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RUTHERFORD BACKSCATTERING AND X-RAY DIFRACTION ANALYSIS OF Ag/ZnS/glass MULTILAYER SYSTEM

Experimental results on the study of the element depth profiles, structural and roughness properties of Ag/ZnS/glass multilayer system are reported. The ZnS films in this system were obtained by close-spaced vacuum sublimation method (CSVS) under different substrate temperature. Examination of layers morphology and structure was performed by optical microscopy with laser interferometry phase shifting and X-ray diffraction method respectively. Element depth profiles and film thickness were studied using energy dispersive X-ray analysis (EDAX), such non-destructive accurate qualitative absolute techniques as Rutherford backscattering spectrometry (RBS) and elastic Backscattering Spectroscopy (BS) of $^4He^+$ and $^1H^+$ ions, respectively. Two temperature ranges where the film growth is going under different mechanism were determined. It was established that ZnS films deposited at $373<T_s<573$ K have ZB structure. At $T_s > 573$ K the traces of WZ phase are appearing in ZnS films, their amount somewhat increases under increasing the T_s. RBS and BS techniques allow to determine atomic concentration of compound elements and atomic concentration of the element depth distributions. It was shown that thickness averaged stoichiometry of ZnS films were determined by deposition regimes.

1. INTRODUCTION

The maximum efficiency of the best thin film solar cells (SC) based on heterojunctions n-CdS/p-CdTe is 16.5%, but the rate of its increasing became considerably slower [1]. The most effective back-contact solar cells have close-spaced chemical deposited semiconductor layers are formed at high temperature (T_n~873 K). This process needs the use of the special heat-resistant glass substrates. Therefore for industry producing of solar cells base layers common use low-temperature (~773 K) method of gas-transport reactions. It enables to use low-cost soda-lime glass substrates. However the efficiency of these solar cells does not exceed 10%, and a prime price of energy is high enough [2].

It is thought that the increase of the efficiency of SCs with CdTe absorbing layer may be achieved by change of the material of optical window [3–5]. Thin ZnS layers (E_g=3.68 eV) can be considered as an alternative to CdS (E_g=2.42 eV) films. Zinc sulfide has a sufficiently larger gap than cadmium sulfide, what makes it possible to expand the photosensitivity range and to increase short circuit currents of the corresponding SCs. ZnS has the same type of the crystal lattice as CdTe and both materials form a continuous row of solid solutions. Besides that, ZnS is not a toxic material due to absence of hard metals as compound components and appears as a friendly material for the environment. At the same time, a large lattice mismatch of ZnS and CdTe (~18%) causes a low efficiency of available ZnS/CdTe SCs (~4%) [3]. However, this disadvantage can be compensated by forming transition layers at the interface under the diffusion process as well as by technological way [4].

The efficiency of ZnO/CBD-ZnS/CIGS solar cells increased to 18.6% in recent years [5]. However vacuum condensates of ZnS as wide-gap solar cell windows in this case practically were not used and their properties are investigated poorly. Optimization of ZnS thin films characteristics is important. Interaction processes also require research between a glass lining and a semi-conductor layer which occur at the moment of halcohenide condensation. It also has caused the work purpose.

2. EXPERIMENTAL DETAILS

Zinc sulfide thin films were deposited on soda-lime glass substrates by the close-spaced vacuum sublimation (CSVS) method [6]. The evaporation of two-phased stoichiometric ZnS powder with exceeded content of hexagonal phase (wurtzite) in the charge was carried out. The temperature T_{ev} of evaporator was 1273 K. The temperature T_s of substrate was varied in the range 373÷973 K.

The thin Ag layer was applied on the ZnS film for support of charge gathering from the film surface during measurements using charge particles. Under such conditions the temperature of the ZnS surface was 573 K.

Surface morphology of the films had been investigated by optical microscopy. The calculation of surface roughness was performed according the standard ISO/R 468 [7], while the average arithmetic deviation R_a of profile was defined by formula $R_a = \frac{1}{n}\sum_{i=1}^{n} y_i$, where y_i — profile deviation of film surface from the mean line, n – the number of profile peaks.

