

Effect of Exciton-Longitudinal Optical Phonon Interaction on Exciton Binding Energies in ZnS/Mg_xBe_yZn_{1-x-y}S Quantum Wells

C. ONODERA^{a,*} AND M. YOSHIDA^b

^aElectronic Engineering Course, Aomori Prefectural Towada Technical Senior High School
215-1 Shimotai Sanbongi, Towada, Aomori 034-0001, Japan

^bHachinohe National College of Technology, 16-1 Uwanotai, Tamonoki, Hachinohe, Aomori 039-1192, Japan

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We study the effects of exciton-longitudinal optical phonon interaction on the exciton binding energies in ZnS/Mg_xBe_yZn_{1-x-y}S single quantum wells. The heavy- and light-hole exciton binding energies increase to the exciton-longitudinal optical phonon interaction. The increase in the maximum heavy-hole (light-hole) exciton binding energy for $x = 0.74$ is 68.3 meV (55.0 meV). In narrow ZnS/Mg_xBe_yZn_{1-x-y}S single quantum wells SQWs, the heavy- and light-hole exciton binding energies exceed the longitudinal optical phonon energy of ZnS when $x \geq 0.1$.

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1. Introduction

Recently, the epitaxial growth of Be-containing II–VI compounds has been reported [1, 2]. The atomic bonds in Be chalcogenides are more covalent than those in other II–VI compounds [3]. Be chalcogenides are considered to be promising candidates for the fabrication of ultraviolet light-emitting devices [4].

The bandgap energy of Mg_xBe_yZn_{1-x-y}S is larger than that of ZnS. In addition, Mg_xBe_yZn_{1-x-y}S can be lattice-matched to ZnS by the adjusting Mg (x) and Be contents (y) of the former. Hence, Mg_xBe_yZn_{1-x-y}S is an excellent barrier material for ZnS Quantum Wells (QWs).

In addition, the exciton binding energies in ZnS/Mg_xBe_yZn_{1-x-y}S single quantum wells (SQWs) are larger than the room-temperature (RT) thermal energy [5]. If the excitons are stable at RT, exciton transitions can be used for the fabrication of light-emitting devices. For this purpose, a large exciton binding energy is required. In our previous study, [5] we calculated the exciton binding energies in ZnS/Mg_xBe_yZn_{1-x-y}S SQWs; for simplification of the calculations, we ignored the effect of exciton-longitudinal optical (LO) phonon interaction on the electron–hole Coulomb interaction. Senger and Bajaj reported that the exciton binding energies calcu-

lated for QWs increase when the effect of the exciton-LO phonon interaction is considered [6]. They calculated the exciton binding energies for various II–VI semiconductor QWs (Zn-, Cd-, and Mg-containing II–VI semiconductor QWs) by considering the effect of the exciton-LO phonon interaction [6, 7]. The results of their calculations showed that the effect of exciton-LO phonon interaction on electron–hole Coulomb interactions plays an important role in increasing the exciton binding energy in II–VI semiconductor QWs [6, 7].

To investigate the increase in the exciton binding energy caused by the exciton-LO phonon interaction in ZnS/Mg_xBe_yZn_{1-x-y}S SQWs, we theoretically calculate the heavy- and light-hole exciton binding energies by considering the effect of the abovementioned interaction after lattice-matching of ZnS and Mg_xBe_yZn_{1-x-y}S at RT.

2. Calculation methods

Senger and Bajaj have reported a detailed method of calculating the exciton binding energies in QWs by considering the effect of electron-LO phonon interaction [6]. The exciton Hamiltonian [6] is given as:

$$H = -\frac{\hbar^2}{2\mu_{\pm}} \frac{1}{\rho} \frac{\partial}{\partial \rho} \frac{\partial}{\partial \rho} - \frac{\hbar^2}{2m_e^*} \frac{\partial^2}{\partial z_e^2} - \frac{\hbar^2}{2m_{\pm}} \frac{\partial^2}{\partial z_h^2} - \frac{e^2}{\epsilon_s r} + V_e + V_h + V_{PB} + E_{self} + V_{KT}, \quad (1)$$

where μ_{\pm} is the reduced mass of the exciton, ϵ is the dielectric constant, and $r = \sqrt{\rho^2 + (z_e - z_h)^2}$. V_e and V_h

* corresponding author; e-mail: ycd1ngt@yahoo.co.jp

are the conduction band and valence band offsets, respectively. For simplification of our calculations, the effective masses of the electron, heavy-hole, and light-hole are assumed to be position independent; further, these effective masses are equal to those of ZnS.

