposited at the sprayed initial precursor volume of $V_s = 5$ ml. The increase of the substrate temperature up to 673 K caused the significant improvements in the stoichiometry of ZnO films. The optimal stoichiometry ratio of CZTS films for application in solar cells was obtained at $V_s = 3$–$4$ ml. Optical study of ZnO films showed that these films have a high-transmission coefficient values of $T = 60$–$80\%$. To the best of our knowledge, there is the lack of works devoted to the study of CZT films obtained by spray pyrolysis technique.

Keywords: ZnO, Cu$_2$ZnSnS$_4$, Cd$_{1-x}$Zn$_x$Te, thin films, pulsed spray pyrolysis

1. Introduction

ZnO is an $n$-type direct-gap semiconductor with a wide band gap ($E_g = 3.37$ eV at $T = 300$ K) having the highest value of exciton energy (60 meV) among the binary compounds [1]. This material is a perspective for application in microelectronics, nanoelectronics, optoelectronics, sensors, solar cells among others due to its unique physical, electrical, and optical properties, non-toxic nature, and chemical and thermal stability in the ambient
It should be noted that, at present, Ukrainian sector of renewable energy, in particular solar, is developing rapidly. First of all it is made possible, thanks to the government support policy. In turn, it leads to an increased interest in the development of new solar cell designs to create further production of solar modules higher efficiency [3, 4]. Due to the absence of rare and toxic elements in zinc oxide compound and possibility to apply low-cost deposition techniques, this material may be an alternative to the traditional ITO (\(\text{In}_2\text{O}_3\)) and FTO (SnO\(_2\):F) transparent conductive layers in thin-film solar cells (SCs) and another optoelectronic device [5]. Nowadays, the perspective substitution of the traditional Si, CdTe, Cu(In,Ga)(S,Se)\(_2\) absorption layers in thin-film SCs is considered Cu\(_2\)ZnSnS\(_4\) (CZTS) semiconductor compound which has the optimal optical properties (\(E_g = 1.5\) eV, \(\alpha \sim 10^4\)–\(10^5\) cm\(^{-1}\)) [6].

Cd\(_{1-x}\)Zn\(_x\)Te (CZT) solid solutions are perspective alternative absorption materials to Cu(In,Ga) (S,Se)\(_2\) in the tandem solar cells having the band gap value of \(E_g = 1.1\) eV. The appealing advantage of CZT compound is the variation of band gap by changing the zinc concentration. The optimal CZT solid solution with \(E_g \sim 1.7\) eV can be obtained at the chemical composition of \(x \sim 0.2\) [7]. To achieve the best working characteristics of devices, ZnO, CZTS, and CZT films must have the single-phase structure with large coherent domain sizes (CDS) \(L_c\), low levels of microdeformations \(\varepsilon\), microstresses \(\sigma\), dislocation concentrations \(\rho\), and well-controlled elemental composition. Unfortunately, typically these films have a high level of defects and secondary phases with different band gaps worsening the performance of the devices based on them. ZnO and CZT films in solar cells should possess high-transmission coefficients and controlled band gaps. Moreover, in order to improve the structural and optical properties of films for application in the low-cost optoelectronic devices, ZnO, CZTS, and CZT films should be deposited by low-cost, non-vacuum methods with optimized physical and technological deposition conditions.

Among the methods to deposit the ZnO, CZT, and CZTS films, special attention is paid to the spray pyrolysis technique having unique advantages: simplicity, efficiency, and cheapness. This technique provides the non-vacuum deposition of a large-area thin film with well-controlled properties.

It was shown [8, 9] that the greatest influence on physical properties and elemental composition of ZnO film has a substrate temperature \(T_s\), CZTS film—the sprayed initial precursor volume \(V_s\). It should be noted that until now CZT films deposited by spray pyrolysis technique are not well-studied, except some works [10, 11].

Thus, the investigation of the influence of deposition conditions on structural, substructural, and optical properties of ZnO, CZTS, and CZT films deposited by spray pyrolysis technique is the perspective in terms of its application in highly efficient optoelectronic devices.

2. ZnO, CZTS, and CZT thin films deposition methods. Peculiarities of the spray pyrolysis technique

The wide range of methods is well developed to deposit ZnO, CZT, and CZTS films which split into physical (for example, magnetron sputtering [12–14]) and chemical (for example,
spray pyrolysis (5, 8–10) techniques. Typically, the physical methods allow to obtain more perfect films with a higher structural quality, and these methods provide a precise control of the films thickness and low content of defects in deposited material compare to chemical methods, but physical deposition techniques require the usage of more complicated equipment and presence of high level of vacuum, thus they are energy-consuming. In contrary, chemical techniques to deposit ZnO, CZTS, and CZT films are low-cost and energy savers. Among them, spray pyrolysis method is considered as the most promising technique. This technique is simple and non-vacuum providing the deposition of the continuous, porous, nanostructured films, and multilayered structures [15].