Structural investigations of the films were performed with X-ray diffractometer DRON 4-07 using Ni-filtered K_α Cu radiation source and conventional Bragg-Brentano geometry. Continuous mode scanning over the range of diffraction angles $20° \le 2\theta \le 60°$ (where 2θ is the Bragg angle) was applied to examine the surface of the samples Obtained diffraction patterns were normalized to the intensity of (111) peak

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of the cubic phase. Phase analysis was done by comparison of interplane distances and relative intensities from the investigated samples and references according to Joint Committee on Powder Diffraction Standards (JCPDS) data [8].

Chemical composition and films thickness studied by energy dispersive X-ray analysis (EDAX) and Rutherford back scattering (RBS) method of protons and high energy (2,5 MeV) helium ions [9]. Distribution of concentration in EDAX method was probed in five points on films surfaces.

As the source of charged protons (in RBS method) the electrostatic accelerator on 2 MeV (Institute of nuclear physics, Frankfort University, Germany) was utilized. As the source of helium ions was used electrostatic accelerator on 2.5 MeV (Scientific institute of nuclear physics, Moscow State University, Russia). The primary beam of protons bombarded the target normally, scattering angle was 170° and 171° respectively. As the detecting system the semiconductor detector of charged particles were used. The energy resolution of this detector was ~15 keV.

SIMNRA and DVBS programs performed the RBS spectra processing. It is considered that oxygen is compulsory part of A_2B_6 compounds. Coming from it chemical composition of ZnS films is certain in supposition, that in a layer except for basic material is contained this impurity and hydrogen, absorbable from substrate.

3. RESULTS AND DISCUSSION

Surface morphology and condensate structure studies showed that zinc sulfide films are transparent, polycrystalline and homogeneous in area with a good adhesion to the substrate. Growth of ZnS layers takes place as follows. A fine-grained transition region is forming on the substrate with following overgrowth of crystallites oriented by the (111) plane parallel to the substrate.

The increase of crystallite sizes *D* with the increasing film thickness *l* as a consequence of a secondary nucleation during their condensation is almost not occurred at T_s < 720 K. As a result, the grains become a form close to a uniaxial one. Increasing the substrate temperature leads to another growth mechanism: a columnar-like mechanism becomes dominant.

The rise of condensation temperature is going with increase in height of layers relief and therefore it's surface roughness. The typical micrographs of condensates surfaces and surface profilograms are presented in fig. 1.

The determination of parameter R_a shows that under rising in temperature from T_s = 423 K to 863 K the surface roughness in increasing from R_a ≈0.062 μm to 0.147 μm at L~3 μm. The dependence of profile average arithmetic deviation for ZnS films versus T_s is shown in fig. 2. The sharper arising of average arithmetic deviation R_a of films surface profile occurs in the range of deposition temperature, where the column mechanism of film growth is realized.

Analysis of XRD patterns demonstrated that ZnS films deposited at 373<T_s<573K have ZB structure. Hexagonal phase in the as-grown films is not observed in X-ray diffractograms of the condensates (fig.3) despite the double-phase composition of the initial charge characterized by dominating WZ amount. As a rule, XRD patterns show reflexes from (111), (311), (222), (331) planes of ZB. The (111) peaks with dominant maximum intensities are presenting in most cases and exhibit the strong texture of the films.

