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EFFECTS OF EXCITON–LONGITUDINAL OPTICAL PHONON INTERACTION AND QUANTUM CONFINEMENT ON EXITON BINDING ENERGIES IN $ZnS_{1-x}Se_x/ZnS$ SINGLE QUANTUM WELLS

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We study the effects of the exciton–longitudinal optical (LO) phonon interaction and quantum confinement on the exciton binding energies in $ZnS_{1-x}Se_x/ZnS$ single quantum wells (SQWs) for an Se alloy content (x) range of 0.1–0.3. In narrow $ZnS_{1-x}Se_x/ZnS$ SQWs, the heavy-hole (light-hole) exciton binding energy calculated by taking into account the exciton–LO phonon interaction for values of x in the range of 0.2–0.3 (0.3) exceeds the LO phonon energy of $ZnS_{1-x}Se_x$. The difference between the maximum heavy-hole (light-hole) exciton binding energy for $x = 0.3$ and the LO phonon energy is less than 1.5 meV (1.0 meV). This SQW shows a weak quantum confinement due to a small conduction-band offset.

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I. INTRODUCTION

$ZnS_{1-x}Se_x/ZnS$ quantum wells (QWs) have been experimentally studied from the viewpoint of their applications to the fabrication of UV optoelectronic devices [1, 2]. The bulk exciton binding energy of ZnS (36 meV) is greater than the room-temperature (RT) thermal energy (approximately 25 meV) [3]. If the excitons are stable at RT, exciton transitions can be used to generate light in light-emitting devices. For this purpose, a large exciton binding energy is required.

Exciton stability depends on their interactions with longitudinal optical (LO) phonons. When excitons exist at RT, they have greater energy than LO phonons. In the case of ZnS, the bulk exciton binding energy is lower than the LO-phonon energy (44 meV) [4]. Because the exciton binding energy in QWs is usually enhanced by a factor of 1.5–2.0 owing to quantum confinement, the exciton binding energy in $ZnS_{1-x}Se_x/ZnS$ QWs is greater than the LO phonon energy. As a result, the exciton stability in the $ZnS_{1-x}Se_x/ZnS$ QWs is greater than that in bulk ZnS.

Zheng and Matsuura presented a theoretical method for investigating the properties of exciton optical phonon interaction in polar semiconductor QWs in detail [5]. They calculated the exciton binding energies in polar semiconductor QWs by taking into account the interaction of the exciton with confined LO phonons, interface phonons, and half-space phonons [6]. They extended their work to excitons in QWs composed of alloy material and studied the properties of the exciton–LO phonon interactions in II-VI semiconductor QWs (ZnCdSe/ZnSe QWs, ZnCdS/ZnS QWs, ZnCdTe/ZnTe QWs, and ZnSSe/ZnS QWs) [7].

Recently, Senger and Bajaj presented a simple theoretical method for calculating the exciton binding energies by taking into account the exciton–LO phonon interaction in polar semiconductor QWs [8]. In their study, the effect of the exciton–LO phonon interaction is described by an effective potential between an electron and a hole as derived by Pollmann and Büttner using the exciton–LO phonon Hamiltonian [8]. Their method has the advantage of being considerably simpler than the more rigid approach of Zheng and Matsuura. They calculated the exciton binding energies for various II-VI semiconductor QWs (ZnSe/MgS QWs, ZnSe/MgZnSe QWs, ZnS/MgZnS QWs, CdZnSe/ZnSe QWs, and ZnO/MgZnO QWs) by taking into account the effect of the exciton–LO phonon interaction [4, 8]. The results of their calculations showed that the effect of the exciton–LO phonon interaction on electron-hole Coulomb interactions plays an important role in increasing the exciton binding energy. Moreover, we calculated increased in exciton binding energies for CdZnS/ZnS QWs by taking into account the effect of the exciton–LO phonon interaction [9].

To investigate the increase in the exciton binding energy caused by the exciton–LO phonon interaction in $ZnS_{1-x}Se_x/ZnS$ QWs, we theoretically calculate the heavy- and light-hole exciton binding energies using Senger and Bajaj's approach. Moreover, to observe the effect of quantum confinement on exciton binding energies in QWs under small conduction-band offset conditions, we compare the exciton binding energies in $ZnS_{1-x}Se_x/ZnS$ QWs with and those in $Cd_xZn_{1-x}S/ZnS$ QWs.

