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X-RAY STRUCTURAL AND PHOTOELECTRIC PROPERTIES OF SnO_2, ZnO, AND Zn_2SnO_4 METAL OXIDE FILMS

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The conditions and parameters for the synthesis of metal oxide films (ZnO, SnO_2, and Zn_2SnO_4) by spray pyrolysis have been determined. The films were synthesized from aqueous solutions; the main differences between the methods were in the composition of the precursors, in the modes and time of deposition. The crystal structure of the Zn_2SnO_4 film corresponds to the cubic lattice, which belongs to the space group Fd3m with blocks 53 nm in size and lattice parameters a = 6.238 Å. Films of SnO_2 and ZnO nanocrystallites 28 and 31 nm in size coherently arranged with lattices in the volume of thin Zn_2SnO_4 films can exhibit quantum size effects, which is of interest for modern nanotechnology. The crystals of the obtained SnO_2 films have a tetragonal Bravais lattice with the space group P4 2/mnm with lattice parameters $a = b = 4.836$ Å and $c = 3.245$ Å, and the size of the SnO_2 film subcrystals is 61 nm. The resulting ZnO films belong to the C6/mmc space group and the crystal lattice has a hexagonal syngony with the wurtzite structure with parameters $a = b = 0.3265$ nm and $c = 0.5212$ nm. It has been determined that, on the surface of the thin film grown, zinc oxide bumps with sizes $L_{ZnO} \approx 84$ nm appear, which affect the unique properties of the samples. It is shown that the resulting thin Zn_2SnO_4, SnO_2, and ZnO films can be used in a wide range of applications from sensitive sensor elements to coatings in transparent electronics in terms of their optical parameters.
Keywords: *Film; Space group; Subcrystal; Nanocrystal; Quantum size effect; Lattice parameter; Transparent electronics; Band gap*
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1. Introduction

Semiconductor metal oxides have been used in photovoltaic technology for many years. The versatility of their properties and the possibility of using the simplest, inexpensive, and easily reproducible manufacturing methods make them promising materials for the manufacture of photovoltaic devices [1, 2] Metal oxides (Sn, Zn) are semiconductors with a band gap from 3 to 3.6 eV. Wide-gap semiconductors (ZnO, SnO_2, Zn_2SnO_4) [3–5] have n-type conductivity due to oxygen vacancy and deviations from stoichiometry, and are transparent in the visible region of the optical spectrum. Thin films of metal oxides are widely used in optoelectronics, gas sensors, and transparent electronics. The electrical properties of metal oxides depend not only on their elemental composition, but also on the method of their synthesis. Thin films of metal oxides can be obtained by sol-gel technology [6], magnetron sputtering [7], electron beam evaporation [8], and other methods. In this work, the spray pyrolysis method was used in a way, which is not laborious and allows obtaining the required materials with the necessary characteristics and a minimum number of technological operations. Spray pyrolysis is a method that based on spraying an aerosol into a heated substrate. The aerosol, forming the necessary substance in the course of a chemical reaction is obtained from a solution of metal salts; it evaporates and then after hitting the substrate, sprayed under pressure [9,10].

The purpose of this work is to determine the optimal parameters for the production of metal oxide films by spray pyrolysis, as well as to study the structural and optical parameters of the fabricated ZnO, SnO_2, and Zn_2SnO_4 films.

2. EXPERIMENTAL TECHNIQUE

The synthesis of SnO_2 and ZnO was carried out from aqueous solutions of the corresponding metal salts. To synthesize a tin oxide film, tin chloride [$SnCl_2$•$2H_2O$] was used as a precursor; a zinc oxide solution was synthesized from zinc acetate [$Zn(CH_3COO)_2$•$2H_2O$]. water in a volume of 200 ml. In order to avoid hydrolysis of the tin chloride salt in water, hydrochloric acid was added in an amount of 1 ml. To synthesize a zinc stannate film, zinc acetate ($Zn(CH_3COO)_2$•$2H_2O$] and tin chloride [$SnCl_2$•$2H_20$] were chosen as precursors. Zinc acetate ($Zn(CH_3COO)_2$•$2H_2O$] was used as a source of zinc oxide, and tin chloride [$SnCl_2$•$2H_2O$] as a source of tin oxide in the synthesis of the compound Zn_2SnO_2. The molar ratio of zinc acetate and tin chloride in the solution was selected as 2:1. The calculated amount of tin chloride and zinc acetate was dissolved in distilled water to form two solutions. Hydrochloric acid HCl was added to prevent hydrolysis of the salt, then the two solutions were mixed and a precipitate formed in the final solution, and more hydrochloric acid was added.