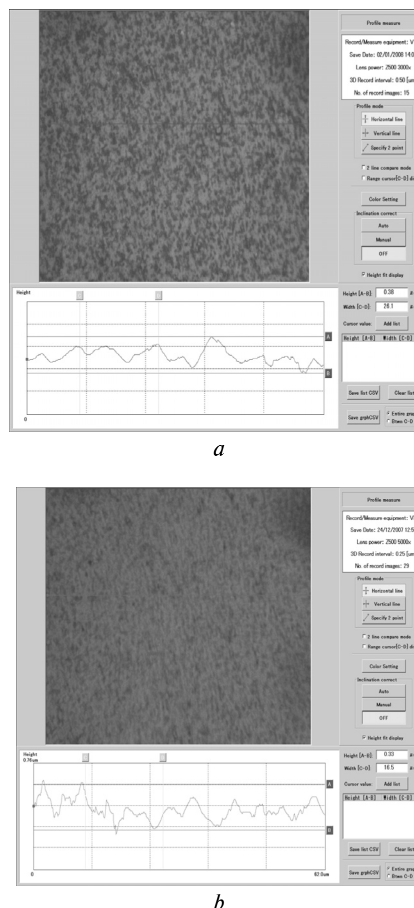

Fig. 1 – The optical morphology with surface profiles of the films grown under different substrate temperatures: T_s =573 K (*a*); T_s = 863K (*b*)

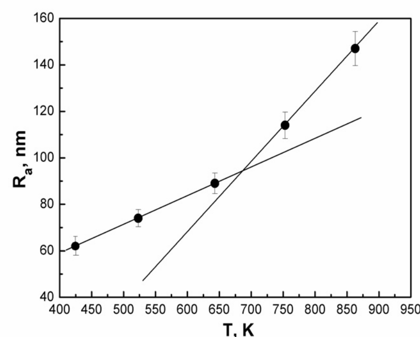

Fig. 2 – Dependencies of arithmetic average to absolute surface deviation R_a values on the substrate temperatures T_s

At T_s > 573 K the traces of WZ phase are appearing in ZnS films, their amount somewhat increases under increasing the T_s. It should be noted that in bulk samples theWZ phase is stable at T>1297 K. XRD patterns mainly demonstrate reflexes only from (101) wurtzite plane and indicate existence of texture in

this phase. In the issue the high-temperature condensates of ZnS are double-phased compounds. X-ray analysis not found out oxides and other extraneous phases.

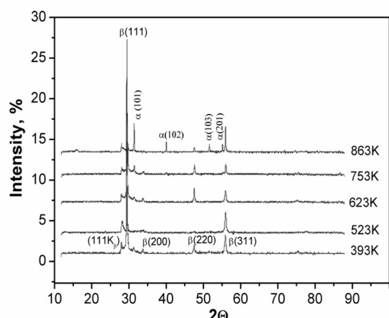

Fig. 3 – X-ray patterns of ZnS films obtained under different condensation temperatures T_s

The typical EDAX spectrums from the "ZnS/sodalime glass" films is illustrated in fig. 4. Along with lines from Zn and S on spectrums there are lines from Si, Ca, K, which belong to lining material. It is related to the small thickness of investigational films by comparison to the depth of X-radiation. The lines of Na, which is one of basic constituents of substrate, coincide with lines of other elements and that is why does not appear.

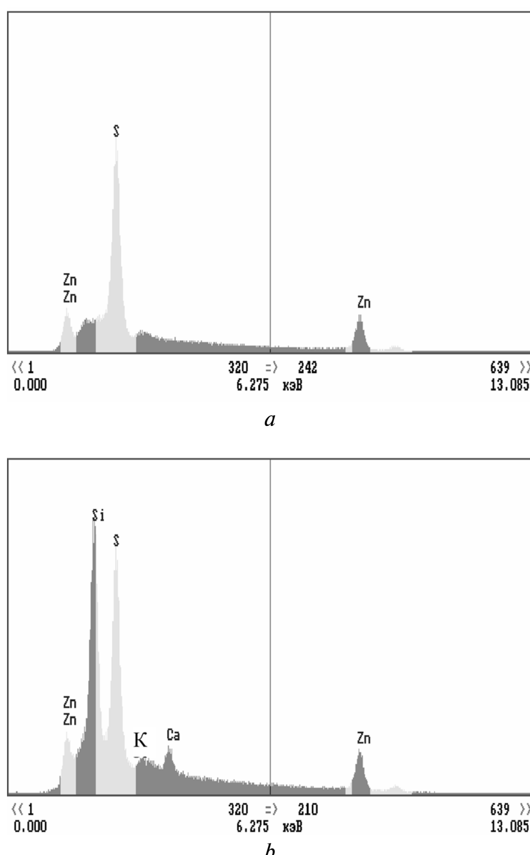

Fig. 4 – Typical EDAX spectrums of the ZnS films on sodalime glass substrates: *a* — depth L=3,2 μm; *b* — L=1,1 μm