The effect of exciton-LO phonon interaction is described by the effective potential V_{PB} between an electron and a hole (PB potential) with a self-energy term E_{self} , which was derived from the exciton-LO phonon Hamiltonian by Pollmann and Büttner [8]. The PB potential and the self-energy terms are given as [2]:

$$V_{\text{PB}} = -\frac{e^2}{\epsilon^* r} \left[\frac{C^4}{B^4} - \frac{m_e^* h_e}{\Delta m} \exp\left(-\frac{r A_e}{R_e}\right) + \frac{m_h^* h_h}{\Delta m} \exp\left(-\frac{r A_h}{R_h}\right) - \left(h_\mu + \frac{C^3 r}{2B^3 a_{\text{ex}}} \right) \exp\left(-\frac{r B}{R_\mu}\right) \right], \quad (2)$$

$$E_{\text{self}} = -(\alpha_e g_e + \alpha_h g_h - \alpha_\mu g_\mu) \hbar \omega_{\text{LO}}, \quad (3)$$

where $\epsilon^* = (1/\epsilon_\infty - 1/\epsilon_s)^{-1}$, and ϵ_s and ϵ_∞ are the static and optical dielectric constants for the well, respectively. $\Delta m = m_h^* - m_e^*$ is the mass difference. $M = m_h^* + m_e^*$ is the total mass of the exciton. a_{ex} is the exciton size, and $\hbar \omega_{\text{LO}}$ is the LO phonon energy. Reference [6] provides the details of the method of calculating the a_{ex} , the dimensionless charge-phonon coupling constants (α_e , α_h , and α_μ), the characteristic polaron radii for the electron, hole, and the excitons with a reduced mass (R_e , R_h , and R_μ), and the remaining coefficients (A_e , A_h , B , C , h_e , h_h , h_μ , g_e , g_h , and g_μ). The material parameters appearing in the equation for the PB potential are considered to be those for the well material [6]. Details of the method of calculating the exciton binding energies by considering the effect of the exciton-LO phonon interaction are also provided in Ref. [6].

To account for the effect of dielectric confinement on the electron-hole Coulomb interaction, we use the effective potential term V_{KT} , which was defined by Kumagai and Takagahara (KT), in the image-charge method [9]. The expression for the abovementioned potential term is given in the form of an infinite series. For example, when the electron and holes are in the well, V_{KT} is given as [10]:

$$V_{\text{KT}} = - \sum_{n=-\infty}^{\infty} \frac{\xi^{|n|}}{\epsilon_s \sqrt{\rho^2 + (z_e - (-1)^n z_h + n L_w)^2}}, \quad (4)$$

where $\xi = (\epsilon_s^w - \epsilon_s^b)/(\epsilon_s^w + \epsilon_s^b)$. ϵ_s^w and ϵ_s^b are the static dielectric constants for the well and the barrier, respectively, and L_w is the well width. Reference [9] includes the details of the method of calculating the exciton binding energies by considering the effect of dielectric confinement on the electron-hole Coulomb interaction.

To calculate the ground-state energies of the heavy- and light-hole excitons, we minimize the expectation values of the Hamiltonian calculated using a trial function with two variational parameters [6]. The trial function [6] is given as:

$$\varphi(z_e, z_h, \rho) = \phi_e(z_e) \phi_h(z_h) \times \exp\left(-\alpha (\rho^2 + \beta(z_e - z_h)^2)^{1/2}\right), \quad (5)$$

with

$$\phi_e(z_e) = \begin{cases} B_e \exp(-\lambda_e z_e) & \text{for } |z_e| \leq L_w/2, \\ \cos(k_e z_e) & \text{for } |z_e| > L_w/2, \end{cases} \quad (6)$$

$$\phi_h(z_h) = \begin{cases} B_h \exp(-\lambda_h z_h) & \text{for } |z_h| \leq L_w/2, \\ \cos(k_h z_h) & \text{for } |z_h| > L_w/2, \end{cases} \quad (7)$$

where $\phi_e(z_e)$ and $\phi_h(z_h)$ are the electron and hole wave functions, respectively. $\phi_e(z_e)$ and $\phi_h(z_h)$ are taken to be the lowest subband energy solutions for finite square-well potentials. The electron and hole subband energies are determined by numerically solving the equation for finite-square potential wells. B_e , B_h , λ_e , λ_h , k_e and k_h are obtained by the interface conditions between the well and barrier layers. α and β are the variational parameters.