II. CALCULATION METHODS

Senger and Bajaj have reported a detailed method for calculating the exciton binding energies in QWs, wherein the effect of electron–LO phonon interaction was taken into account [8]. The exciton Hamiltonian [8] is given as

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

where $\mu_{\pm}$ is the reduced mass of the exciton. The value of $\mu_{\pm}$ [7] is given as

$$\frac{1}{\mu_{\pm}} = \frac{1}{m_e^*} + \frac{1}{m_0}\,(\gamma_1 \pm \gamma_2), \tag{2}$$

where m_0 is the free-electron mass and m_e^*, the electron effective mass. The quantity $m_{\pm}$ is the hole effective mass [10] and is given as

$$\frac{1}{m_{\pm}} = \frac{1}{m_0}\,(\gamma_1 \mp 2\gamma_2). \tag{3}$$

To simplify our calculations, the effective masses of the electron, heavy-hole, and light-hole are assumed to be position independent; further, their effective masses are assumed to be equal to those of the electrons, heavy-holes, and light-holes in $ZnS_{1-x}Se_x$. $V_e(z_e)$ and $V_h(z_h)$ are given as [10]

$$V_e(z_e) = \begin{cases} 0\ (|z_e| \le L_w/2) \\ \\ V_e\ (|z_e| > L_w/2) \end{cases} \tag{4}$$

and

$$V_h(z_h) = \begin{cases} 0\ (|z_h| \le L_w/2) \\ \\ V_{hh} \text{ or } V_{lh}\ (|z_h| > L_w/2) \end{cases}. \tag{5}$$

Here, V_e, V_{hh}, and V_{lh} are the conduction, heavy-hole and light-hole band offsets, respectively, and L_w is the well width. We define the origin of the coordinate system as the center of the well layer [7].

Band offsets are calculated using the "model-solid approach". [11] The heavy-hole band offset V_{hh} (light-hole band offset V_{lh}) is calculated as the difference between the energies at the top of the heavy-hole (light-hole) bands in $ZnS_{1-x}Se_x$ and ZnS, and the conduction band offset V_e is calculated as the difference between the energies at the bottom of the conduction bands in $ZnS_{1-x}Se_x$ and ZnS.

The energy at the bottom of the conduction band in unstrained $ZnS_{1-x}Se_x$ is calculated by linear interpolation without using a bowing parameter. On the other hand, the energy at the top of the valence band in unstrained $ZnS_{1-x}Se_x$ is calculated by linear interpolation using a bowing parameter. In $ZnS_{1-x}Se_x$, the anions (S and Se) have a strong influence on the valence band, whereas Zn cations determine the energy at the bottom of the conduction band. Therefore, the effect of bandgap bowing is taken into account when calculating the energy at the top of the valence band.

The energy at the top of the heavy-hole (light-hole) band in strained $ZnS_{1-x}Se_x$ is defined as the sum of the energy at the top of the valence band in unstrained $ZnS_{1-x}Se_x$ and the energy shift of the heavy-hole (light-hole) band in strained $ZnS_{1-x}Se_x$. On the other hand, the energy at the bottom of the conduction band in strained $ZnS_{1-x}Se_x$ is defined as the sum of the energy at the bottom of the conduction band in unstrained $ZnS_{1-x}Se_x$ and the energy shift of the conduction band in strained $ZnS_{1-x}Se_x$.

The following relations are used to calculate the energy shifts of the strained conduction (dE_c), heavy-hole (dE_{hh}), and light-hole (dE_{lh}) bands: [12]

$$\varepsilon = \frac{a_b - a_w}{a_w}, \tag{6}$$

$$\varepsilon_{zz} = -\frac{2C_{12}}{C_{11}}\varepsilon, \tag{7}$$

$$E_S = -b(\varepsilon_{zz} - \varepsilon), \tag{8}$$

$$E_H = a_v(2\varepsilon + \varepsilon_{zz}), \tag{9}$$

$$dE_c = a_c(2\varepsilon + \varepsilon_{zz}), \tag{10}$$

$$dE_{hh} = E_H + E_S, \tag{11}$$

$$dE_{lh} = E_H - \frac{\Delta_{so}}{2}(1+x) + \frac{\Delta_{so}}{2}(1 - 2x + 9x^2)^{1/2}, \tag{12}$$

where a_w and a_b are the lattice constants of the $ZnS_{1-x}Se_x$ wells and ZnS barriers, respectively. ε is the in-plane strain ($x-y$ plane); ε_{zz}, the perpendicular strain (z direction); and C_{ij}, is the elastic stiffness constant. $x = E_S/\Delta_{so}$, where Δ_{so} is the spin-orbit splitting energy. a_v and a_c are the hydrostatic deformation potentials in the valence and conduction bands, respectively, and b is the shear deformation potential.

