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Properties of the Window Layers for the CZTSe and CZTS Based Solar Cells

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The paper presents complex investigation of optical characteristics and some structural parameters of ZnS and ZnSe films obtained by the close-spaced sublimation technique under different growth condition. Investigation of optical characteristics was carried out in the $\lambda = 350$-900 nm wavelength range for ZnS and $\lambda = 300$-600 nm for ZnSe. Spectral distributions of transmission $T(\lambda)$ and reflection spectra $R(\lambda)$ and their dependence on the deposition temperature of ZnS and ZnSe films are obtained from optical studies.

Keywords: Thin films, Solar cells, Properties, ZnS, ZnSe, CZTS, CZTSe.

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1. INTRODUCTION

Presently maximal efficiency of the best thin films solar cells based on n-CdS/*p*-CdTe is 17.1 %. For the *n*-CdS/*p*-$CuInSe_2$ (CIS) and n-CdS/*p*-$CuIn_{1-x}Ga_xSe_2$ (CIGS) based solar cells the higher efficiency values 17.8 % and 20.4 % are already achieved [1].

However these solar cells have several disadvantages that complicate their extensive use. Among them, low transmission coefficient of the CdS window layer in the ultraviolet region of the spectrum. Also such solar cells contain rare and expensive (In, Ga) or toxic (Cd) materials. Today multicompound thin films $Cu_2ZnSnSe_4$ (CZTSe), Cu_2ZnSnS_4 (CZTS), and $Cu_2ZnSn(S, Se)_4$ (CZTSSe) are considered as alternatives to CIS, CIGS and CdTe base layers [2]. These compounds are composed of earth-abundant elements which is advantageous in terms of price. Fig. 1 shows the relationship between sufficiency and prices of materials, which are used for solar energy. We can see that sulfur, zinc, tin and copper, following this ratio have a much better characteristics than cadmium and indium [3].

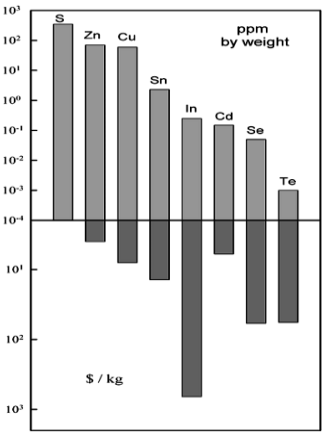

Fig. 1 – Relationship between abundance and price for major solar cell materials **[3]**

The band-gap of CZTSe has been controversial for some time, but a band-gap energy value of 1.0 eV has been established recently [4]. CZTS, on the other hand, has a band gap energy of 1.5 eV [5]. Since the alloy of the CZTS and CZTSe, CZTSSe, can cover the importanct range of (1.0-1.5 eV), this alloy system is considered to be an ideal replacement for CIGS for thin-film solar cell applications. Currently, however, the highest reported efficiency of solar cells made of these compounds is 10.1 % for the *n*-CdS/*p*-CZTS,Se structure [6], which is much smaller than the record efficiency (20.4 %) for CIGS-based solar cells (Fig. 2) [1, 7]. The main problems seem to be dominant interface recombination, short minority carrier lifetime, and high series resistance [6]. Improvement of the efficiency of solar cells based on these multicompound thin films may be achieved by optimization of the absorber layer (CZTSSe) properties or by replacing the CdS ($E_g = 2.42$ eV) window layer with ZnS (ZnSe) which has a wider band-gap ($E_g = 3.67$ eV, $E_g = 2.67$ eV) [8].

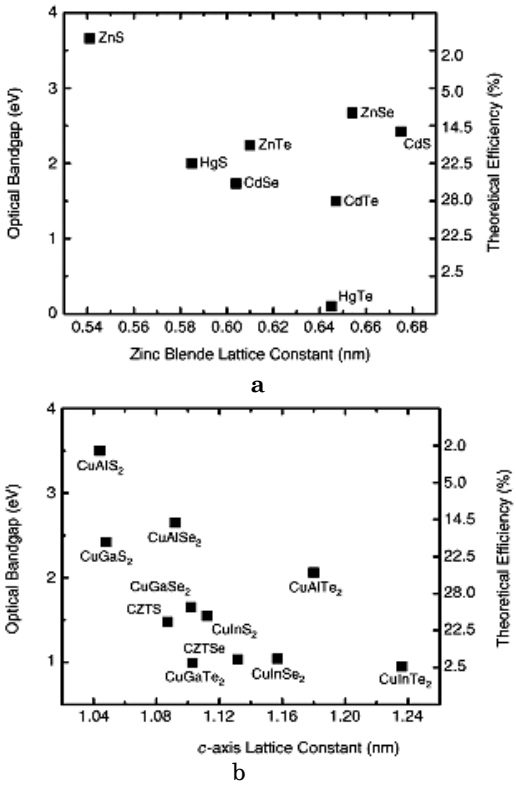

Fig. 2 – Optical bandgap and theoretical single-junction AM1.5 global spectrum efficiency versus lattice constant for zinc blende II-VI (a), chalcopyrite I-III-VI_2 and CZTS, CZTSe compound semiconductors (b) [3]

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In addition, at the large-scale use, important from the ecological point of view, is that the row of these connections (ZnS, ZnSe) does not contain a heavy metal – cadmium in the composition.

