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Band-gap engineering of $\text{ZnO}_{1-x}\text{S}_x$ films grown by rf magnetron sputtering of ZnS target

V.Khomyak¹, I.Shtepliuk^{2,3}, V. Khranovskyy², R. Yakimova²

¹ Fedkovich Chernivtsi National University, 2 Kotsubinsky str., 58012 Chernivtsi, Ukraine

²Department of Physics, Chemistry and Biology, Linköping University, SE-58183, Linköping, Sweden

³ Frantsevich Institute for Problems of Materials Science NAS of Ukraine, 3 Krzhizhanivsky str., 03680 Kyiv, Ukraine

Abstract

Structural and optical properties of $\text{ZnO}_{1-x}\text{S}_x$ ($0 \leq x \leq 1.0$) thin films grown onto sapphire substrates ($c\text{-Al}_2\text{O}_3$) at 300 °C by radio frequency (rf) magnetron sputtering of ZnS ceramic target are studied. A possibility of purposeful controlling sulfur content and, as consequence, $\text{ZnO}_{1-x}\text{S}_x$ band gap energy via changing the ratio of the partial pressures of argon and oxygen are revealed. Linear dependence of ZnO lattice parameter c on S content suggests that structural properties of single-phase ternary alloys in the composition range between ZnO and ZnS obey Vegard's law. The mechanisms of influence of gas mixing ratio on film growth and band gap energy are discussed. Cu(In,Ga)Se₂ (CIGS)-based heterojunction solar cells with $\text{ZnO}_{1-x}\text{S}_x$ buffer layers were fabricated by one-cycle magnetron sputtering procedure. Electrical characteristics of Cd-free devices are comparable to those of CdS-containing photovoltaic heterostructures, thereby indicating prospects of using $\text{ZnO}_{1-x}\text{S}_x$ layers for fabrication of CIGS solar cells.

Keywords: ZnO, ZnS, band-gap energy, film deposition, bowing parameter, solar cells

Corresponding author: Ivan Shtepliuk, Linköping University, Department of Physics, Chemistry, and Biology (IFM), 583 81 Linköping, Sweden, phone: 0762644554, e-mail: ivan.shtepliuk@liu.se

Zinc oxide (ZnO) and zinc sulfide (ZnS) are among the most intensively investigated semiconductor materials. It is triggered by the broad spectrum of their physical characteristics being appropriate for designing various devices, such as ultraviolet (UV) light emitting diodes (LEDs), electroluminescent displays, gas sensors, anti-reflection coatings, transparent electrodes and windows in thin-film solar cells. The great interest into these materials is mainly driven by their wide band gap energy ($E_g \sim 3.3\text{-}3.4$ eV for ZnO and $E_g \sim 3.4\text{-}3.8$ eV for ZnS), meaning a high transparency in visible and near-UV range. The latter makes it possible to increase the number of photons passing to absorbing and/or active layers in optoelectronic and photovoltaic devices [1, 2]. Moreover, both ZnO and ZnS have large values of the exciton binding energy

(~ 60 and 40 meV, respectively), which can provide an efficient UV emission at room and higher temperatures [3]. Furthermore, much attention is recently paid to the possibility of using thin layers of these materials for replacement of highly toxic CdS, which is commonly used today for buffer layers in fabrication of Cu(In,Ga)Se₂-based heterojunction photovoltaic cells with efficiency as high as 20 % [4]. In this regard, it is necessary to develop technological approaches for obtaining Cd-free high-quality thin-film buffer layers for solar cells. Various technological methods were used for growing ZnO and ZnS films including molecular beam epitaxy, chemical vapor deposition by organometallic compounds, sol-gel deposition, rf and direct current magnetron sputtering, spray pyrolysis and pulsed laser deposition [5-10]. Properties of materials obtained by these methods were found to be strongly determined by growth conditions, different types of impurities and post-growth annealing. In this context, it is very important to define a correlation between the growth conditions and the materials' properties.