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 [13]. The PB potential and the self-energy term are respectively given as [8]

$$V_{PB} = -\frac{e^2}{\epsilon_s r} - \frac{e^2}{\epsilon^* r}\left[\frac{C^4}{B^4} - \frac{m_e^* h_e}{\Delta m}\, e^{-\frac{-rA_e}{R_e}} + \frac{m_h^* h_h}{\Delta m} e^{-\frac{rA_h}{R_h}} - \left(h_\mu + \frac{C^3 r}{2B^3 a_{ex}}\right) e^{-\frac{rB}{R_\mu}}\right], \tag{13}$$

$$E_{self} = -(\alpha_e g_e + \alpha_h g_h - \alpha_\mu g_\mu)\hbar\omega_{LO}, \tag{14}$$

where $r = \sqrt{\rho^2 + (z_e - z_h)^2}$, $\epsilon^* = (1/\epsilon_\infty - 1/\epsilon_s)^{-1}$, and ϵ_s and ϵ_∞ are the static and optical dielectric constants, respectively, for the well. $\Delta m = m_h^* - m_e^*$ is the mass difference. $M = m_h^* + m_e^*$ is the total mass of the exciton. a_{ex} is the exciton size and $\hbar\omega_{LO}$, is the LO phonon energy. The material parameters in the expression for calculating the PB potential are those of the $ZnS_{1-x}Se_x$ well [8]. The hole mass is taken as $m_h^* = 1/\gamma_1$. For a more realistic understanding of the exciton binding energy calculated by taking into account the effect of the PB potential, an insight into the effect of independent hole masses on the PB potential is necessary. However, it is difficult to gain this insight. To simplify our calculations, we use the weighted average of the hole masses to determine the PB potential. Reference 8 provides details of a method for calculating a_{ex}; dimensionless charge-phonon coupling constants (α_e, α_h, and α_μ); characteristic polaron radii for the electron, hole, and excitons with reduced masses (R_e, R_h, and R_μ, respectively); and miscellaneous coefficients (A_e, A_h, B, C, h_e, h_h, h_μ, g_e,

g_h, and g_μ). The details of the method for calculating the exciton binding energies by taking into account the effect of the exciton–LO phonon interaction are also provided in ref. [8].

To account for the effect of dielectric confinement on the electron-hole Coulomb interaction, Senger and Bajaj used the effective potential term, V_{KT}, as defined by Kumagai and Takagahara (KT) in the image-charge method [14]. In this study, we ignore V_{KT} because the difference between the static dielectric constants of ZnS (8.9) and ZnSe (8.8) is small [4].

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 [8]. The trial function [8] is expressed as

$$\varphi(z_e, z_h, \rho) = \phi_e(z_e)\phi_h(z_h) \times \exp\left\{-\alpha\left[\rho^2 + \beta\,(z_e - z_h)^2\right]^{1/2}\right\}, \quad (15)$$

with

$$\phi_e(z_e) = \begin{cases} B_e \exp(-\lambda_e z_e)\ (|z_e| \le L_w/2) \\ \cos(k_e z_e)\ (|z_e| > L_w/2) \end{cases}, \quad (16)$$

$$\phi_h(z_h) = \begin{cases} B_h \exp(-\lambda_h z_h)\ (|z_h| \le L_w/2) \\ \cos(k_h z_h)\ (|z_h| > L_w/2) \end{cases}, \quad (17)$$

where $\phi_e(z_e)$ and $\phi_h(z_h)$ are the wave functions of the electron and the hole, respectively. $\phi_e(z_e)$ and $\phi_h(z_h)$ are considered as the lowest subband-energy solutions for finite square-well potentials [7]. 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 using the interface conditions between the well and the barrier layers. α and β are the variational parameters.

The heavy-hole exciton transition energy is determined by subtracting the heavy-hole exciton binding energy from the effective heavy-hole bandgap energy; the effective heavy-hole bandgap energy is determined by the summing of the minimum conduction subband energy, minimum heavy-hole subband energy, and heavy-hole bandgap energy of the well layer. The light-hole exciton transition energy is calculated in a similar manner.