The ZnO, SnO_2, and Zn_2SnO_4 films were deposited at an air pressure of 2 bar at a rate of 8 ml/min. The distance from the spray head to the preheated glass slide was 85 cm. The film of ZnO, SnO_2, and Zn_2SnO_4 was deposited in one layer for 18 minutes. Multilayer deposition of the ZnO film took place for 1 min with a subsequent break of 30 seconds to restore the substrate temperature.

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Structural studies of thin metal oxide films of SnO_2, ZnO, and Zn_2SnO_4 were performed on an XRD-6100 X-ray diffractometer. X-ray voltage 40.0 kV, current 30.0 mA. The scanning range is 8.0-9.0, the scanning speed is 2 deg/min, the sampling step is 0.02 degrees. The experimental results obtained with the XRD-6100 were processed by the Rietveld method using the Fullprof program.

3. RESULTS AND DISCUSSION

On Fig. 1*a* shows X-ray patterns of the Zn_2SnO_4 films and shown that a well-crystallized Zn_2SnO film is obtained, as indicated by clear peaks of reflections from different crystal planes, which can all be attributed to the zinc-stannate phase. This indicates sufficient crystallization immediately after spray pyrolysis application. The X-ray pattern of the Zn_2SnO film has the following reflections, which are presented in Table 1.

Table 1. Diffraction positions observed in X-ray spectra of Zn_2SnO_4 metal oxide films (HKL – crystallographic orientations, d - interplanar spacing, 2θ – angle)

	2θ	*hkl*	*d, Å*	Composition
1	16.077	002	5.3954	SnO_2
2	18.867	111	4.6513	Zn_2SnO_4
3	22.23	110	3.9871	ZnO
4	28.8	220	3.1258	Zn_2SnO_4
5	33.91	311	2.6417	Zn_2SnO_4
6	35.46	222	2.5313	Zn_2SnO_4
7	41.183	400	2.1921	Zn_2SnO_4
8	46.408	211	1.9572	ZnO
9	51.03	422	1.7918	Zn_2SnO_4
10	54.372	511	1.6872	Zn_2SnO_4
11	59.65	440	1.5523	Zn_2SnO_4
12	67.57	620	1.3865	Zn_2SnO_4
13	70.42	533	1.3374	Zn_2SnO_4
14	71.357	622	1.3221	Zn_2SnO_4
15	76.82	444	0.8812	Zn_2SnO_4

Table 1 and the diffraction pattern show that the main high-intensity (5×10^3 pulses^{-1}) reflection is present at d/n = 0.46513 nm (18.867) and this indicates that the film surface corresponds to the crystallographic plane (111). We analyzed the experimental results of this reflection using the Fullprof program, and determined the crystal structure of the Zn_2SnO_4 film corresponds to the cubic lattice, which belongs to the space group Fd3m (Fig. 1*a*). Also using the Nelson-Riley extrapolation function [11]

$$\xi = (1/2)\cdot[(\mathrm{Cos}^2\theta/\theta + (\mathrm{Cos}^2\theta/\mathrm{Sin}\theta)], \tag{1}$$

the cubic lattice parameter of the Zn_2SnO_4 film was determined from reflections – (111), which amounted to about 6.238 Å.

