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Valence band structure and optical properties of $\text{ZnO}_{1-x}\text{S}_x$ ternary alloys

I.Shtepliuk^{1,2}, V.Khomyak³, V. Khranovskyy¹ and R. Yakimova¹

¹*Department of Physics, Chemistry and Biology, Linköping University, SE-58183, Linköping, Sweden*

²*Frantsevich Institute for Problems of Materials Science NAS of Ukraine, 3 Krzhizhanivsky str., 03680 Kyiv, Ukraine*

³*Fedkovich Chernivtsi National University, 2 Kotsubinsky str., 58012 Chernivtsi, Ukraine*

Abstract

The k,p method and the effective mass theory are applied to compute valence-band electronic structure and optical properties of $\text{ZnO}_{1-x}\text{S}_x$ ternary alloys under biaxial strain. A significant modification of the band structure with increasing sulfur content is revealed. Features of wave-functions and matrix elements in the transverse electrical (TE) and transverse magnetic (TM) regimes for three valence subbands are studied and discussed. The results of calculations of interband transition energy and spontaneous emission spectra are in agreement with experimental data for $\text{ZnO}_{1-x}\text{S}_x$ films grown by radiofrequency magnetron sputtering technique.

Keywords: optical materials, electronic band structure, computer simulations, optical properties

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

1. Introduction

Light-emitting devices (LEDs) and thin-film heterojunctions are desirable for different optoelectronics and photovoltaic applications such as displays, sustainable light sources and solar cells. Among the available semiconductors which can possess direct band gaps, zinc oxide (ZnO) offers the promise of the LEDs and toxic-free photoelectric transducers [1, 2]. Band gap engineering (BGE) of ZnO could make it accessible to solar cell applications, since the semiconductor systems with tuned band-gap may be used as intermediate layers to adjust the band offsets between different layers in heterojunction solar cells. In general, BGE is the process of altering the band gap of a material by controlling the composition of certain semiconductor alloy. In this regard, it is very important to choose an appropriate doping source providing the BGE of ZnO. Sulfur is intriguing isoelectronic impurity for anion substitution in ZnO [3]. Recently, much attention has been paid to the synthesis of $\text{ZnO}_{1-x}\text{S}_x$ alloys [4-8]. However, a large difference in the electronegativities between oxygen and sulfur causes changes

in both the lattice potential and the electron potential, thereby leading to band-gap bowing in the $\text{ZnO}_{1-x}\text{S}_x$ alloys [9]. Since the larger the bowing is related to the greater the miscibility gap [10], then the growth of $\text{ZnO}_{1-x}\text{S}_x$ alloys across the entire composition range is a big challenge [11, 12]. For these reasons, the information about the fundamental properties of $\text{ZnO}_{1-x}\text{S}_x$ is very essential in the terms of both material science and possible applications. A solution of the BGE problem can be achieved via a clear understanding both the band structure of $\text{ZnO}_{1-x}\text{S}_x$ alloys and a nature of optical processes occurring in such materials. Theoretical calculations in the frames of semi-empirical k,p approach is an effective tool for investigation of band dispersion and can adequately explain the impact of different realistic effects (strain, spin-orbit splitting, etc.) on the electronic properties of grown films [13]. Of particular interest is the theoretical study of optical matrix elements and the wave functions depending on the sulfur content because their behavior is crucial to understanding and in-depth description of both light absorption and spontaneous emission processes. Thus, a comprehensive theoretical analysis of the electronic band structure and optical properties of $\text{ZnO}_{1-x}\text{S}_x$ films is performed in this study.

2. Theoretical framework

All interband optical processes in $\text{ZnO}_{1-x}\text{S}_x$ alloys are primarily determined by the interband matrix elements of momentum operator at the edges of the conduction and valence band. These matrix elements determine not only the intensity of the absorption and emission, but also the polarization selection rules due to crystal symmetry. For correct calculation of matrix elements is necessary to find Bloch wave functions that describe the holes in the valence band and the valence band dispersion taking into account valence band degeneracy, spin-orbit interaction, crystal field splitting, the spin degeneracy and the strain. Modified six-by-six k,p theory, which takes into account all mentioned interactions and effects can give an adequate description of valence band dispersion in the vicinity of the Γ point using a small number of physical parameters [13]. This model involves solving the Schrödinger equation, which includes a modified Pikus-Bir Hamiltonian [13]:

$$[\mathbf{H}_v(k_x, k_y, k_z)]\Psi_H^i = E_H^i \Psi_H^i \quad (1)$$

To find the wave functions and Eigen-energies of electrons in the conduction band is necessary to solve the usual Schrödinger equation with the following Hamiltonian:

$$\begin{cases} \mathbf{H}_c(k_x, k_y, k_z) = E_c + a_{c1}e_{zz} + a_{c2}(e_{xx} + e_{yy}) + \frac{\hbar^2(k_x^2 + k_y^2)}{2m_{\parallel}} + \frac{\hbar^2k_z^2}{2m_{\perp}} \\ a_{c1} = a_1 + D_1 \\ a_{c2} = a_2 + D_2 \end{cases} \quad (2)$$

where $m_{\parallel}, m_{\perp}$ are longitudinal and transverse effective mass of the electron, a_1 and a_2 are deformation potentials of the conduction band.