Further development of the optoelectronic and photoelectric devices requires an achievement of controllable band-gap engineering (BGE). One way of BGE is an isoelectronic replacement of host anions or cations in ZnO and ZnS by elements of the same group in periodic table, which leads to formation of ZnO_{1-x}S_x alloys [11-14]. During the last decade the number of theoretical and experimental works devoted to growth and characterization of ZnO_{1-x}S_x thin films has been increasing due to their ability to be used as a buffer layer in solar cells [11, 15]. Main parameters of alloy films (especially sulfur dependent band-gap energy) obtained by different research groups sufficiently differ from each other because of different growth methods. Among other methods, magnetron sputtering technique is very promising approach for growth of large-area thin films with controllable optical and structural properties through tuning the growth conditions. There are, nevertheless, a lack of literature data related to ZnO_{1-x}S_x films deposited by rf magnetron sputtering of ZnS target in Ar-O₂ gas mixture and their properties. Investigation of ZnO_{1-x}S_x films with low sulfur content grown at reduced O₂ content in gas mixture (only ~2-4%) was reported by Refs. [16, 17]. Other authors [11] reported about composition dependent band gap energy $E_g(x)$ of single-phase ZnO_{1-x}S_x films within the whole composition range. However reports about a direct correlation between the Ar-O₂ ratio during sputtering of ZnS target and sulfur content in ZnO_{1-x}S_x are missing. Understanding such a correlation may help to achieve desirable properties of ZnO_{1-x}S_x ternary alloys.

Despite the published results the relationship between the deposition conditions of ZnO_{1-x}S_x thin films and their characteristics is still not fully understood and even controversial. Therefore, further study is of considerable interest to optimize the deposition technology of

ZnO_{1-x}S_x films with controllable properties, appropriate for replacement of Cd-containing buffer layer in solar cells.

The aim of our study is to obtain ZnO_{1-x}S_x thin films over the entire range of compositions by reactive rf magnetron sputtering of ZnS target and study the effect of the oxygen and argon partial pressures ratio on their structural and optical properties. Additional aim of this work is to fabricate CIGS-based solar cells with Cd-free buffers layers and find out their electrical parameters and role of BGE.

ZnO_{1-x}S_x films were grown on sapphire substrates *c*-Al₂O₃ at $T_S = 300$ °C by reactive rf magnetron sputtering of ZnS ceramic target (5N purity) in the gas mixture of high-purity O₂ and Ar (99.99%). All layers were deposited at a frequency of 13.56 MHz. The pressure of gas mixture in the chamber during the sputtering process was $\sim 10^{-3}$ Torr and RF power was maintained at 50 W. The target-substrate distance was 40 mm. Films were deposited at a different ratio of partial pressures P_{O_2}/P_{Ar} varying from 0 to 2.0 in order to obtain ZnO_{1-x}S_x alloys with different sulfur content *x*. The gas mixing ratio is the very important control parameter, which is determining for both composition of the films and their structural quality. To provide the necessary gas mixing ratio we used gas bottle, which was filled with argon/oxygen mixture. This mixture with specified values of partial pressures was supplied to vacuum chamber via gas reducer. The thickness of the obtained films was evaluated by both interference microscope MII-4 and interference patterns in transmission spectra and was in the range of 500 - 600 nm. The crystal structure of the grown films was studied using X-ray diffraction (XRD) by DRON-4 (running at 40 kV and 30 mA) with CuK_α source ($\lambda = 0.154056$ nm). Elemental analysis of ZnO_{1-x}Se_x films was performed by X-ray photoelectron spectrometry (XPS) using UHV-Analysis-System SPECS (Germany). Optical transmission spectra *T* were measured using improved versatile setup that works in two modes: normal (classic methods of measurement) and λ -modulation [18]. All studies were performed at room temperature. Fabrication of Al/*n*⁺-ZnO/*i*-ZnO/*n*-ZnO_{1-x}S_x/*p*-CuIn_{0.8}Ga_{0.2}Se₂/Mo (*x*=0, 0.19, 0.32) and Al/*n*⁺-ZnO/*i*-ZnO/*n*-CdS/*p*-CuIn_{0.8}Ga_{0.2}Se₂/Mo solar cells was performed in one technological cycle using the rf and dc magnetron sputtering with three targets and without decompression of working vacuum chamber. Light current-voltage (*I*-*V*) characteristics were measured under the AM1.5 (100 mW/cm²) spectral conditions at solar illumination.