Taking into account the increased interest to the nanosized materials with properties, significantly different to bulk materials (caused by quantum-size effect), several scientific groups have obtained the nanocrystalline ZnO and CZTS films [16, 17]. It is important to note that the works dedicated to the study of the nanosized structures used chemical techniques for films deposition. ZnO, CZTS, and CZT films deposited by spray pyrolysis technique are not yet well-studied; this fact conditioned the aim of our study.

The image of laboratory setup developed for the deposition of ZnO, CZTS, and CZT films by pulsed spray pyrolysis is showed in Figure 1. It consists of a spraying gun with initial precursor volume reservoir (1), spraying nozzle (2), and microcontroller block (3), allowing the control of the number of spraying cycles, time, and pauses between cycles. To the spraying gun, the compressor with pressure regulator (4) is connected with the aim of producing the air flow for transportation of the dispersed precursor onto heated substrate surface. Between the spraying gun and the compressor, an electromagnetic valve (5) is installed, where the “open” and “closed” regimes are controlled by the microcontroller block (3). The heating of substrate (6) is provided by the heating plate (7). During the deposition of films by spray pyrolysis technique, the properties of ZnO, CZTS, and CZT condensates are dependent on the precursor choice and physical, chemical deposition conditions. Table 1 presents the overview of deposition conditions and precursors typically used to deposit the ZnO, CZTS, and CZT films by spray pyrolysis technique.

Figure 1. Image of the experimental setup for ZnO, CZTS, and CZT films deposition by pulsed spray pyrolysis: (1) spraying gun with initial precursor volume reservoir, (2) spraying nozzle, (3) microcontroller block, (4) compressor, (5) electromagnetic valve, (6) substrate, and (7) heating plate [18, 19].
It should be noted that in order to obtain initial molecular solution for the deposition, the typical materials are metal salts dissolved in polar solvents, particularly in water, ethanol, etc. The most common substrates used are the non-oriented glass and silicon slides. The average substrate temperature is in the range of 250–823 K. It should be noted that these values are lower in comparison to the substrate temperatures used in physical methods.

| №  | Initial precursor                        | Solvent                  | Concentration (M) | Substrate type | Substrate temperature, $T_s$ (K) | Ref. |
|----|-----------------------------------------|--------------------------|-------------------|----------------|----------------------------------|------|
| 1  | Zinc chloride ($\text{ZnCl}_2$)          | $\text{H}_2\text{O}$     | 0.10              | Silicon        | 623–823                         | [21] |
|    |                                         | $\text{H}_2\text{O}$     | 0.10              | Glass          | 773                             | [22] |
|    |                                         | $\text{H}_2\text{O}$     | 0.10              | Glass          | 523–723                         | [23] |
| 2  | Zinc acetate ($\text{Zn(CH}_3\text{COO)}_2\cdot\text{2H}_2\text{O}$) | $\text{H}_2\text{O}$     | 0.04              | Glass          | 573                             | [24] |
| 3  | Zinc acetate ($\text{Zn(CH}_3\text{COO)}_2$) | $\text{H}_2\text{O} + \text{CH}_3\text{OH}$ | 0.20              | Glass          | 693                             | [25] |
|    |                                         | $\text{H}_2\text{O}$     | 0.50              | Glass          | 453–723                         | [26] |
|    |                                         | $\text{H}_2\text{O}$     | 0.10              | Glass          | 623                             | [27] |

### CZT films deposition

| 4  | Cadmium chloride ($\text{CdCl}_2$) Zinc chloride ($\text{ZnCl}_2$) Tellurium chloride ($\text{TeCl}_4$) | $\text{H}_2\text{O}$     | 0.02 (1:1:3) | Glass          | 250–325                         | [10, 11] |

### CZTS films deposition

| 5  | Copper chloride ($\text{CuCl}_2$) Zinc chloride ($\text{ZnCl}_2$) Tin chloride ($\text{SnCl}_2$) Thiourea ($\text{CS(NH}_2\text{)}_2$) | ($\text{CH}_3\text{)}_2\text{SO}$ | 0.010          | Soda-lime glass | 623                             | [28] |
|    |                                                                 |                                      | 0.005          |                 |                   |      |
|    |                                                                 |                                      | 0.005          |                 |                   |      |
|    |                                                                 |                                      | 0.040          |                 |                   |      |
| 6  | Copper chloride ($\text{CuCl}_2$) Zinc chloride ($\text{ZnCl}_2$) Tin chloride ($\text{SnCl}_2$) Thiourea ($\text{CS(NH}_2\text{)}_2$) | $\text{H}_2\text{O} + \text{C}_2\text{H}_5\text{OH}$ | 0.020          | Soda-lime glass | 553–633                         | [29] |
|    |                                                                 |                                      | 0.010          |                 |                   |      |
|    |                                                                 |                                      | 0.010          |                 |                   |      |
|    |                                                                 |                                      | 0.080          |                 |                   |      |

Table 1. Precursors and physical-chemical conditions to deposit the ZnO, CZTS, and CZT films by spray pyrolysis method.
3. Morphological, structural, and substructural properties of ZnO and CZTS films obtained by spray pyrolysis technique

The surface morphology, structural, substructural, optical properties, and chemical composition of ZnO and CZTS films deposited by spray pyrolysis method are determined by its physical, chemical, and technological deposition conditions.