Optical matrix elements for interband transitions can be expressed by the following formula [14]:

$$|\hat{\mathbf{e}}\mathbf{M}^{\eta}|^2 = \left| \langle \Psi_c | \hat{\mathbf{e}} \cdot \mathbf{p} | \Psi_v^i \rangle \right|^2 \quad (3)$$

where $\eta = \uparrow$ and $\downarrow$ depending on the spin orientation. Ψ_c, Ψ_v^i are wave functions of the conduction and three valence subbands.

Matrix elements in the case of TE-polarization for $\eta = \uparrow$ were determined by the following equation [14]:

$$|M_x|^2 = \left| -\frac{1}{\sqrt{2}} P_x \langle g_m^1 \Psi_c \rangle + \frac{1}{\sqrt{2}} P_x \langle g_m^2 \Psi_c \rangle \right|^2 \quad (4)$$

While for TM-polarized matrix elements one can be written [34]:

$$|M_z|^2 = \left| -\frac{1}{\sqrt{2}} P_z \langle g_m^3 \Psi_c \rangle \right|^2 \quad (5)$$

where g_m^1, g_m^2 and g_m^3 are components of Bloch wave functions that correspond heavy-hole band ($m=HH$), light-hole band ($m=LH$) and crystal-field split-off hole band ($m=CH$), correspondingly. Kane parameters P_x and P_y , present in expressions (4) and (5), can be found using the formulas in Ref. [14]. Spontaneous emission spectra were calculated using the formalism described in [15]. It should be noted that the interpolation relationships between physical parameters of wurtzitic zinc oxide and zinc sulfide were used for calculations (Table 1).

Table 1. Some physical parameters of $\text{ZnO}_{1-x}\text{S}_x$ alloys

Parameters	Symbol	Unit	Linear interpolation	References
Elastic constant	C_{13}	GPa	$121 - 75.5x$	[16, 17] ^{theory}
Elastic constant	C_{33}	GPa	$225 - 85.4x$	[16, 17] ^{theory}
Lattice parameter	a	Å	$3.25 + 0.573x$	[18, 19] ^{experiment}
Band-gap energy	E_g	eV	$3.62x + 3.3(1-x) - 3.5(1-x)x$	our experiment
Valence-band effective-mass parameters	A_1 A_2 A_3 A_4 A_5 A_6	-	-6.68036+2.47836x; -0.45388-0.97412x; 6.1275-2.6505x; -2.70374+1.11874x; -2.7669+2.9789x; -4.62566+7.68566x;	[20, 21] ^{theory}
Deformation potentials	D_1 D_2 D_3 D_4 D_5 D_6	eV	-3.90 -4.13 -1.15 -1.22 -1.53 -2.88	[22] ^{theory}

Conduction-band effective masses	$m_{\parallel}$ $m_{\perp}$	m_0	$0.24+0.019x$ $0.28-0.053x$	[21, 23] ^{theory}
Splitting energies	Δ_{cr} $\Delta_{so}/3$	eV	$0.050+0.008x$ $0.0016666+0.02903x$	[18, 24] ^{experiment}

3. Experimental details

In order to compare results of theoretical investigation with experimental data, we studied the compositional dependence of the band-gap energy of $\text{ZnO}_{1-x}\text{S}_x$ films ($x=0.0, 0.007, 0.052, 0.11, 0.14, 0.19, 0.26, 0.32, 0.96$ and 1.00) grown onto *c*-sapphire substrates at $T_S = 300$ °C by reactive rf magnetron sputtering of ZnS ceramic target (5N purity) in the gas mixture of high-purity O_2 and Ar (99.99%). Control of the sulfur content was performed via tuning the ratio of partial pressures $P_{\text{O}_2}/P_{\text{Ar}}$ from 0 to 2.0. 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. 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). XRD characterization confirmed that the films obey the Vegard's law and have hexagonal wurtzite structure with a preferred *c*-axis orientation along (002) plane. Elemental analysis of $\text{ZnO}_{1-x}\text{S}_x$ films was performed by X-ray photoelectron spectrometry (XPS) using UHV-Analysis-System SPECS (Germany). The band-gap energy of the $\text{ZnO}_{1-x}\text{S}_x$ films was determined from investigation of optical transmission spectra measured at room temperature. The values of E_g were 3.30, 3.29, 3.12, 3.00, 2.90, 2.85, 2.73, 2.70, 3.48 and 3.62 eV for $\text{ZnO}_{1-x}\text{S}_x$ films with $x=0.0, 0.007, 0.052, 0.11, 0.14, 0.19, 0.26, 0.32, 0.96$ and 1.00 , respectively.