The average subcrystal size of the Zn_2SnO_4 film (*D*) was calculated by the Solyakov-Scherrer formula [11] using X-ray data, which was 53 nm. The formula is given in the ratio, and the calculated values are given in table 1:

$$D = \frac{k\lambda}{\omega cos\theta}, \tag{2}$$

where *k* is a constant (0.94), *D* is the size of subcrystals (blocks in nm), λ is the length

X-ray wavelength (1.5406 Å), ω is the full width at half maximum (FWHM in radians) and θ is the Bragg diffraction angle

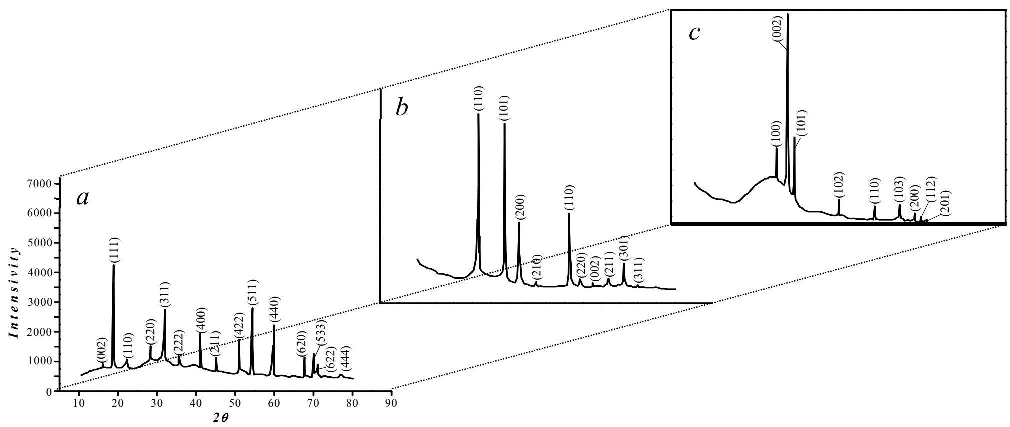

Figure 1. X-ray diffraction pattern of thin metal oxide films of Zn_2SnO_4 (*a*), SnO_2 (*b*), and ZnO (*c*)

However, films of SnO_2 and ZnO nanocrystallites 28 and 31 nm in size coherently arranged with lattices in the volume of thin Zn_2SnO_4 films can exhibit quantum size effects, which is of interest for modern nanotechnology.

The experimental data obtained using the X-ray diffraction method for thin layers of metal oxide SnO_2 are shown in Fig. 1*b*. An analysis of the X-ray diffraction pattern of the SnO_2 film shows that several structural reflections (Fig. 1*b*) of a selective nature with different intensities are observed in the diffraction pattern. The observed diffraction reflection from SnO_2 films with an intense reflection of (110) SnO_2 at $2\theta = 26.8°$ and its other order of (101) SnO_2 at $2\theta = 34.1°$, their FWHM(110) $\approx 6.1\times10^{-3}$ rad and FWHM(101) $\simeq 4.33\times10^{-3}$ rad) indicates the perfection of crystalline tin dioxide. Intense reflections from different crystal planes and their analysis of experimental results show that SnO_2 crystals have a Bravais tetragonal lattice with space group P4_2/mnm with lattice parameters $a = b = 4.836$ Å and $c = 3.245$ Å.

In addition, new structural reflections with different intensities appeared which are presented in Table 1.

Table 1. Diffraction positions observed in X-ray spectra of SnO_2 metal oxide films (HKL – crystallographic orientations, d – interplanar distance, θ, 2θ – angle, I – intensity)

No.	HKL	d, Å	*θ*, deg	2 *θ*, deg	I
1	110	3.333	13° 23′	26° 46′	100
2	101	2.631	17° 03′	34° 06′	80
3	200	2.359	19° 05′	38° 10′	30
4	210	2.012	21° 10′	42° 20′	7
5	211	1.758	26° 00′	52° 00′	40
6	220	1.612	27° 09′	54° 18′	20
7	002	1.584	29° 04′	58° 08′	5
8	310	1.495	31° 02′	62° 04′	10
9	301	1.410	33° 10′	66° 20′	20
10	202	1.320	35° 44′	71° 28′	5

The average size of subcrystals of the SnO_2 film (*D*) was calculated by formula (2), which is 61 nm.