Figure 1a shows the XRD patterns from ZnO_{1-x}S_x thin films deposited at $T_S = 300$ °C and at different ratios of partial pressures of oxygen and argon (P_{O_2}/P_{Ar}).

Fig. 1. (a) XRD patterns of $\text{ZnO}_{1-x}\text{S}_x$ thin films deposited at different ratios of partial pressures of oxygen and argon $P_{\text{O}_2}/P_{\text{Ar}}$: 1 – 2.0; 2 – 1.0; 3 – 0.7; 4 – 0.43; 5 – 0.25; 6 – 0.10; 7 – 0.05; 8 – 0.03; 9 – 0.01; 10 – 0.0. (b) Dependence of the lattice parameter c on the sulfur content in the film

θ - 2θ scan data of $\text{ZnO}_{1-x}\text{S}_x$ films exhibit a strong peak corresponding to the (002) reflection of hexagonal structure. The observation of the strong (002) peak indicates that the films are grown with c -axis orientation. With increasing the $P_{\text{O}_2}/P_{\text{Ar}}$ ratio from 0 to 2.0 the maximum of (002) peak shifted towards larger Bragg angles from 28.63° for ZnS films to 34.46° for ZnO by a nearly linear dependence, indicating the formation of $\text{ZnO}_{1-x}\text{S}_x$ ternary alloys over the entire range of chemical composition x (see Table 1). The sulfur content x in $\text{ZnO}_{1-x}\text{S}_x$ films was defined by XPS measurements and changed from 1 to 0, depending on the $P_{\text{O}_2}/P_{\text{Ar}}$ ratio during the sputtering procedure (see Table 1). Our results are in good agreement with the data presented in Ref. [11]. The values of the full width at half maximum (FWHM) for (002) crystallographic plane are shown in Table 1. The FWHM for ZnS is 0.43° and decreases to 0.14° for ZnO, suggesting a high crystal quality of the $\text{ZnO}_{1-x}\text{S}_x$ films. Structural parameters of $\text{ZnO}_{1-x}\text{S}_x$ ($0 \leq x \leq 1$) films are listed in Table 1.

Table 1

Parameters of $\text{ZnO}_{1-x}\text{S}_x$ films grown by rf reactive magnetron sputtering technique at $T_S = 300^\circ\text{C}$

Sulfur content x in $\text{ZnO}_{1-x}\text{S}_x$	$P_{\text{O}_2}/P_{\text{Ar}}$	Diffraction angle $2\theta_{002}$, deg.	FWHM, deg.	Lattice parameter c , nm	Crystallite size D , nm	E_g , eV
0.00	2.0	34.46	0.14	0.5199	35	3.30
0.007	1.0	34.40	0.16	0.5208	32	3.29
0.052	0.7	34.03	0.19	0.5263	27	3.12
0.11	0.43	33.83	0.21	0.5296	24	3.00

0.14	0.25	33.61	0.23	0.5329	21	2.90
0.19	0.10	33.07	0.29	0.5412	17	2.85
0.26	0.05	32.81	0.37	0.5457	13	2.73
0.32	0.03	32.33	0.41	0.5531	12	2.70
0.96	0.01	28.87	0.51	0.6180	10	3.48
1.00	0.00	28.63	0.43	0.6231	11	3.62

With increasing the P_{O_2}/P_{Ar} ratio (increase in oxygen content in gas mixture) from 0 to 2.0 the lattice parameter c is reduced by a linear law from 0.6231 nm for ZnS films to 0.5199 nm for ZnO films (Table 1). Such a change in lattice parameter along the c -axis of $ZnO_{1-x}S_x$ indicates the fulfillment of the Vegard's law (Fig. 1b). Worth mentioning is that, it was previously reported about a non-linear behavior of the c -lattice parameter depending on the S content in $ZnO_{1-x}S_x$ [19]. This discrepancy is associated with the different methods of growing $ZnO_{1-x}S_x$ thin films, as was also shown by B. K. Meyer *et al.* [11]). It can be seen that in our results the c value of ZnO film is 0.5199 nm. It is slightly smaller than that of bulk ZnO (0.5205 nm) [20]. Similar to the biaxial strain model described in Ref. [21], we have calculated the film stress σ_{film} with consideration of both residual strain ε and thermoelastic strain ε_T , arising from the difference in thermal expansion coefficients of ZnO and Al_2O_3 . The calculated value of stress $\sigma_{film}(ZnO)$ as high as 3.70 GPa suggests the ZnO films undergo compressive stress along the c axis.