3.1. The morphological properties

SEM images of ZnO films deposited at different substrate temperatures are presented in Figure 2a–d [19, 20]. It has been shown that at substrate temperatures higher than 473 K, crack-free and continuous nanocrystalline ZnO films with a good adhesion to substrate were formed.

The average grain size in the condensates was in the range of $D_c = (25–270)$ nm (see inset in Figure 2d), increasing under the increase the deposition temperature up to 673 K. Whereas, the film thickness determined by the cross-sectional image was $d = 0.8–1.2$ μm.

One of the main film parameters of CZTS films is its thickness, which is typically controlled by the dispersed precursor volume $V_s$. Dependence CZTS films properties vs. films thickness in the range of $d = 0.244–0.754$ μm was studied by authors [9]. These values are not optimal for absorption of nearly 100% solar radiation because of the necessity CZTS films with thickness of $d = 1–3$ μm [6].

Thus, we have studied the CZTS films deposited by spray pyrolysis technique at different sprayed initial precursor volumes which had the higher thickness than studied in Ref. [9].

In Figure 2e–h, the SEM images of CZTS films and its cross-section deposited at different $V_s$ are presented. It can be seen that in the range of studied values continuous films were formed,

![Figure 2. SEM images of ZnO films surface deposited at different temperature $T_s$, K: 473 (a), 573 (b), 623 (c), and 673 (d). Inset (d) shows the film surface with high resolution obtained at 673 K [19] and CZTS films surface deposited at different dispersed initial precursor volumes $V_s$, ml: 2 (e), 3 (f), 4 (g), and 5 (h). Inset (h) shows the films’ cross-section [20].](image-url)
which had a well adhesion to substrate and characterized by the absence of cracks and holes on their surfaces. The maximal layer thickness is determined by the cross-section method and it was \( d = 1.3 \, \mu m \) at \( V_s = 5 \, ml \) (Figure 2h).

### 3.2. Structural and substructural properties

Structural and substructural properties of ZnO and CZTS films have a significant influence on functional characteristics of devices [18–20]. Thus, its study is an important scientific objective. For example, band gap of zinc oxide films can be significantly increased by means of nanostructuring due to the quantum-size effects. At the same time, CZTS films as the absorber layers is SC should have the crystallites with sizes larger that diffusion length of minority charge carriers [6]. However, the films obtained by spray pyrolysis are usually characterized by high levels of microdeformations, microstresses, and density of dislocations in comparison to the values observed in the condensates deposited by physical vacuum methods, e.g., thermal evaporation, magnetron sputtering, etc.

The detailed description of methods applied to study structural, substructural, and optical properties of films is described elsewhere [18–20].

In Figure 3a, the XRD patterns of ZnO films deposited at different substrate temperatures are presented. On the diffraction patterns of the low-temperature films is dominated the diffraction line at angles 35.60–36.10° that corresponds to the reflection from (101) plane of ZnO hexagonal phase. On the diffraction patterns of the films deposited at \( T_s > 573 \, K \), the lines at angles 31.80° and 34.80° are dominated, which correspond to the reflections of (100) and (002) crystallographic planes, respectively. X-ray analysis has been shown that deposited samples are single-phase and contain ZnO hexagonal phase. Secondary phases have not been determined by XRD analysis.

In Figure 3b, the X-ray patterns of CZTS films deposited at different dispersed solution volumes are shown. As can be seen from Figure 3b, on X-ray patterns is dominated the line on angles 28.05–28.50° which corresponds to the reflection from (112) CZTS tetragonal phase.
crystallographic plane. There are also presented lines at angles 47.15°–47.50° and 55.55°–56.45° which correspond to the reflection from (220) and (312) CZTS planes, respectively. It should be noted that during the increasing of precursor volume the intensity of peaks is increased and its half-width is decreased. It may be caused by the increasing of film thickness and by improvement of the films’ crystalline quality. It is well-known that intensities ratio between the number of diffraction reflections from kesterite and stannite crystallographic planes is different [30]. Taking into account this fact, determination of these ratios gives an opportunity to estimate precisely the materials dominate phase. The measured intensity ratio \( I_{(112)}/I_{(220)} \) from (112) and (220) crystallographic planes films was 2.23–2.56. These values are similar to the values, determined for undoped films with kesterite phase \( I_{(112)}/I_{(220)} \approx 2.80 \) [31]; thus, most probably, the investigated films have a kesterite phase. This conclusion is confirmed by the experimental measurements of lattice constants ratio \( c/2a = 0.9970–1.0203 \), that was similar to 1.0. These values are typical for kesterite [32].

Lattice parameter of the materials is a characteristic which is very sensitive to stoichiometry varying, impurities introduction, oxidation, etc. Thus, the precise determination of these values allows us to study the corresponding processes.