4. Results and discussion

Figure 1 depicts dispersion curves of the valence band of wurtzitic $\text{ZnO}_{1-x}\text{S}_x$ alloys with different sulfur content. It is clearly seen that the two highest valence subbands ascribed to heavy hole and light hole are close to each other at the center of Brillouin zone due to low value of spin-orbit splitting energy Δ_{SO} . The third CH subband is separated from HH and LH band because of crystal field splitting by Δ_{cr} . It should be noted that in the case of low concentrations of sulfur dispersion law for all subbands is close to isotropic parabolic.

Fig. 1. Valence band structure of ZnO_{1-x}S_x alloys for different values of sulfur content: (a) – $x=0.05$, (b) – $x=0.11$ and (c) – $x=1$. The axis of abscissas is the quasi-wave vector in [100] and [001] directions, respectively.

The enlargement of the sulfur content in the alloy leads to significant modification of band spectrum. In particular, there is a noticeable increment of spin-orbit interaction energy and crystal field splitting energy, i.e. the increase in splitting of the valence band within the whole range of quasi-wave vector $\mathbf{k}$ (decoupling of the valence subbands). Another important point is the anisotropy of the valence band spectrum. One can clearly see that the dispersion of heavy hole subband along the hexagonal c axis is substantially different from the dispersion in the direction perpendicular to the axis c . Fig. 2 demonstrates the constant energy contour plots of the topmost valence subbands evidencing such anisotropy. It is obvious that such features of band structure will cause anisotropy of the optical properties of alloys. In addition, the increase in the sulfur content leads to changes in the energy, which corresponds to the center of the Brillouin zone ($k_x=k_y=k_z=0$) and, as a consequence, to the change of energy of optical transition between the conduction band and valence subbands.

Fig. 2. The constant energy contour plots of heavy hole (HH) band for $\text{ZnO}_{1-x}\text{S}_x$ alloys with different S content: (a) – $x=0.05$, HH; (b) – $x=0.11$, HH; (c) – $x=1$, HH;

As mentioned before, due to lattice mismatch between alloy and substrate the resulting film is under stress. Therefore, it is very important to investigate how type of elastic deformation affects the band structure of $\text{ZnO}_{1-x}\text{S}_x$. Three cases are considered: compressive strain ($e_{xx} < 0$), tensile strain ($e_{xx} > 0$) and absence of strain ($e_{xx} = 0$). It is noticeable that the energy levels of all valence subbands in the vicinity of the center of the Brillouin zone shifted up in the energy scale in the case of compressive strain and down in the energy scale in the case of tensile strain. In addition, energy distance between subbands in the case of compressive deformation increases with respect to the relaxed state, and decreases when tensile strain is occurred. Thus, the type of strain can affect the energy of optical transitions. Fig. 3 represents the dependences of the C-HH (conduction band-heavy hole band) transition energy on the sulfur content for different cases of strain. Characteristic features of presented dependences are their nonlinearity and sensitivity to strain type. In other words, there are two regions with different trends in band-gap energy. The initial increase in the sulfur content to a value ~ 0.42 causes the reduction of band-gap energy, while a further growth of the S content gives a rise to an enlargement of optical transition energy. As can be seen from Fig. 3, blue circles corresponding to our experimental values of E_g (determined from the analysis of the fundamental absorption edge) for $\text{ZnO}_{1-x}\text{S}_x$ film grown by rf

magnetron sputtering are in good agreement with our theoretical results. The slight discrepancy between theory and experiment can be explained by technological growth features of the individual film (since sulfur content was controlled by changing the ratio of the partial pressures of oxygen and argon) and presence of mechanical stresses caused by both local deformation and crystal lattice mismatch.

Fig.3. Dependence of the C-HH optical transition energy on the sulfur content in $\text{ZnO}_{1-x}\text{S}_x$ for different types of strain e_{xx} : curve 1 corresponds to compressive strain -2.5 %, curve 2 is related to relaxed case and curve 3 represents tensile strain +2.5 %. Blue circles correspond to our experimental values of band gap energy of $\text{ZnO}_{1-x}\text{S}_x$ films, which were determined from analysis of the absorption spectra.