This is why such techniques as RBS and BS were applied to explore an elemental composition of the multilayer Ag/ZnS/glass system. It is necessary to mention that these techniques were used very seldom to study ZnS films [10–12]. The BS has improved sensitivity to detect low-Z traces in high-Z matrix and deeper probing. At the same time, the RBS technique has better sensitivity to analyze high-Z elements in low-Z substrates, lower value of profiling depth. From the other side RBS has higher depth resolution and more accurate detection of the absolute trace element concentration [10]. Thus both techniques are complementary each other and give us possibility to obtain more detailed information about the ZnS film depth, thickness averaged stoichiometry of ZnS films and roughness of the Ag-ZnS and ZnS-glass interface layers.

Typical BS and RBS spectra obtained from Ag/ZnS/glass system are shown in Fig. 5,6. As we can see, overlapping of the partial spectra from the matrix and thin layers occurs. Values of thickness were extracted from BS spectra and found out to be L=1.1, 1.8 and 3.2 μm.

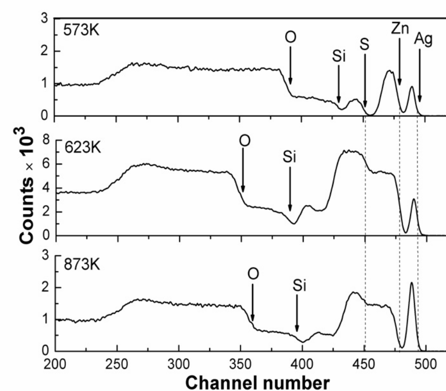

Fig. 5. Elastic proton backscattering spectras from multilayer Ag/ZnS/glass system obtained by different grow conditions. Kinematic edges of the elemental partial spectra are shown by arrows

Fig. 5 shows that the peaks from Zn, S are good separated from each other at 573 K in the case of ZnS thin film (L=1.1 microns), but in the case of more thick layers (L=1.8-3.2 microns) the partial spectra overlap at 623 and 873 K, and it makes data handling more difficult. Using $^4He^+$ analysing beam, the spectra overlap even in the case of ZnS thinnest layer (Fig. 6).

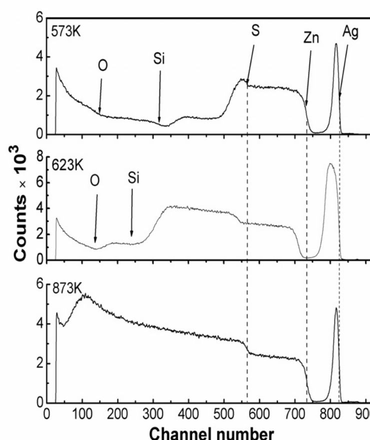

Fig. 6. Energetic $^4He^+$ RBS spectra from multilayer Ag/ZnS/glass systems obtained by different grow conditions. Kinematic edges of the elemental partial spectra are shown by arrows

As a result of the simulations using SIMNRA and DVBS codes, depth concentration distribution of the multi-layer system was extracted. Some results of the data handling for the sample prepared at T_s = 873 K are presented in Table 1.

Table 1

Elemental depth distribution in multilayer Ag/ZnS/glass system

L, nm	*C*, атоmic %									
	Ag	Zn	S	Ca	Si	Al	Mg	Na	O	H
104,7	73,0	24,6	2,4	0	0	0	0	0	0	0
166,5	17,2	32,7	48,9	0	0	0	0	0	0	1,1
219,0	1,2	34,9	51,5	0	0	0	0	0	6,7	5,6
250,4	0	42,1	55,3	0	0	0	0	0	1,7	1,0
399,2	0	43,1	55,8	0	0	0	0	0	0	1,1
763,8	0	43,6	56,1	0	0	0	0	0	0	0,2
1146,9	0	43,8	56,0	0	0	0	0	0	0	0,2
1534,2	0	43,8	56,0	0	0	0	0	0	0	0,2
1836,8	0	43,1	55,1	0	0	0	0	0	0	0,8
1989,6	0	37,4	54,4	0,4	0,1	0	0	0	7,7	0,7
2096,7	0	32,7	49,4	2,5	2,9	0	0	0	9,2	3,3
2350,8	0	25,1	38,6	2,3	12,3	0	0	0	10,9	10,8
2611,1	0	13,5	8,0	2,7	17,4	0	0	0	29,3	29,0
35340,5	0	0	0	3	25	1	1	10	60	0