In Figure 4, the dependencies of ZnO and CZTS films lattice parameters \( a, c \) vs. deposition conditions are presented. In Figure 4a, it can be seen that during the increase of substrate temperature, measured parameters \( a, c \) for ZnO films are approached to the reference data that may be caused by the film stoichiometry improvement. High-temperature condensates composition approaching to the stoichiometric is confirmed by the chemical composition analysis data. In case of CZTS films (Figure 4b) most similar to the reference data \( a \) and \( c \) values are obtained by us at \( V_s = 4–5 \text{ ml} \), that is well-correlated with elemental composition analysis. It was estimated that lattice parameters are varied in the range of \( a_{\text{ZnO}} = 0.32477–0.32554 \text{ nm}, c_{\text{ZnO}} = 0.51507–0.52111 \text{ nm}, c/2a_{\text{ZnO}} = 1.5822–1.6046, a_{\text{CZTS}} = 0.5423–0.5480 \text{ nm}, c_{\text{CZTS}} = 1.0823–1.1182 \text{ nm}, \) and \( c/2a_{\text{CZTS}} = 0.9970–1.0203 \), the unit cell volume was in the range of \( V_{\text{cell(ZnO)}} = 0.0427–0.0477 \text{ nm}^3 \) and \( V_{\text{cell(CZTS)}} = 0.3183–0.3358 \text{ nm}^3 \), that is well-correlated to the reference data [31] and values obtained for ZnO and CZTS films deposited by spray pyrolysis technique in Ref. [34].

![Figure 4](image-url)

**Figure 4.** The dependencies of the lattice parameters \( a, c \) on the physical and technological deposition conditions [substrate temperature \( T_s, \text{ K} \)—for ZnO films (a) dispersion solution volume \( V_s, \text{ ml} \)—for CZTS films (b)]. Horizontal lines are corresponding to the stoichiometric material.
In Figure 5, the results of measurements $L$ and $\varepsilon$ parameters in studied films by threefold convolution method are presented. As can be seen from Figure 5a, in ZnO films during the increasing of substrate temperature from 473 to 673 K, there is a tendency of the CDS values increasing in direction of [100]—from $L \sim 14$ to $\sim 21$ nm, in direction of [101]—from $L \sim 11$ to $\sim 20$ nm and in direction of [102]—from $L \sim 10$ to $\sim 63$ nm. Similar $L-T_s$ dependencies are observed in our previous works [33], where II-VI type compounds (CdTe, ZnS, ZnSe, and ZnTe) were obtained by close-spaced vacuum sublimation technique. At the same time, the microdeformations level in ZnO films in direction of [100] is decreased from $\varepsilon \sim 1.6 \times 10^{-5}$ to $\sim 0.5 \times 10^{-5}$, in direction of [101]—from $\varepsilon \sim 3.5 \times 10^{-5}$ to $\sim 1.2 \times 10^{-5}$, in direction of [102]—from $\varepsilon \sim 1.0 \times 10^{-5}$ to $\sim 0.7 \times 10^{-5}$, at the same substrate temperatures range (Figure 5b). Similar $\varepsilon$ decreasing at substrate temperatures of $T_s > 573$ K is observed in CdTe and ZnTe films [35].

As can be seen from Figure 5c, in CZTS films during the increasing of the dispersion solution volume from 2 to 5 ml, CDS values are almost were not changed: $L \sim 24–26$ nm (for (112)–(220) planes pair), $L \sim 25–27$ nm (for(112)–(312) planes pair), and $L \sim 39–40$ nm (for (220)–(312) planes pair). Consequently, $V_s$ varying influence on CDS sizes is negligible. It should be noted that obtained results of $L$ measurements are well-correlated to the results presented in Refs. [36], where CZTS films were deposited under the similar experimental conditions. At the

Figure 5. Influence of the substrate temperature on CDS values (a) and microdeformations level (b) of ZnO films on direction normal to the (100)–(200) (1), (101)–(202) (2), (102)–(103) (3) crystallographic planes and of the dispersion solution volume $V_s$ on $L$ (c) and $\varepsilon$ (d) for CZTS films on direction normal to the (112)–(220) (1), (112)–(312) (2), (220)–(312) (3) planes. The threefold convolution technique was used.
same time, the microdeformations level in CZTS films for the directions normal to (112)–(220) crystallographic planes is varied in the range of \( \varepsilon \approx (0.93–0.99) \times 10^{-3} \); for (112)–(312) planes—\( \varepsilon \approx (0.76–0.77) \times 10^{-3} \); for (220)–(312) planes—\( \varepsilon \approx (0.65–0.71) \times 10^{-3} \) (Figure 5d). It should be noted that measured microdeformations values in CZTS films are lower than presented in Ref. [37], where \( \varepsilon \approx (1.26–6.60) \times 10^{-3} \). The measured level of microdeformations allowed us to determine the level of microstresses (\( \sigma \)) in nanocrystalline ZnO and CZTS films. It was estimated that microstresses levels in ZnO and CZTS films varied in the ranges of \( \sigma_{\text{ZnO}} = 0.48–1.53 \) MPa, \( \sigma_{\text{CZTS}} = 5.2–20.3 \) MPa, respectively. The influence of \( T_s \) onto \( \sigma \) level in ZnO films was also studied in Refs. [8], where authors estimated that during the increase of \( T_s \) from 623 to 723 K the compression stress level \( \sigma \) was decreased (1.77–1.47 GPa).