The wave-function of each valence subbands consists of three components that determine both the physical nature corresponding subband and optical matrix elements. Figure 4 depicts dependences of g_1^2 , g_2^2 and g_3^2 coefficients on the quasi-wave vector for heavy hole band (HH), light-hole band (LH) and crystal-field split-off hole band (CH). It can be observed the dominant nature of quasi-wave vector dependent g_1^2 component for HH band. As a result of the spin-orbit splitting, HH band in the center of the Brillouin zone is characterized by the following values of coefficients of Bloch wave-function: $g_1^2=1$, $g_2^2=0$ and $g_3^2=0$. At the same time, in the vicinity of Γ point the g_1^2 component for LH and CH bands is zero. In the case of LH and CH bands (Fig. 4 b, c) one can note the dominance of g_2^2 and g_3^2 components around the center of the Brillouin zone. It is obvious that in the case of heavy hole band an increase in wave vector leads to a sharp drop of g_1^2 component, substantial increment of g_2^2 and small growth of g_3^2 . In the range of quasi-wave vectors $0.1-0.2 \text{ \AA}^{-1}$ one can see the superposition of g_1^2 and g_2^2 components. An

enhancement of k_t causes the reduction of g_2^2 (g_3^2) coefficient for LH band (CH band), and rise in g_2^2 (g_1^2) and g_3^2 (g_2^2) coefficients followed by their subsequent superposition.

Fig. 4. Normalized values of the wave functions for different valence subbands of $\text{ZnO}_{0.89}\text{S}_{0.11}$ alloy under tensile strain $e_{xx}=+2.5\%$: (a) heavy hole band, (b) light hole band (c) crystal-field split-off hole band.

Based on the analysis of the Bloch wave-functions the matrix elements of the interband transition between conduction band and valence subbands for cases of TE- and TM-polarization can be calculated [25]. It is appropriate to note that in the case of TM-polarization electric field vector is directed along the c axis ($\mathbf{E} \parallel \mathbf{c}$), whereas in the case of TE-polarization $\mathbf{E} \perp \mathbf{c}$ [26, 27]. At the same time, TM-polarization in many cases is undesirable, because the output radiation with such a polarization from the wide-gap semiconductors in directions perpendicular to the (0001) plane is actually impossible [28]. Fig. 5 illustrates typical dependences of matrix elements on the wave vector for strained film of $\text{ZnO}_{0.89}\text{S}_{0.11}$ alloy. It is noticeable that in the TE-polarized mode the matrix elements of the C-HH and C-LH transitions are much greater than in the case of TM-polarization. First of all, this can be explained by the ratio between the energies that correspond to the absorption edge for C-LH and C-CH transitions. In the case of $\text{ZnO}_{1-x}\text{S}_x$ alloy, the crystal field splitting energy is larger than the spin-orbit splitting energy. On the other hand, the matrix elements in the case of TM-polarization are mainly determined by the behavior of g_3^2 component

of the wave function, which has the maximum value for CH subband. That is why the matrix elements for C-HH and C-LH interband transitions in wurtzitic alloys are much higher for $E^\perp c$, while the matrix element of C-CH transition is greater for $E\parallel c$. It should also be noted that the increase in the wave vector causes a considerable enlargement of matrix elements of C-LH for the TM-polarization, which is caused by enhancement of the g_3^2 component for LH band (Fig. 4b).

Fig. 5. Optical matrix elements for direct interband transitions (conduction band – heavy hole band, light hole band and crystal-field split-off hole band) in $\text{ZnO}_{0.89}\text{S}_{0.11}$ alloy with consideration of the tensile strain ($e_{xx}=+2.5\%$) for (a) TE i (b) TM-polarized modes.

It was also investigated the dependence of the optical transition matrix elements for C-HH on the sulfur content in the alloy (see. Fig.6). It is significant that the increase in the sulfur content leads to a reduction of matrix elements in the TE-polarized mode, and their growth in TM regime. This is due to the change of the physical nature of the components of the wave function due to change of composition. However, the interband matrix elements of the main direct transition for TE-polarization in the zinc sulfide in a small vicinity of the center of the Brillouin zone are characterized by the highest values compared to those of other samples, gradually decreasing with increasing quasi-wave vector (see. Fig. 6).

Fig. 6. Dependence of the optical matrix elements for direct interband transition «conduction band – heavy hole band» on the sulfur content with consideration of the tensile strain ($e_{xx}=+2.5\%$) for (a) TE i (b) TM-polarized modes.