From Table 1 one can see the decrease in the crystallite size with increasing sulfur content. This is due to the fact that the deposition rate of $ZnO_{1-x}S_x$ films is dependent on the P_{O_2}/P_{Ar} ratio. In the absence of oxygen ($P_{O_2}/P_{Ar}=0$), the deposition rate was as high as 0.28 nm/s for ZnS. With increasing the O_2 content in the gas mixture (reducing the value of P_{O_2}/P_{Ar}), the deposition rate decreases, reaching the minimum value of 0.093 nm/s for ZnO films. It is caused by reducing the number of high-energy Ar ions bombarding the target. Such a small crystallite size for zinc sulfide films is apparently associated with a large number of adatoms (and thus nucleation centers) in the early stages of film growth. Moreover, since the vapor pressure of sulfur is several orders greater than the saturated vapor pressure of zinc [22], then sulfur will evaporate more rapidly than zinc from the target and reach the substrate surface faster. Therefore, the formation of chemical bonds between sulfur and zinc occurs on the substrate surface, while in the case of undoped zinc oxide Zn is mainly oxidized before deposition on the substrate. An additional step of forming Zn-S chemical bonds on the interface leads to growth of films with poorer crystal quality as was reported by Aita *et al.* [23]. Thus the ZnS films had a poor structural quality. At the same time, increasing the partial pressure of oxygen in the chamber leads to the fact that part of the sputtered sulfur atoms condenses on the substrate and

another part interacts with oxygen and forms SO_2 gas. Therefore, the formation of the Zn-O-S chemical bonds occur both in a space between a sputtering target and a substrate surface and directly on the substrate. Thus, increasing the oxygen content in the gas mixture is accompanied by a decrease in the sulfur content in the film (because a smaller number of sulfur adatoms is available to form chemical bonds with zinc). At the maximum value of the ratio of the partial pressure ($P_{\text{O}_2}/P_{\text{Ar}}=2.0$), almost all sputtered sulfur species react exothermically with oxygen and do not have enough time to reach the substrate surface. A direct condensation of molecular ZnO onto substrate is most probable at such conditions. Due to the low growth rate, surface diffusion of condensed adatoms promotes a coalescence of growing islands, thereby increasing the crystallite size in the ZnO film.

Fig. 2a shows the optical transmission spectra of $\text{ZnO}_{1-x}\text{S}_x$ ($0 \leq x \leq 1.0$) grown at different ratio of partial pressures of argon and oxygen. The $\text{ZnO}_{1-x}\text{S}_x$ films are characterized by high transparency in visible ($60 \div 85\%$). The sharp fundamental absorption edge and clear interference pattern indicate the high optical quality of grown films within the entire range of chemical compositions x .

Fig. 2. (a) The spectral dependence of the optical transmission of $\text{ZnO}_{1-x}\text{S}_x$ thin films deposited at different values of $P_{\text{O}_2}/P_{\text{Ar}}$ ratio: 1 – 2.0; 2 – 0.7; 3 – 0.25; 4 – 0.1; 5 – 0.05; 6 – 0.03; 7 – 0.01; 8 – 0.0. (b) Dependence of the band gap energy on the sulfur content in the film

The values of E_g determined by extrapolating of $\alpha^2(h\nu)$ curve to $\alpha^2 = 0$ are presented in Fig. 2b. It is clearly seen that the band gap energy of $\text{ZnO}_{1-x}\text{S}_x$ varies non-linearly with changing the sulfur content. Changing x from 1.0 to 0, i.e. reduction of S content and increase in O content, E_g initially decreases, reaching the minimum at $x=0.32$ ($E_g=2.7$ eV), and then increases to 3.30 eV (ZnO). Behavior of $\text{ZnO}_{1-x}\text{S}_x$ band gap energy can be described as [24]