In CZTS films, during the increase of the dispersion solution volume microstresses level is decreased, wherein the smallest \( \sigma \) values are observed in layers obtained at \( V_s = 5 \) ml.

In Figure 6, the results of measurements of the dislocations concentration on the boundaries (\( \rho_L \)) and within volume (\( \rho \)) CSDs blocks and of the general dislocations concentration (\( \rho \)) in direction normal to (100) crystallographic plane for ZnO films or (112) crystallographic plane for CZTS films are presented. Studied ZnO layers are characterized by rather low values of \( \rho = (1.3–6.1) \times 10^{13} \) lines/m\(^2\) compare to the results obtained by other authors. As it can be seen from Figure 6a, during the increase of \( T_s \) there is a tendency to decrease \( \rho \) values. In Ref. [38], authors have estimated that in ZnO nanocrystalline films with thickness of \( d = 0.135–0.392 \) \mu m, deposited at \( T_s = 473 \) K, the dislocation concentration values are higher (\( \rho = (1.29–4.15) \times 10^{13} \) lines/m\(^2\)) than determined here. In Ref. [39], authors have also obtained higher values (\( \rho = (2.4–5.8) \times 10^{13} \) lines/m\(^2\)) compared to our results. It has been shown that during the increase of \( V_s \) (Figure 6b) in CZTS films general dislocation density \( \rho \) does not almost change in all investigated directions.

The smallest values of \( \rho = (17.0–19.3) \times 10^{15} \) lines/m\(^2\) are obtained in case of film deposited at dispersion volume of \( V_s = 5 \) ml. It should be noted that these values \( \rho \) are smaller than observed earlier for CZTS films deposited by chemical methods (spray pyrolysis – \( \rho = (11.6–80.3) \times 10^{16} \) lines/m\(^2\)) [35], and higher compare to the films obtained by vacuum methods (thermal evaporation – \( \rho = (0.64–4.00) \times 10^{14} \) lines/m\(^2\)) [40].

Figure 6. The influence of substrate temperature \( T_s \) (in case of ZnO films (a)) and dispersed initial solution volume \( V_s \) (in case of CZTS films (b)) on dislocations density \( \rho \): on the sub-grain boundaries (1), within CDS units (2) and general dislocations concentration (3) for the direction normal to (100)–(200) planes for ZnO and to (112)–(220) planes for CZTS. The measurements error was varied in the range of 15–20%.
3.3. The study of the stoichiometry

Energy dispersed analysis of the X-ray spectra (EDAX) allows us to determine the elemental composition of ZnO and CZTS films obtained in present work. Results determined for films deposited at different physical-chemical and technological conditions are presented in Table 2. As it can be seen, ZnO films have some oxygen surplus on zinc. Besides, films stoichiometry is increased during the increasing of the substrate temperature. This fact is confirmed by the concentration ratios $C_O / C_{Zn}$ that are parts of compound ($\gamma_{ZnO} = 1.4 - T_s = 473 \text{ K}, \gamma_{ZnO} = 1.2 - T_s = 623 \text{ K}$). The impurities connected to the films contamination by the precursor materials have not been determined.

The control of CZTS films elemental composition is a complex and important task because of its probable determination of the phase conditions, crystal structure, optical, and electrical properties of investigated layers. It was estimated that in CZTS films some copper, zinc, and tin are present in surplus and has some sulfur deficiency. Sulfur losses in films during the pyrolytic reaction of the initial precursor near the surface of the heated substrate may be caused by its high volatility [41]. It should be noted that stoichiometry of studied films is some improved during the increasing of dispersed precursor volume. Also, the obtained ratio $\gamma_{CZTS_1} = (0.80–0.84)$ in CZTS films deposited at precursor dispersion with volume of $V_s = 2–3 \text{ ml}$ is close to the optimal values necessary to develop SCs with high solar energy conversion efficiency ($\gamma_{CZTS_1} = (0.8–0.9), \gamma_{CZTS_2} = (1.1–1.2)$) [40, 42]. For film obtained by dispersion precursor volume of $3 \text{ ml}$ for this requirement corresponds the next ratio $\gamma_{CZTS_2} = 1.2$. Impurities related to the films’ contamination by the precursor’s materials have also not been observed in CZTS layers.