However problem of the practical use of zinc chalcogenide films is not decided to this time the solar power engineering as a result of absence of scientific bases of pellicle material science of binary compounds and technologies of receipt mono- and multilayered structures on their basis with, reproductive and stable in time preset parameter.

The main task of this study was research some structural and optical properties of the ZnS and ZnSe thin films as window layers for CZTSe and CZTS based heterojunction (HJ) solar cells.

2. METHODS OF SAMPLE MANUFACTURING AND ANALYSIS

For the thin films deposition the close-spaced vacuum sublimation method was used [9-10]. Thin films were deposited in VUP-5M vacuum system on ultrasonically cleaned glass substrates. The powders of compound were used as charge. The evaporation temperature during ZnSe thin films deposition was $T_e = 1073$ K and for the ZnS $T_e = 1273$ K, substrate temperature T_s is changed from 373 to 973 K.

The measurement of the transmission $T(\lambda)$ and reflection spectra $R(\lambda)$ was performed by the SF-26 and SF-46 spectrophotometers in $\lambda = 350$-900 nm wavelength range for ZnS and $\lambda = 300$-600 nm for ZnSe. The two-beam measurement system used allows to avoid the influence of substrate on final experimental results [10]. The study of the ZnS optical properties was carried out also with spectrophotometer "Ocean Optics USB–200" with the help of Spectra Suite application.

Absorption spectra were obtained from the transmission and reflection spectra following to the next method [11]. For the band-gap energy calculation we have used following equation:

$$\alpha h\nu = A_0(h\nu - E_g)^{1/2}, \qquad (1)$$

where A_0 is constant (depend on effective mass of the free carrier), $h\nu$ is quantum energy.

Structural investigations of the films were performed with an X-ray diffractometer DRON 4–07 in the range of diffraction angles $20° \le 2\theta \le 60°$ (where 2θ is the Bragg angle) using a Ni-filtered $K_\alpha Cu$ radiation source. The lattice parameter was calculated by the Nelson-Riley extrapolation method [12].

Method of structural parameters determine presented in [9-10].

3. RESULTS AND DISCUSSION

Analysis of X-ray diffraction patterns demonstrated that ZnS films grown at $373 < T_s < 573$ K have cubic crystalline structure. At $T_s > 573$ K the traces of hexagonal phase are appearing in ZnS films, their amount somewhat increases under increasing the substrate temperature [10]. ZnSe have almost cubic crystalline structure, and paths the hexagonal phase were observed only in samples obtained at $T_s > 773$ K [13].

It was determined that the lattice parameter of the cubic phase of the ZnS films is changed in the range $a = (0.54060\text{-}0.54196)$ nm and for the hexagonal phase $a = (0.3802\text{-}0.3861)$ nm and $c = (0.6220\text{-}0.6316)$ nm. Measurement of the ZnSe lattice parameter has shown that a is changed from 0.56864 nm ($T_s = 373$ K) to 0.56653 nm ($T_s = 973$ K) (Table 1).

Table 1 – Lattice parameter of ZnS and ZnSe films cubic phase

T_s, K	a, nm	
	ZnS	ZnSe
charge	0,54163	0,56661
373	0,54196	0,56864
473	0,54060	0,56692
573	0,54189	0,56700
673	-	0,56644
723	0,54171	-
773	-	0,56572
803	0,54182	-
873	-	0,56674
973	0,54182	0,56653
Reference	0,54060 [14]	0,566882 [14]
Literature	0,5409-0,5428 [15]	(0,566-0,571 [16]

It is well known that charge transport mechanism from HJ and an efficiency of solar cells determine by state of interface between materials [17]. At the lattice mismatch of semiconductors ($\Delta a = \alpha(a_1 - a_2)/(a_1 + a_2)$) less than 1 % observed their hetero-epitaxial conjugation, in result near-surface states on hetero-boundary are practically not form. At more large lattice mismatch (> 1 %) on hetero-boundary formed a dislocations grid, which has an effective recombination of charge carriers that significantly decreases an efficiency of photo-transformers. At last, when lattice mismatch is more than 7 % on it's interface formed very large number of near-surface states ($N_s > 10^{14}$ cm^{-2}) where recombined practically all charge carriers, which created as a result of photo-generation.

So, were measured by us distances between the closest surface defects which may formed on HJ with different window layers (CdS, ZnS, ZnSe) and absorber layers CZTS, CZTSe because of distance between the near-surface defects (x_N) and minimal concentration of near-surface states (N_s).