We determine the heavy- and light-hole masses in the z -direction of the QW and for the x - y plane in terms of the well-known Luttinger parameters [11]. The condition for lattice-matching between ZnS and $\text{Mg}_x\text{Be}_y\text{Zn}_{1-x-y}\text{S}$ is $y = 0.35x$ [5]. This condition is valid until $x = 0.74$, where the Zn content ($1 - x - y$) becomes zero. The valence band offset V_h is calculated as the difference between the energies at the top of the valence bands in ZnS and $\text{Mg}_x\text{Be}_y\text{Zn}_{1-x-y}\text{S}$. The conduction band offset V_e is calculated as the difference between the energies at the bottom of the conduction bands in ZnS and $\text{Mg}_x\text{Be}_y\text{Zn}_{1-x-y}\text{S}$.

3. Results and discussion

The values of the physical parameters used for our calculation are listed in Table I. The parameters corresponding to alloy material are derived by linear interpolation. The effective masses of the heavy- and light-holes in the z -direction are calculated to be $m_{+z} = 0.96m_0$ and $m_{-z} = 0.44m_0$, respectively. The effective masses of the heavy- and light-holes in the x - y plane are calculated to be $m_{//+} = 0.30m_0$ and $m_{// -} = 0.56m_0$, respectively.

We calculate V_e and V_h in ZnS/ $\text{Be}_x\text{Zn}_{1-x}\text{S}$ SQWs when x is in the range 0.1–0.74. By analyzing the calculated data, we obtain the following simple equations for estimating V_e and V_h in ZnS/ $\text{Be}_x\text{Zn}_{1-x}\text{S}$ SQWs:

$$V_e [\text{meV}] = 543.9x^2 + 927.9x (0.1 \leq x \leq 0.74), \quad (8)$$

$$V_h [\text{meV}] = 273.2x (0.1 \leq x \leq 0.74), \quad (9)$$

We calculate the heavy- and light-hole exciton binding energies by ignoring (ignoring the V_{PB} , E_{self} , and V_{KT} in Eq. (1)) and considering (using the whole of Eq. (1)) the effect of the exciton-LO phonon interaction. Figs. 1a and b show the heavy- and light-hole exciton binding energies calculated by considering and ignoring the effect of the exciton-LO phonon interaction in ZnS/ $\text{Mg}_x\text{Be}_y\text{Zn}_{1-x-y}\text{S}$ SQWs, respectively, for $x = 0.14$. For comparison of the theoretical results with the experimen-

tal results, the heavy- and light-hole exciton binding energies measured for ZnS/Mg_xZn_{1-x}S SQWs at $x = 0.19$ [12] are also plotted. The bandgap discontinuity ΔE in ZnS/Mg_xBe_yZn_{1-x-y}S SQWs for $x = 0.14$ is estimated to be 178.8 meV, whereas that in ZnS/Mg_xZn_{1-x}S SQWs for $x = 0.19$ is estimated to be 174.0 meV [7].

The difference in ΔE between ZnS/Mg_xBe_yZn_{1-x-y}S SQWs for $x = 0.14$ and ZnS/Mg_xZn_{1-x}S SQWs for $x = 0.19$ is 4.8 meV; therefore, we assume that the effect of quantum confinement on the excitons in ZnS/Mg_xBe_yZn_{1-x-y}S SQWs at $x = 0.14$ is equivalent to that in ZnS/Mg_xZn_{1-x}S SQWs at $x = 0.19$.

TABLE I

Physical parameters used in the calculation.

	ZnS	BeS	MgS
Bandgap energy E_g [eV]	3.68 [12]	5.66 [13]	4.8 [14]
Bowing parameter for ZnMgS		0.0698 [15]	
Bowing parameter for ZnBeS		0.94 [16]	
Bowing parameter for BeMgS		0 [17]	
Energy at the top of the valence band E_{v0} [eV]	-11.84 [18]	-12.35 [19]	-11.93 [20]
Effective mass of electron effective m_e [m_0]	0.28 [11]		
Luttinger parameter γ_1	2.54 [11]		
Luttinger parameter γ_2	0.75 [11]		
Static dielectric constant ϵ_s [ϵ_0]	8.9 [7]	5.67 [21]	4.506 [22]
Optical dielectric constant ϵ_∞ [ϵ_0]	5.10 [7]		
LO phonon energy [meV]	44.0 [7]		

TABLE II

Increase in the maximum heavy- and light-hole exciton binding energies [meV].