| ZnO | $T_s$ (K) | $C_{Zn}$ (at. %) | $C_O$ (at. %) | $\gamma_{ZnO}$ |
|-----|-----------|-----------------|---------------|---------------|
| 473 | 41.8      | 58.2            | 1.4           |
| 523 | 42.3      | 57.7            | 1.4           |
| 573 | 42.6      | 57.4            | 1.3           |
| 623 | 44.3      | 55.7            | 1.2           |
| 673 | 44.0      | 56.0            | 1.2           |
|     | Stoichiometry | 50.0            | 50.0          | 1.0           |

| CZTS | $V_s$ (ml) | $C_{Cu}$ (at. %) | $C_{Zn}$ (at. %) | $C_{Sn}$ (at. %) | $C_S$ (at. %) | $\gamma_{CZTS_1}$ | $\gamma_{CZTS_2}$ | $\gamma_{CZTS_3}$ |
|------|-----------|-----------------|-----------------|-----------------|-------------|-----------------|-----------------|-----------------|
| 2    | 28.6      | 21.4            | 14.3            | 35.8            | 0.8         | 1.5             | 0.8             |
| 3    | 27.0      | 17.3            | 14.7            | 40.8            | 0.8         | 1.2             | 0.7             |
| 4    | 27.7      | 16.3            | 15.1            | 40.9            | 0.9         | 1.0             | 0.6             |
| 5    | 26.4      | 15.2            | 15.4            | 43.0            | 0.9         | 1.0             | 0.6             |
|     | Stoichiometry | 25.0            | 12.5            | 12.5            | 50.0        | 1.0             | 1.0             | 0.5             |

Table 2. Measurement results of the chemical composition for ZnO and CZTS films obtained at different conditions.
4. Optical properties of ZnO and CZTS films obtained by spray pyrolysis technique

4.1. Optical properties

The study and control of the optical properties of ZnO, CZTS, and CZT films is an important task with the aim of their usage in optoelectronic devices, especially for SCs development. It is well-known that optical characteristics of these films heavily depend on morphological, structural, substructural properties, chemical composition, and physical (chemical) and technological deposition conditions.

In present work, the transmission light coefficient of ZnO films was in the range of $T = 60\text{–}80\%$ at the wavelength range of $\lambda = 430\text{–}800$ nm. The highest transmission values had films obtained at $T_s = 673$ K. It was estimated that measurement $E_g$ values for ZnO films were in the range of $3.18\text{–}3.30$ eV and were also dependent on $T_s$.

As can be seen from Figure 7a, band gap $E_g$ of zinc oxide during the increasing of the deposition temperature is at first increased and in further decreased. This complex dependence of $E_g$ may be caused by increasing of the grain sizes in films and by improvement of their structural quality during the increasing of $T_s$. It is well known [43] that in nanocrystalline films ($D_C < 100$ nm) band gap is determined by quantum effects, that leads to the increasing of $E_g$ compare to the values observed in bulk materials. During the increasing of the grain size, quantum effects are gradually decreased. At the same time, due to the high level of the substructural defects (primarily dislocations) in nanocrystalline films, that have been given the local deformations on the materials lattice, its average $E_g$ have been smaller than in bulk materials [16]. At high substrate temperatures, films with sufficient large grain size and low structural defect concentration were formed. As a result, the band gap of semiconductor is approaching the bulk value. Similar tendencies of $E_g$ changing depending on the deposition temperature were observed in Refs. [44].

In Figure 7b, dependence of the materials $E_g$ on the dispersed solution precursor volume $V_s$ is presented. It should be noted that the smallest $\alpha$ values have been obtained for layers

![Figure 7. Band gap ($E_g$) dependencies on substrate temperature $T_s$ in ZnO films (a) and on dispersion solution volume $V_s$ in CZTS films (b). Dashed line corresponds to band gap value in bulk ZnO ($E_g = 3.37$ eV) and bulk CZTS ($E_g = 1.50$ eV).](http://dx.doi.org/10.5772/intechopen.72988)
deposited at volume of $V_s = 2$ ml, the highest values—at $V_s = 5$ ml, respectively. It is quite typical because of the smallest and highest thickness values of the corresponding layers. During the increasing of dispersed initial precursor solution volume, the values of band gap were varied in the range of $E_g = 1.06–1.30$ eV and were approximately approached to the values typical for bulk stoichiometric material ($E_g = 1.5$ eV). It indicates on increasing of grain sizes and decreasing of films deficiency during the increasing of their thickness. Similar tendencies have been observed in Ref. [9].

4.2. Raman and Fourier transform IR (FTIR) spectra

Raman spectroscopy is an additional to X-ray diffraction analysis method of studying the phase composition and quality of ZnO, CZTS, and CZT thin films.