$$E_{g\text{ZnOS}}(x) = xE_{g\text{ZnS}} + (1-x)E_{g\text{ZnO}} - b(1-x)x, \quad (1)$$

where $E_{g\text{ZnS}}$ and $E_{g\text{ZnO}}$ are band gap energy of binary compounds at 300 K (3.62 eV and 3.30 eV, respectively), a is the bowing parameter. According to our data, its value is 3.5 eV. Nonlinear dependence of the band gap energy is caused by difference in electronic properties of oxygen and sulfur anions in the zinc oxide lattice. Since oxygen electronegativity ($\chi = 3.44$) is higher than that of sulfur ($\chi = 2.58$), the density of charge around the oxygen atom is larger than that of sulfur atom. In other words, the distance between Zn 3d and O 2p orbital energy levels, forming the top of the valence band of zinc oxide is less than the distance between the Zn 3d and S 3p orbitals in the case of ZnS binary compound. Stronger p-d repulsion leads to a shift of the valence band maximum (VBM) upwards in energy. That's why zinc oxide has smaller band-gap energy in comparison to zinc sulfide. Reducing the sulfur content in $\text{ZnO}_{1-x}\text{S}_x$ from $x=1$ to $x=0.42$ causes the band-gap shrinkage. It is due to a small contribution of S 3p orbitals to the states near the VBM and appearance of the O 2p orbitals, which leads to enhancement of the p-d repulsion. Further decreasing the S content from $x=0.42$ to $x=0$ is accompanied by the increase in E_g . It is caused by hybridization between Zn 3d, S 3p and O 2p electron levels and asymmetric distribution of charge density around anions, which lead to downward movement of the VBM. On the other hand, rearrangement of chemical bonds in the simultaneous presence of oxygen and sulfur anions as well as volume deformation can also contribute to non-trivial dependence of the band gap energy on the sulfur content [25]. Such a behavior is typical for many other alloys based on $\text{A}^{\text{II}}\text{B}^{\text{VI}}$ compounds [26], including the $\text{ZnO}_{1-x}\text{S}_x$ [11]. Our values for ZnO and ZnS are in good agreement with known literature data [3, 5, 27, 28]. This is also confirmed by our recent studies of band structure parameters of ZnO using high-sensitive modulation spectroscopy [3, 29]. The parameters E_g , Δ_{so} i Δ_{cr} , which are 3.30 eV, 5 i 49 meV respectively, are consistent with other published data [27, 30].

Effect of band gap engineering of $\text{ZnO}_{1-x}\text{S}_x$ clearly manifests itself in electrical properties of CIGS solar cells. Indeed, changeable band-gap energy of $\text{ZnO}_{1-x}\text{S}_x$ buffer layer expands the energy range of incident photons moving to CIGS active layer, thereby improving the overall photo-conversion efficiency. Figure 3 shows the light I - V characteristics of Cd-free $\text{Al}/n^+-\text{ZnO}/n-\text{ZnO}_{1-x}\text{S}_x/p-\text{CuIn}_{0.8}\text{Ga}_{0.2}\text{Se}_2/\text{Mo}$ heterostructures with different sulfur content in $\text{ZnO}_{1-x}\text{S}_x$ buffer layer (curves 1-3). For comparison we also depicted the I - V curve for solar cell with CdS buffer layer (curve 4). The main electrical parameters (short circuit current I_{SC} , open circuit voltage V_{OC} , fill factor FF and efficiency η) of fabricated solar cells are determined from careful analysis of the I - V curves and are listed in Table 2. We can see that the solar cells with $n-\text{ZnO}_{0.81}\text{S}_{19}$ and $n-\text{ZnO}_{0.68}\text{S}_{32}$ buffer layers demonstrate enhanced efficiency of photo-conversion in comparison to heterostructures with undoped ZnO buffer layer. It can be explained by both BGE effect via the changing the sulfur content and tuning lattice mismatch between heterostructure's

components. Nevertheless, establishing the exact mechanism requires further experimental and theoretical verification. At the same time, the $\text{ZnO}_{1-x}\text{S}_x$ -containing solar cells possess comparable properties to photovoltaics devices with toxic CdS buffer layers. It indicates the prospects of the using the Cd-free buffer layers with controllable parameters for fabrication of CIGS solar cells by one-cycle magnetron sputtering technique.