	$x = 0.1$	$x = 0.2$	$x = 0.3$	$x = 0.4$	$x = 0.5$	$x = 0.6$	$x = 0.7$	$x = 0.74$
Heavy-hole	13.9	19.3	25.5	32.3	40.9	50.6	62.7	68.3
Light-hole	9.6	13.5	18.5	24.5	31.3	39.8	50.2	55.0

The changes in the binding energies of the heavy- and light-hole excitons with L_w are essentially similar. Even after considering the effect of the exciton-LO phonon interaction, no notable change is observed in the shape of the curve obtained for the dependence of the heavy- and light-hole exciton binding energies on L_w . The maximum heavy-hole (light-hole) exciton binding energy obtained by considering the effect of the exciton-LO phonon interaction is 58.9 meV (51.1 meV); on the other hand, the maximum heavy-hole (light-hole) exciton binding energy obtained by ignoring the effect of exciton-LO phonon interaction is 42.8 meV (40.8 meV). The maximum heavy- and light-hole exciton binding energies are smaller than those calculated by Senger and Bajaj for ZnS/Mg_xZn_{1-x}S SQWs at $x = 0.19$ [7]. This difference may be attributed to the fact that the heavy-hole (light-hole) mass in the x - y plane ($0.30m_0$ ($0.56m_0$)) used in our calculation is smaller than that used in Senger and Bajaj's calculation ($0.73m_0$) [7]. The increase in the maximum heavy-hole (light-hole) exciton binding energy in ZnS/Mg_xBe_yZn_{1-x-y}S SQWs for $x = 0.14$ estimated to

be 16.1 meV (10.3 meV) by considering the effect of the electron-LO phonon interaction. The estimated increase in the maximum heavy-hole exciton binding energy is equivalent to that calculated by Senger and Bajaj [7] for ZnS/Mg_xZn_{1-x}S SQWs at $x = 0.19$.

The light-hole exciton binding energy measured by Urbaszek et al. for ZnS/Mg_xZn_{1-x}S SQWs for $x = 0.19$ and $L_w = 3.5$ nm is considerably larger than that calculated by considering the effect of the exciton-LO phonon interaction. However, the heavy-hole exciton binding energy measured by Urbaszek et al. for ZnS/Mg_xZn_{1-x}S SQWs at $x = 0.19$ for $L_w = 4$ nm is only slightly larger than that calculated by considering the effect of the exciton-LO phonon interaction. The measured heavy- and light-hole exciton binding energies show a marked decrease when the value of L_w increases from 3 nm to 5 nm. The reason for this anomalous behavior is unknown. The heavy- and light-hole exciton binding energies measured for wide wells are larger than those calculated by ignoring the effect of the exciton-LO phonon interaction, and smaller than those calculated by considering this effect. How-

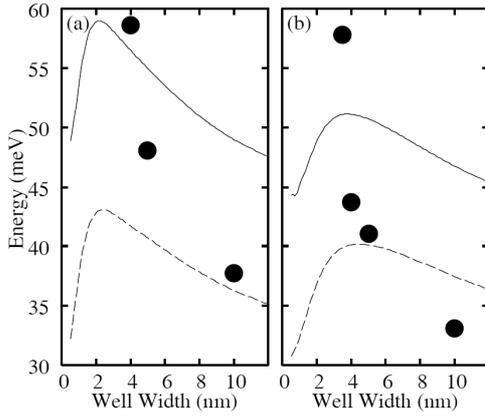


Fig. 1. (a) Heavy-hole and (b) light-hole exciton binding energies calculated by considering and ignoring the effect of exciton-LO phonon interaction in $\text{ZnS}/\text{Mg}_x\text{Be}_y\text{Zn}_{1-x-y}\text{S}$ SQWs as functions of L_w for $x = 0.14$. Solid and dashed curves indicate the exciton binding energies obtained by considering and ignoring the effect of electron-LO phonon interaction, respectively. Closed circles indicate the experimental data reported by Urbaszek et al. [12] for $\text{ZnS}/\text{Mg}_x\text{Zn}_{1-x}\text{S}$ SQWs at $x = 0.19$.

ever, the light-hole exciton binding energy measured for $L_w = 10$ nm is lesser than that calculated by ignoring the effect of exciton-LO phonon interaction. Possible explanations for the large discrepancy between the theory and experimental data are the neglect of effective-masses mismatch between the well and barrier layers, the neglect of off-diagonal terms in the Luttinger–Kohn exciton Hamiltonian, and the neglect of nonparabolicity of the energy bands in a quantum-well situation [24]. Further research is necessary for a fair comparison of the theoretical results with the experimental results.