It is noteworthy that knowing the dependence of matrix elements for all types of direct interband transitions in alloy gives a possibility to calculate the spontaneous emission spectra taking into account the TE and TM polarization regimes [15]. The results of these calculations are presented in Fig. 7.

Fig. 7. The calculated spectra of spontaneous emission, depending on the sulfur content in the $\text{ZnO}_{1-x}\text{S}_x$ alloy.

In general, the maxima of spectra correspond to the experimental values of the band gap (including its nontrivial depending on the sulfur content) that was determined from the fundamental absorption edge analysis. It is obvious that increasing the sulfur content leads to a shift in the spectrum of spontaneous emission towards low-energy region. For large values of sulfur content in the alloy one can observe the displacement of the emission peak maximum towards the high-energy region. Moreover, due to a decrease of matrix elements in the case of films with a high sulfur content and because of large values of spin-orbit splitting and crystal field splitting energies (depending on the sulfur content) the spontaneous emission spectrum of zinc sulfide is rather broad and asymmetric compared with those of un-doped ZnO films and $\text{ZnO}_{0.9}\text{S}_{0.1}$ and $\text{ZnO}_{0.7}\text{S}_{0.3}$ alloys.

5. Conclusions

The theoretical study of the electronic and optical properties of $\text{ZnO}_{1-x}\text{S}_x$ ternary alloys was performed using the semi-empirical k.p method. Computation of valence-band electronic spectrum of $\text{ZnO}_{1-x}\text{S}_x$ ternary alloys showed increase in anisotropy of valence band dispersion and increment of energy distance between subbands, because of the concentration dependence of the splitting parameters. The nature of the wave functions and matrix elements in the TE and TM

polarization modes for all three valence subbands depending on the quasi-wave vector and sulfur content were studied. The dominant contribution of components of the wave function of the valence subbands to interband matrix elements of C-HH, C-LH and C-CH transitions was revealed. The calculated spectra of spontaneous emission were characterized by initial redshift with increasing sulfur content to 42 at. % followed by blue shift at higher concentrations of sulfur. There was good agreement between theoretical calculations of interband transition energy and spontaneous emission spectra with experimentally determined values of band gap. The obtained results open the way for realization of effective ZnO band gap engineering and provide understanding of the nature of optical processes in $\text{ZnO}_{1-x}\text{S}_x$ semiconductor films.

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List of Tables

Table 1. Some physical parameters of $\text{ZnO}_{1-x}\text{S}_x$ alloys

List of Figure Captions

Fig. 1. Valence band structure of $\text{ZnO}_{1-x}\text{S}_x$ alloys for different values of sulfur content: (a) – $x=0.05$, (b) – $x=0.11$ and (c) – $x=1$. The axis of abscissas is the quasi-wave vector in [100] and [001] directions, respectively.

Fig. 2. The constant energy contour plots of heavy hole (HH) band for $\text{ZnO}_{1-x}\text{S}_x$ alloys with different S content: (a) – $x=0.05$, HH; (b) – $x=0.11$, HH; (c) – $x=1$, HH;

Fig.3. Dependence of the C-HH optical transition energy on the sulfur content in $\text{ZnO}_{1-x}\text{S}_x$ for different types of strain e_{xx} : curve 1 corresponds to compressive strain -2.5 %, curve 2 is related to relaxed case and curve 3 represents tensile strain +2.5 %. Blue circles correspond to our experimental values of band gap energy of $\text{ZnO}_{1-x}\text{S}_x$ films, which were determined from analysis of the absorption spectra.

Fig. 4. Normalized values of the wave functions for different valence subbands of $\text{ZnO}_{0.89}\text{S}_{0.11}$ alloy under tensile strain $e_{xx}=+2.5\%$: (a) heavy hole band, (b) light hole band (c) crystal-field split-off hole band.

Fig. 5. Optical matrix elements for direct interband transitions (conduction band – heavy hole band, light hole band and crystal-field split-off hole band) in $\text{ZnO}_{0.89}\text{S}_{0.11}$ alloy with consideration of the tensile strain ($e_{xx}=+2.5\%$) for (a) TE i (b) TM-polarized modes.

Fig. 6. Dependence of the optical matrix elements for direct interband transition «conduction band – heavy hole band» on the sulfur content with consideration of the tensile strain ($e_{xx}=+2.5\%$) for (a) TE i (b) TM-polarized modes.

Fig. 7. The calculated spectra of spontaneous emission, depending on the sulfur content in the $\text{ZnO}_{1-x}\text{S}_x$ alloy.