Fig.3. Light I - V characteristics of solar cells with different buffer layers:
 1 – $\text{Al}/n^+-\text{ZnO}/n-\text{ZnO}_{1-x}\text{S}_x/p-\text{CuIn}_{0.8}\text{Ga}_{0.2}\text{Se}_2/\text{Mo}$, $x=0.19$; 2– $\text{Al}/n^+-\text{ZnO}/n-\text{ZnO}_{1-x}\text{S}_x/p-\text{CuIn}_{0.8}\text{Ga}_{0.2}\text{Se}_2/\text{Mo}$, $x=0.32$; 3 – $\text{Al}/n^+-\text{ZnO}/n-\text{ZnO}_{1-x}\text{S}_x/p-\text{CuIn}_{0.8}\text{Ga}_{0.2}\text{Se}_2/\text{Mo}$, $x=0$;
 4– $\text{Al}/n^+-\text{ZnO}/i-\text{ZnO}/n-\text{CdS}/p-\text{CuIn}_{0.8}\text{Ga}_{0.2}\text{Se}_2/\text{Mo}$

Table 2.

Main output electrical parameters of heterojunction solar cells based on $\text{ZnO}_{1-x}\text{S}_x$ films

Heterostructure	Short circuit current, J_{sc} , mA/cm^2	Open circuit voltage, U_{oc} , V	Fill factor, FF	η , %
$\text{Al}/n^+-\text{ZnO}/n-\text{ZnO}_{1-x}\text{S}_x/p-\text{CuIn}_{0.8}\text{Ga}_{0.2}\text{Se}_2/\text{Mo}$, $x=0.19$	33.79	0.48	61.52	9.98
$\text{Al}/n^+-\text{ZnO}/n-\text{ZnO}_{1-x}\text{S}_x/p-\text{CuIn}_{0.8}\text{Ga}_{0.2}\text{Se}_2/\text{Mo}$, $x=0.32$	30.03	0.49	56.74	8.35
$\text{Al}/n^+-\text{ZnO}/n-\text{ZnO}_{1-x}\text{S}_x/p-\text{CuIn}_{0.8}\text{Ga}_{0.2}\text{Se}_2/\text{Mo}$, $x=0$	30.19	0.49	51.08	7.52
$\text{Al}/n^+-\text{ZnO}/i-\text{ZnO}/n-\text{CdS}/p-\text{CuIn}_{0.8}\text{Ga}_{0.2}\text{Se}_2/\text{Mo}$	37.93	0.55	63.97	13.29

We have investigated the composition dependence of the fundamental band gap of single-phase $\text{ZnO}_{1-x}\text{S}_x$ ($0 \leq x \leq 1.0$) films grown by rf magnetron sputtering. Controlling the sulfur content and band-gap engineering was preformed via changing the ratio of partial pressures of

argon and oxygen. The different regimes of the film growth governing by gas mixing ratio were discussed. The films were characterized by linear dependence of the lattice parameter and nontrivial behavior of band gap energy (with large bowing parameter as high as 3.5 eV) with a change in sulfur content. Nonlinear band gap energy change was explained in terms of different values of electronegativities of oxygen and sulfur. In contrast to Bruno Meyer's report [11] the direct correlation between gas mixing ratio, growth regimes, structural and optical properties of the $\text{ZnO}_{1-x}\text{S}_x$ ternary alloys was revealed and discussed. We have also fabricated $\text{Al}/n^+-\text{ZnO}/n-\text{ZnO}_{1-x}\text{S}_x/p-\text{CuIn}_{0.8}\text{Ga}_{0.2}\text{Se}_2/\text{Mo}$ solar cells, where all layers were deposited by one-cycle magnetron sputtering without a decompression of working chamber. The electrical parameters of $\text{ZnO}_{1-x}\text{S}_x$ -containing devices were similar to those of solar cells with CdS buffer layers, thereby suggesting the feasibility of Cd-free solar cells with enhanced performance. Our approach to fabrication of CIGS solar cells with $\text{ZnO}_{1-x}\text{S}_x$ buffer layers offers ecological and economic advantages over technology of Cd-containing photovoltaic devices.

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