Traces of Si, Ca, Na diffused from glass substrate to chalcogenide were explored in ZnS film at high temperatures of the layer growth T_n. Some small concentration of W impurity caused by using of tungsten evaporator for the deposition to obtain ZnS films was detected on the surface of the films. Oxygen was observed only in the near-surface layers of the film where the oxide phase formation is possible, for example, ZnO, and in the film interface layers. It is necessary to mention that oxygen concentration reaches 3–8% in the ZnS films prepared by pyrolysis and chemical solutions methods and such films are rather solid state solution like ZnS_xO_{1-x} [3]. In the vacuum condensates, typical concentration of oxygen does not exceed 1–2% which has been confirmed experimentally. Carbon impurities were also found out on the surface of ZnS films. As additional studies have shown, these impurities ingress into samples from the residual gas atmosphere of the vacuum scattering chamber of RBS beam lines. For RBS spectra simulation hydrogen concentration is usually used in the sample composition as a model of the film pores, single vacancies etc.

Fig.7 shows the resulted types of depth distributing of concentrations components (Zn, S) of Ag/ZnS/glass multilayer structure obtained by RBS method. Results of «tailing» size of Zn/S concentration profiles in the transitional layer of Ag-ZnS in number and high-quality conform to information from measuring of roughness of films surfaces resulted on Fig. 2.

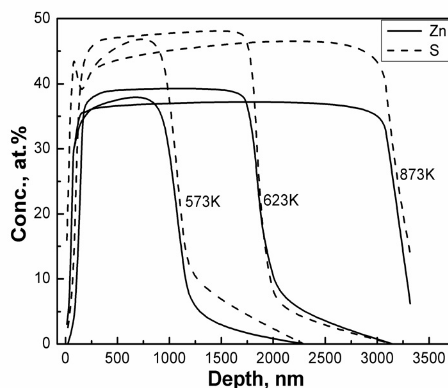

Fig. 7 – Effective elemental depth profiles of Ag/ZnS/glass system obtained by Elastic backscattering spectrometry

Fig. 7 shows that stoichiometry of ZnS films depending on T_s and layer thickness. For the film deposited at T_s = 863 K, it is observed some increasing in S in the narrow near-surface sublayer.

Table 2 presents the results of average layer ZnS film stoichiometry obtained using RBS and BS techniques.

Table 2

Estimation of the effective stochiometric composition of ZnS layer

Sample	T_e, K	T_s, K	BS data			RBS data		
			C_{Zn}, at.%	C_S, at.%	C_{Zn}/C_S	C_{Zn}, at.%	C_S, at.%	C_{Zn}/C_S
ZnS-1	1373	573	49,5	48,9	1,01	39,0	49,0	0,80
ZnS-3	1373	623	43,8	56,1	0,78	39,5	49,0	0,81
ZnS-2	1373	873	42,6	57,2	0,75	38,0	49,0	0,77

A relative error of the effective stoichiometry composition value of ZnS layer extracted from the BS data could be more than 20%, at the same time that derived from the RBS spectra does not exceed 2–4%. Comparing the results obtained using different techniques, it is clear that those are within the limits of experimental error.

The obtained element concentration ratio C_{Zn}/C_S ~0.8 of the compound is found out quite unexpected and require to be elucidated using different analysing techniques. According to RBS results, ZnS films ought to be double phase and sulphur reached. But XRD, optical and SEM data are in contradiction with the RBS findings. The last techniques do not detect the sulphur precipitates.