For cubic lattices these values may be measured by following equations [18]:

$$x_N = \frac{a_1 a_2}{\sqrt{2}(a_1 - a_2)}, \quad N_S = \frac{4(a_1^2 - a_2^2)}{a_1^2 a_2^2}, \qquad (2)$$

where a_1, a_2 are lattice parameters of HJ contact materials.

Appropriate measuring presented in Table 2. As we can see from this table the best conjugation of the lattices observed for *n*-ZnS-*p*-CZTS and *n*-ZnSe-*p*-CZTSe HJ. Lattice mismatches for these HJs are not more than 0.3-0.5 %, so they are the most useful for solar cells application.

Typical transmission spectra obtained at different substrate temperature are presented on Fig. 3.

It was determined that films with thickness about 1.5 μm have transmission coefficients about (70-95) %. The ZnS films have especially high transmission coefficients. For ZnS a low reflection coefficient of 1-2 % was also observed. ZnSe films have optical properties

Table 2 – HJ parameters between II-VI and CZTS(Se) compounds

HJ	Stable phase	a_1, nm	a_2, nm	Δa, %	x_N, nm	$N_s \cdot 10^{-14}$, cm^{-2}
n-CdS-*p*-Cu_2ZnSnS_4	W-Kest.	0,41368	0,54335	27,1	1,23	9,83
n-ZnS-*p*-Cu_2ZnSnS_4	ZB-Kest.	0,54060	0,54335	0,5	75,53	0,14
n-ZnSe-*p*-Cu_2ZnSnS_4	ZB-Kest.	0,56688	0,54335	4,2	9,26	1,10
n-CdS-*p*-$Cu_2ZnSnSe_4$	W-Stan.	0,41368	0,56840	31,5	1,08	11,0
n-ZnS-*p*-$Cu_2ZnSnSe_4$	ZB-Stan	0,54060	0,56840	5,0	7,82	1,31
n-ZnSe-*p*-$Cu_2ZnSnSe_4$	ZB-Stan.	0,56688	0,56840	0,3	150,09	0,066

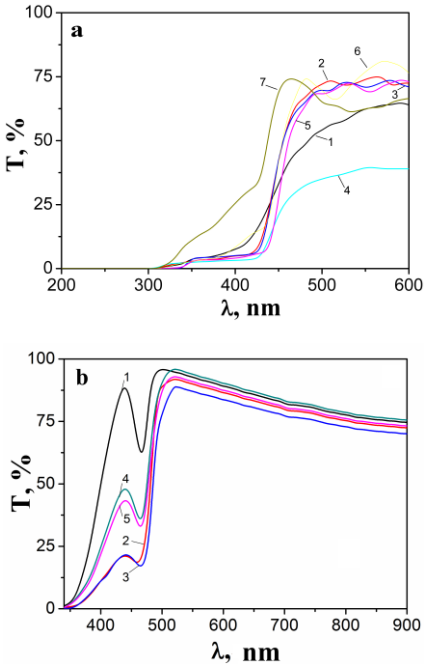

Fig. 3 – Transmission spectra of ZnSe T_s, K: 373 – *1*; 473 – *2*; 573 – *3*; 673 – *4*; 773 – *5*; 873 – *6*; 973 – *7* (a) and ZnS T_s, K: 373 – *1*; 473 K – *2*; 573 K – *3*; 723 K – *4*; 973 K – *5* (b) films obtained under various substrate temperatures

slightly worse than those of ZnS films. Changes in the transmission spectra of the films obtained under different growth conditions can be explained by the different crystal and phase structure of the samples as well as influences of grain boundaries and surface roughness.

According to optical analysis, SEM images and X-ray study, those films with column-like structure have the best properties, and low concentration of extended defects are obtained at optimal growth conditions (T_s = 600-800 K).

The influence of growth conditions on band-gap energy is also determined. Band gap energy is decreased from E_g = 3.68 eV to 3.64 eV in substrate temperature range from T_s = 473 K to T_s = 973 K and increased to 3.82 eV with substrate temperature. In case of ZnSe wide band gap was 2.57-2.62 eV.

4. CONCLUSIONS

High values of transmission coefficient of ZnS and ZnSe films make it possible to consider these materials as a window layers in CZTSe and CZTS based solar cells. Since ZnS and ZnSe compounds have band-gaps wider than that of CdS, it is possible to expand the photosensitivity range of the solar cells. It was determined that lattice parameters of ZnS and ZnSe films are well matched with CZTSe and CZTS lattice parameters (a_{CZTS} = 0.5426-0,5432 nm; a_{CZTSe} = 0.5681-0.5688 nm). Therefore, it may be possible to substantially increase the performances of the solar cells based on CZTSe and CZTS based materials by employing ZnS and ZnSe window layers

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