Raman spectra of ZnO films measured in the range of frequencies 90–800 cm$^{-1}$ are presented in Figure 8a. In spectra, a number of different intensity lines on the next frequencies: 95–98, 333–336, 415, 439–442, 572, and 578–587 cm$^{-1}$ are observed. Using the reference data, these lines were interpreted by us as the next phonon modes: $E_2^{\text{low}}$(Zn) [43–45], $E_2^{\text{high}}$–$E_2^{\text{low}}$ [46], $E_1$(TO) [45], $E_2^{\text{high}}$(O) [43–47], $A_1$(LO) [43] and $E_1$(LO) [45–46]. In Figure 8a, two intensive peaks, which correspond to $E_2$ mode, are also observed: peak $E_2^{\text{high}}$, which is relative to the oxygen anions, is localized at frequency of 439–442 cm$^{-1}$ and peak $E_2^{\text{low}}$, which is relative to zinc cations, is localized at frequency of 95–98 cm$^{-1}$. It is well known [49] that the crystalline quality of ZnO films has a direct influence on the mode $E_2$ intensity. Besides, $E_2^{\text{high}}$(O) peak is very sensitive to the presence of inner defects of material. The deviation of the frequency $E_2^{\text{high}}$(O) peak from the value typical for bulk ZnO (437 cm$^{-1}$), that is observed by us in low-temperature condensates, indicates about the presence in zinc oxide high level of microstresses and stretched defects (dislocations) density of the lattice. It should be noted that during the increase of the substrate temperature, the $E_2^{\text{high}}$(O) peak position is some red-shifted from 442 cm$^{-1}$ to the typical bulk ZnO values—439 cm$^{-1}$, which indicates the decrease of $\sigma$ and $\rho$ levels.

FTIR spectroscopy is an addition to X-ray diffraction analysis and Raman spectroscopy technique, which allows to obtain an information about the elemental composition of the studied material and its contamination by the precursor impurities. The number of frequencies,
where the light absorption and transmission in films are performed, allows us to determine the functional links between chemical elements which are part of the studied materials.

In **Figure 8b**, FTIR reflection spectra of ZnO films deposited at different substrate temperatures are presented. Although that thin films were deposited in air by chemical technique obtained spectra were comparatively pure.

At low frequencies (460–475 cm\(^{-1}\)), there is observed minima, which due to the reference data [48], correspond to Zn-O vibrational mode. It should be noted that FTIR spectra obtained on films deposited in all range of substrate temperatures have a C-Cl vibrational mode [50]. The presence of this connection may be caused by the usage of HCl acid, which was added as a precursor during its preparation. The acid paths are also observed in films. In FTIR spectra of ZnO films deposited at \(T_s < 573\) K, peaks on the frequencies 1405 and 1560 cm\(^{-1}\) are presented; they were interpreted by us as symmetric and asymmetric C-O vibrational modes [50]. The absence of C-O connections in films deposited at \(T_s > 573\) K indicates about the total precursor decomposition near the substrate surface at these temperatures. It eliminates the possibility of adsorption of the acetate elements on ZnO films surface during the pyrolysis, and it leads to the formation of single-phase zinc oxide polycrystalline films.

It is well known that in CZTS films, the presence of secondary phases, such as Cu\(_x\)S\(_y\) Zn\(_x\)S\(_y\), Sn \(_x\)S\(_y\), CuSnS\(_y\), ZnO, and Zn SnO\(_y\) is available [39, 51–53]. They are characterized by affiliated lattices, and they indicate on XRD patterns refractions on similar angles. It complicates the phase analysis by XRD technique. Thus, for precise identification of the secondary phases in CZTS compound, the researchers often use Raman spectroscopy in addition to XRD analysis [54]. It allows to identify not only secondary phases, but also kesterite and stannite. In **Table 3**, we present experimental data on Raman shifts for CZTS films obtained by different lasers and compare them with literature data.

| **Experimental data** | **Literature data** |
|-----------------------|--------------------|
| \(V_\text{s}, \text{ml}\) | Raman shift, cm\(^{-1}\) | Symmetry | Mode | Reference |
| 2                     | 142                 | 143–144 | E     | CZTS E   | [56]          |
|                       | 340                 | 338–339 | A     | CZTS A   | [54]          |
| 664                   | 672                 | 672     | A     | 2a CZTS A | [56]          |
| **Green-laser (\(\lambda = 514.5\) nm)** |  |  |  |  |
| 339                   | 338–339             | A       | CZTS A | [52]          |
| 663                   | 672                 | 672     | A     | 2a CZTS A | [57]          |
| **Red laser (\(\lambda = 632.8\) nm)** |  |  |  |  |
| 340                   | 341                 | 341     | A     | CZTS A   | [56]          |
|                       | 560                 | 560     | A     | ZnO      | [45]          |
| 664                   | 672                 | 672     | A     | 2a CZTS A | [57]          |

**Table 3.** Peaks interpretation presented on Raman spectra of CZTS films.
the results of study the Raman spectra of CZTS films using as an excitation source the radiation of several lasers are presented. At all spectra regardless on the precursor volume and excitation laser type, the main peak on frequencies of (339–340) cm$^{-1}$ is presented. It is well correlated to the results of previous studies [52, 54, 55]. In Raman spectra obtained using the green laser, lines on the next frequencies: 142, 340, and 664 cm$^{-1}$ are also observed, which correspond to CZTS $E$, CZTS $A$, and 2a CZTS $A$ (CZTS $A$ mode phonon replica) phonon modes, respectively [54–56].