The other literature works on the using of the RBS technique to study of ZnS films show that ratio of C_{Zn}/C_S~0.91 [11], 1.02 [12] and 1.22 [13] that is to say there are enrichment of Zn-atoms in the condensates. From the other side in the Ref. [15] where explored ZnS films were deposited using photo-chemical deposition method and characterised using SEM/EDAX technique the authors had obtained the results similar to our ones — C_{Zn}/C_S~0.71–0.81. The paper [16] attracts especial interest where the authors were studied a variation of the stoichiometric composition ZnS films at different substrate temperatures using SEM/EDAX which is quite similar to RBS technique. It was found out that C_{Zn}/C_S ratio increase from 0.88 up to 1.19 at increasing of T_s from 473 to 623 K, respectively. The C_{Zn}/C_S ration is also varied in depth from the value of 0.97 naer substrate up to 1.11 near the surface layer, respectively [17].

4. CONCLUSIONS

The structural investigation was spent and nondestructive elemental analysis of multylayer Ag/ZnS/glass structure obtained by CSVS technique under different grow temperatures was carried out. Two temperature ranges where the film growth is going under different mechanism were determined. It was established that ZnS films deposited at $373<T_s<573$ K have ZB structure. At $T_s > 573$ K the traces of WZ phase are appearing in ZnS films, their amount somewhat increases under increasing the T_s. By means of RBS and BS methods the chemical composition of condensates was determined and component distribution of compound as function of multylayer system depth was obtained. It was shown that thickness averaged stoichiometry of ZnS films were determined by deposition regimes and were varying in Zn-to-S ratio range 0.77÷0.81.

5. ACKNOWLEDGEMENT

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А. С. Опанасюк

ДОСЛІДЖЕННЯ ЕЛЕМЕНТНОГО СКЛАДУ ТА СТРУКТУРИ БАГАТОШАРОВОЇ СИСТЕМИ Ag/ZnS/СКЛО

В роботі проведене дослідження профілів розподілу елементів за товщиною, структурних властивостей та шорсткості поверхні плівок ZnS в багатошаровій системі Ag/ZnS/скло. Шари сульфіду цинку в системі були отримані методом вакуумної сублімації в замкнутому об‘ємі (CSVS) при різних температурах конденсації. Вивчення морфології поверхні проводилось за допомогою лазерної інтерферометрії зі зміщеною фазою. Структурні дослідження проводились з використанням методу рентгенівської дифракції (XRD). Вивчення розподілу елементів за товщиною та товщини плівок ZnS було здійснено за допомогою резерфордівського і пружного зворотного розсіювання протонів та іонів гелію-4 (RBS). Показано, що при $373<T_n<573$ K плівки ZnS мають кубічну структуру, в той час як при вищих температурах підкладки вони стають двохфазними. В результаті визначений елементний склад конденсатів, побудований розподіл елементів багатошарової системи та стехіометрія плівок ZnS за товщиною.

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ИССЛЕДОВАНИЕ ЕЛЕМЕНТНОГО СОСТАВА И СТРУКТУРЫ МНОГОСЛОЙНОЙ СИСТЕМЫ Ag/ZnS/СТЕКЛО

В работе проведено изучение профилей распределения элементов по толщине, структурных свойств и шероховатости поверхности для пленок ZnS в многослойной пленочной системе Ag/ZnS/стекло. Пленки сульфида цинка в системе были получены методом вакуумной сублимации в замкнутом объеме (CSVS) при разных температурах конденсации. Изучение морфологии поверхности проводилось с помощью лазерной интерферометрии со смещенной фазой. Структурные исследования проводились с использованием метода рентгеновской дифракции (XRD). Изучение профилей распределения элементов по толщине и толщины пленок ZnS было осуществлено с помощью резерфордовского и упругого обратного рассеяния протонов и ионов гелия-4 (RBS). Показано, что при $373<T_n<573$ K пленки ZnS имеют кубическую структуру, а при более высоких температурах подложки они становятся двухфазными. В результате определен элементный состав конденсатов, построено распределение элементов многослойной системы и стехиометрии пленок ZnS по толщине.