Fig. 1*c* shows an X-ray diffraction pattern of a thin film and, at low angle scattering, a broad diffuse reflection with selective crystallographic orientation reflections is observed at d/n = 0.2774 nm ($2\theta = 31.7°$) (100), d/n = 0 .2723 nm ($2\theta = 32.97°$) at (002) and d/n = 0.249 nm ($2\theta = 36.34°$) (101). Structural line (002), observed at d/n = 0.2723 nm ($2\theta = 32.97°$) on the diffraction pattern, shows that it is high intensity ($\sim10^5$ pulses^{-1}) and thin width (FWHM = $2.62\cdot10^{-3}$ rad). This testifies to the high perfection of the lattice of the thin-layer crystalline film [12]. An analysis of the experimental results of this reflection showed that it belongs to the C6/mmc space group and has a hexagonal syngony with the wurtzite structure in the crystal lattice (due to the bond between zinc-oxygen atoms). The sizes of subcrystals determined from the half-width of this structural peak were 67 nm.

In addition, another diffuse reflection was observed in the X-ray diffraction pattern of a thin ZnO layer at a maximum average angular scattering of $2\theta \approx 42.12°$ (FWHM = 3.03×10^{-1} rad). At the same time, in diffusion reflection of low intensity at d/n = 0.1911 nm ($2\theta = 47.63°$); at $(102)_{ZnO}$, at $(103)_{ZnO}$ d/n = 0.1630 nm ($2\theta = 56.67°$), and d/n = 0.1481 nm ($2\theta = 62.93°$) $(110)_{ZnO}$ - selective reflections were also observed. Theoretical calculations presented in [12,13,14] and obtained on the basis of the analysis of experimental data of X-ray diffraction patterns of a thin layer confirm that these structural reflections arise on the surface of a thin layer due to the formation of ZnO nanocrystallites, while their average size is ZnO at d/n = 0.1911 nm ($2\theta = 47.63°$) $(102)_{ZnO}$, at d/n = 0.1630 nm ($2\theta = 56.67°$) $(103)_{ZnO}$ and d/n = 0.1481 nm ($2\theta = 62.93$)° $(110)_{ZnO}$ which is determined to be 84 nm using experimental results of selective reflections.

Optical data on the films were obtained on a SPECS SSP-715 M spectrophotometer. The transmission spectra of ZnO, SnO_2, and Zn_2SnO_4 are shown in Fig. 2. The transmission spectra for films SnO_2, ZnO, Zn_2SnO_4 have a transparency of more than 80% in the visible and infrared parts of the spectrum. The transparency threshold is in the ultraviolet range. This makes them suitable for use in transparent electronics and solar energy. In accordance with the literature data [15-18], all synthesized metal oxides had a direct band structure.

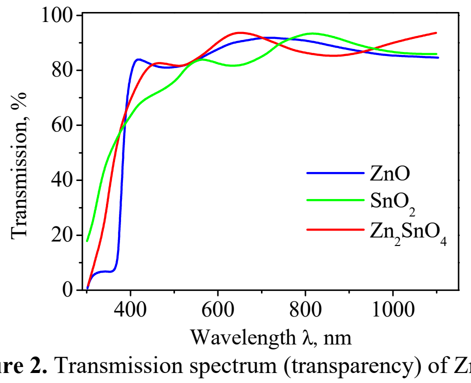

Figure 2. Transmission spectrum (transparency) of ZnO, SnO_2, and Zn_2SnO_4 films

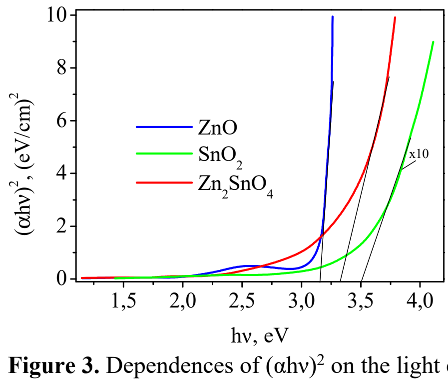

Figure 3. Dependences of $(\alpha h\nu)^2$ on the light energy for ZnO, SnO_2, and Zn_2SnO_4 films

From the absorption thresholds, one can determine the absorption coefficient and band gap of the film in the coordinates $(\alpha h\nu)^2 = f(h\nu)$. The calculation data for the band gap are shown in Fig. 3. The band gap was determined by straightening the graph $(\alpha h\nu)^2 = f(h\nu)$ and amounted to 3.5 eV for Zn_2SnO_4, 3.3 eV for SnO_2 and 3.2 eV for ZnO.