Usage of the red- and UV-lasers as phonons excitation source allows us to increase the method’s sensitivity onto the revealing of compounds with optical band gap close to $E_g \sim 1.96$ and $\sim 3.81$ eV (excitation radiations energies of corresponding lasers). On spectra, obtained using the red- and UV-lasers, are presented lines on frequencies 339–340 cm$^{-1}$, 663–664 cm$^{-1}$ which correspond to the CZTS $A$ and 2a CZTS $A$ phonon modes [52, 56, 57]. The usage of UV-laser in one of the studied films revealed a negligible number of ZnO secondary phase. In addition, these results are supported by the phonon excitation in Raman spectra on the frequency at 560 cm$^{-1}$ on film obtained from the precursor volume dispersion of 3 ml. Other secondary phases in studied films are not revealed. Raman spectra of CZT films measured during the influence of green-laser excitation radiation ($\lambda = 514$ nm, $E = 2.41$ eV) are presented in Figure 9. In the spectra of the CZT sample ($x = 0.32$), peak which corresponds to LO$_2$(ZnTe) mode is observed. In these spectra, intensive peaks which correspond to $A_1$(Te) $E_{TO}$(Te) telluric modes are also detected. In the spectra of the CZT sample ($x = 0.75$), is observed a weak peak that corresponds to $A_1$(Te) mode, peaks of the next modes: LO$_1$(CdTe), TO$_1$(CdTe), TO$_2$(ZnTe), LO$_2$(ZnTe), and also detected the LO$_2$(ZnTe) mode resonant replica.

Figure 9. Raman spectra of CZT films measured during the impact of excitation irradiation of the wavelength 785 nm at room temperature (RT) [7].
5. Conclusions

As a result of the complex study of structure, substructure, optical properties, and elemental composition of ZnO, CZTS, and CZT films obtained by pulsed spray pyrolysis technique dependent on the physical (chemical) and technological deposition conditions, it was determined that ZnO nanocrystalline films have an average grain size of $D_c = 25–270$ nm and their thickness was $d = 0.8–1.2$ μm, and were formed at $T_s > 473$ K. CZTS continuous films with optimal thickness of $d = 1.3$ μm were deposited at dispersed initial precursor volume $V_s = 5$ ml. It was found that ZnO and CZTS films were polycrystalline in nature, single-phase, and had hexagonal and tetragonal phases, respectively. CZTS samples had a kesterite structure.

It has been shown that in ZnO during the increasing of substrate temperature there is a tendency to the increasing of the CDS; however, in CZTS films, their CSD values were weakly depended on the dispersed solution volume.

Lattice parameters values in ZnO and CZTS films deposited at $T_s = 623$ K, $V_s = 4$ ml were well-correlated to the reference data that confirms their optimal stoichiometry and crystalline quality.

It has been estimated that during the increase of $T_s$ the microdeformations level, microstresses, and dislocation density in ZnO films were decreased; in CZTS films, these parameters were weakly dependent on $V_s$.

It has been determined that during the increasing of substrate temperature to 623 K stoichiometry of ZnO layers was improved ($\gamma_{ZnO} = 1.2$). It has been shown that optimal for usage in SCs CZTS films, their stoichiometry ratios $\gamma_{CZTS,1} = 0.8–0.9$, $\gamma_{CZTS,2} = 1.1–1.2$, $\gamma_{CZTS,3} = 0.7$ were obtained at $V_s = 3–4$ ml.

Study of the optical characteristics of ZnO films allow to estimate the high values of transmission coefficient $T = 60–80\%$. Measured $E_g$ values of ZnO layers were determined in the range of 3.18–3.30 eV and had a complex dependence on $T_s$. During the increase of $V_s$, the values of $E_g = 1.06–1.30$ eV of CZTS layers were approximately approached to the reference data $E_g = 1.5$ eV. Raman spectra analysis of ZnO films confirmed the results of the XRD study, namely decreasing $\varepsilon$, $\sigma$, and $\rho$ values during the increase of $T_s$. CZTS films’ Raman spectra analysis has confirmed the single-phase nature of condensates. FTIR study indicated the absence of precursor impurities in ZnO films obtained at $T_s > 573$ K.

CZT film spectra ($x = 0.32$) had a mode $LO_2(ZnTe)$. In these spectra, intensive peaks corresponded to $A_1(Te)$ and $E_{10}(Te)$ tellure modes were also determined. CZT film spectra ($x = 0.75$) have a weak mode $A_1(Te)$, peaks of $LO_1(CdTe)$, $TO_1(CdTe)$, $TO_2(ZnTe)$, and $LO_2(ZnTe)$ modes, and also $LO_2(ZnTe)$ mode resonant replica.

The results of a research study of the ZnO, CZTS, and CZT thin films will be used for the development of the devices, primarily, in third generation high-efficiency thin-film solar cells.
Acknowledgements

This work was supported by the Ministry of the Education and Science of Ukraine (Grants numbers: 0116U002619, 0115U000665c, 0116U006813, and 0117U003929).

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