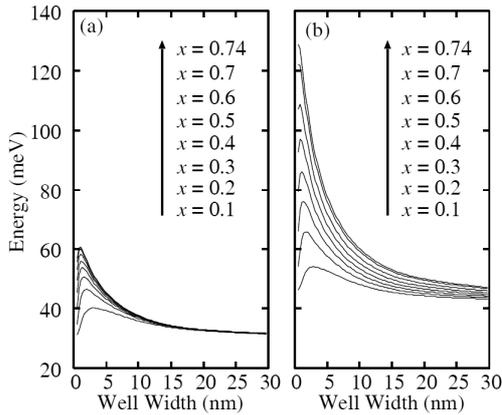


Fig. 2. Heavy-hole exciton binding energies calculated by (a) ignoring and (b) considering the effect of exciton-LO phonon interaction in $\text{ZnS}/\text{Mg}_x\text{Be}_y\text{Zn}_{1-x-y}\text{S}$ SQWs as functions of L_w for $x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7,$ and 0.74 .

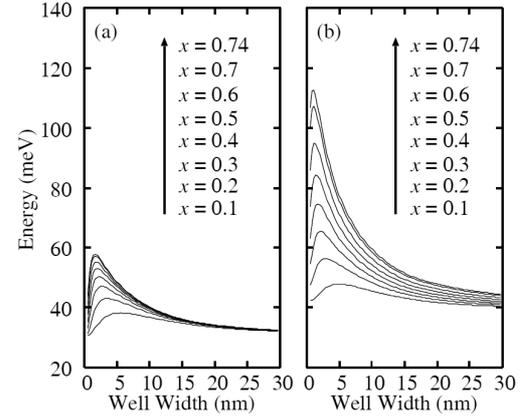


Fig. 3. Light-hole exciton binding energies calculated by (a) ignoring and (b) considering the effect of exciton-LO phonon interaction in $\text{ZnS}/\text{Mg}_x\text{Be}_y\text{Zn}_{1-x-y}\text{S}$ SQWs as functions of L_w for $x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7,$ and 0.74 .

To observe the effect of an increase in ΔE , we calculated the heavy- and light-hole exciton binding energies as functions of L_w by considering and ignoring the effect of the exciton-LO phonon interaction in $\text{ZnS}/\text{Mg}_x\text{Be}_y\text{Zn}_{1-x-y}\text{S}$ SQWs for $x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7,$ and 0.74 . Figures 2a and b show the heavy-hole exciton binding energies calculated by ignoring and considering the effect of the exciton-LO phonon interaction, respectively. Figures 3a and b show the light-hole exciton binding energies calculated by ignoring and considering the effect of the electron-LO phonon interaction, respectively. The heavy-hole (light-hole) exciton binding energy calculated by considering the effect of the exciton-LO phonon interaction increases with x , reaching a value of 129.0 meV (112.8 meV) at $x = 0.74$. The value of L_w at which the exciton binding energy is maximum decreases with an increase in x because both V_e and V_h increase with x . The shape of the curve obtained for the dependence of the heavy- and light-hole exciton binding energies on L_w remains the same, irrespective of whether the effect of the exciton-LO phonon interaction is considered or ignored. Table II shows the increases in the maximum heavy-hole and light-hole exciton binding energies in $\text{ZnS}/\text{Mg}_x\text{Be}_y\text{Zn}_{1-x-y}\text{S}$ SQWs for $x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7,$ and 0.74 . The increase in the maximum heavy-hole (light-hole) exciton binding energy calculated by considering the effect of the exciton-LO phonon interaction increases with x , reaching a value of 68.3 meV (55.0 meV) at $x = 0.74$. In the case of narrow wells, the heavy-hole (light-hole) exciton binding energy calculated by considering the effect of the exciton-LO phonon interaction is larger than the LO phonon energy of ZnS (44 meV) [7].

4. Conclusions

We have calculated the binding energies of heavy- and light-hole excitons in $\text{ZnS}/\text{Mg}_x\text{Be}_y\text{Zn}_{1-x-y}\text{S}$ SQWs by

considering the effect of exciton-LO phonon interaction. The increase in the maximum binding energy of the heavy-hole (light-hole) exciton for $x = 0.74$ is 68.3 meV (55.0 meV). The dependence of the heavy- and light-hole exciton binding energies on L_w is qualitatively the same, irrespective of whether the effect of the exciton-LO phonon interaction is considered or ignored.

The heavy- and light-hole exciton binding energies in narrow ZnS/Mg_xBe_yZn_{1-x-y}S SQWs exceed the LO phonon energy of ZnS when $x \geq 0.1$. Therefore, ZnS/Mg_xBe_yZn_{1-x-y}S SQWs are potential candidates for ultraviolet applications based on RT exciton emission.

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