4. CONCLUSION

Thus, based on the analysis of the technological modes of synthesis and the results of the studies of metal oxide films (ZnO, SnO_2 and Zn_2SnO_4), the following conclusions can be drawn:

- the conditions and parameters for the synthesis of Zn_2SnO_4, SnO_2 and ZnO films using spray pyrolysis were determined. The films were synthesized from aqueous solutions; the main differences between the methods were in the composition of the precursors, in the modes and time of deposition;

-crystal structure of the Zn_2SnO_4 film corresponds to the cubic lattice, which belongs to the space group Fd3m with blocks sized 53 nm and lattice parameters a = 6.238 Å. Films of SnO_2 and ZnO nanocrystallites 28 and 31 nm in size coherently arranged with lattices in the volume of thin Zn_2SnO_4 films can exhibit quantum size effects, which is of interest for modern nanotechnology.

-crystals of the resulting SnO_2 films have a tetragonal Bravais lattice with space group P4_2/mnm with lattice parameters $a = b$ = 4.836 Å and c = 3.245 Å, and the subcrystal size of the SnO_2 film is 61 nm.

The resulting ZnO films belong to the C6/mmc space group and the crystal lattice has a hexagonal syngony with the wurtzite structure with parameters $a = b$ = 0.3265 nm and c = 0.5212 nm. It has been determined that, on the surface of the thin film grown, zinc oxide bumps with sizes $L_{ZnO} \approx 84$ nm appear, which affect the unique properties of the samples.

- studies of the parameters of films Zn_2SnO_4, SnO_2 and ZnO were carried out to assess the possibility of using them as structural elements of a thin-film solar cell. The band gap was determined from the light absorption spectra and was in the range of 3.2 – 3.5 eV for oxides based on Zn and Sn.

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РЕНТГЕНОСТРУКТУРНІ ТА ФОТОЕЛЕКТРИЧНІ ВЛАСТИВОСТІ SnO_2, ZnO, ТА Zn_2SnO_4 МЕТАЛООКСИДНИХ ПЛІВОК

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Визначено умови та параметри синтезу плівок оксидів металів (ZnO, SnO_2, Zn_2SnO_4) методом розпилювального піролізу. Плівки синтезовано з водних розчинів; основні відмінності методів полягали в складі прекурсорів, режимах і часу осадження. Кристалічна структура плівки Zn_2SnO_4 відповідає кубічній ґратці, що належить до просторової групи Fd3m з розміром блоків 53 нм і параметрами ґратки a = 6,238 Å. Плівки нанокристалітів SnO_2 і ZnO розміром 28 і 31 нм, когерентно розташовані з ґратками в об'ємі тонких плівок Zn_2SnO_4, можуть проявляти квантово-розмірні ефекти, що становить інтерес для сучасних нанотехнологій. Кристали отриманих плівок SnO_2 мають тетрагональну ґратку Браве з просторовою групою P4 2/mnm з параметрами ґратки a = b = 4,836 Å та c = 3,245 Å, розмір субкристалів плівки SnO_2 становить 61 нм. Отримані плівки ZnO належать до просторової групи C6/mmc, а кристалічна решітка має гексагональну сингонію зі структурою вюрциту з параметрами a = b = 0,3265 нм і c = 0,5212 нм. Встановлено, що на поверхні вирощеної тонкої плівки виникають горбки оксиду цинку з розмірами $L_{ZnO} \approx 84$ нм, які впливають на унікальні властивості зразків. Показано, що отримані тонкі плівки Zn_2SnO_4, SnO_2 і ZnO можуть бути використані в широкому діапазоні застосувань від чутливих сенсорних елементів до покриттів в прозорій електроніці з точки зору їх оптичних параметрів.

Ключові слова: *плівка; просторова група; субкристал; нанокристал; ефект квантового розміру; параметр решітки; прозора електроніка; заборонена зона*