Here, we assume that the barrier width in ZnS is considerably larger than the critical thickness of the barrier layer; therefore, the lattice constant of the ZnS barrier approaches the bulk value. We also assume that the lattice constant of $ZnS_{1-x}Se_x$ is equal to that of ZnS when the $ZnS_{1-x}Se_x$ well is sandwiched between two ZnS barriers. Under these conditions, we calculate the critical thickness of the $ZnS_{1-x}Se_x$ well in ZnS by using Matthews and Blakeslee's (MB's) mechanical equilibrium model [15]. The critical thickness h_c is given as

$$h_c = \frac{b(1-\nu\cos^2\alpha)}{2\pi f(1+\nu)\cos\lambda}\left(\ln\frac{h_c}{b} + 1\right), \quad (18)$$

where ν is the Poisson ratio; f, the lattice mismatch between $ZnS_{1-x}Se_x$ and ZnS; and b, the Burgers vector. Here, we assume that $b = \sqrt{2}a$, $\cos\alpha = 0$, and $\cos\lambda = 1$ where an edge dislocation is assumed for the critical thickness calculation; a is the lattice constant of the $ZnS_{1-x}Se_x$ well.

III. RESULTS AND DISCUSSION

A. Exciton binding energies for $ZnS_{1-x}Se_x$/ZnS SQWs

The physical parameters used for our calculations are listed in Table I. The parameters corresponding to the alloy material were derived by linear interpolation.

	ZnSe	ZnS
Lattice constant, a (nm)	0.56681 [16]	0.54093 [17]
Bandgap energy at 4.2 K, E_g (eV)	2.82 [18]	3.84 [17]
Energy at the top of the valence band, E_{v0} (eV)	–10.58 [16]	–11.40 [16]
Hydrostatic deformation potential in conduction band, a_c (eV)	–4.17 [16]	–2.78 [17]
Hydrostatic deformation potential in valence band, a_v (eV)	1.65 [16]	1.2 [17]
Shear deformation potential, b (eV)	–1.2 [16]	–0.7 [17]
Elastic stiffness constant, C_{11} (GPa)	81.0 [16]	106.7 [17]
Elastic stiffness constant, C_{12} (GPa)	48.8 [16]	66.6 [17]
Spin-orbit splitting energy, Δ_{so} (eV)	0.45 [16]	0.072 [17]
Effective mass of the electron, m_e (m_0)	0.14 [19]	0.28 [19]
Luttinger parameter, γ_1	2.45 [8]	2.54 [19]
Luttinger parameter, γ_2	0.61 [8]	0.75 [19]
Static dielectric constant, ϵ_s (ϵ_0)	8.8 [4]	8.9 [4]
Optical dielectric constant, ϵ_∞ (ϵ_0)	5.4 [18]	5.1 [18]
LO phonon energy, $\hbar\omega_{LO}$ (meV)	31 [20]	44 [4]
Bowing parameter for $ZnS_{1-x}Se_x$ (eV)	0.43 [16]	

Table I. Physical parameters used in calculations.

The critical thickness h_c of the $ZnS_{1-x}Se_x$ well for $x = 0.1$, 0.2, and 0.3 on ZnS are 540.2, 104.5, and 38.8 nm. respectively. h_c of the $ZnS_{1-x}Se_x$ well decreases with x because the difference between the lattice constants of $ZnS_{1-x}Se_x$ and ZnS increases with x. For calculating the heavy- and light-hole exciton binding energies, the thickness of the $ZnS_{1-x}Se_x$ wells for values of x in the range of 0.1–0.3 is taken as 40 nm.

The values of V_e in the $ZnS_{1-x}Se_x$/ZnS SQWs for $x = 0.1$, 0.2, and 0.3 are 9.5, 18.0, and 25.5 meV, respectively; the corresponding values of V_{hh} are 124.2, 240.4, and 348.7 meV, respectively; and the corresponding values of V_{lh} are 111.3, 213.6, and 306.9 meV, respectively. The values of V_e, V_{hh}, and V_{lh} are listed in Table II.

QWs	x	V_e	V_{hh}	V_{lh}	V_e/V_{hh}	V_e/V_{lh}
$ZnS_{1-x}Se_x$/ZnS	0.1	9.5	124.2	111.3	29/71	21/79
	0.2	18.0	240.4	213.6	30/70	23/77
	0.3	25.5	348.7	306.9	32/68	23/77
$Cd_xZn_{1-x}S$/ZnS	0.1	122.8	20.6	1.5	86/14	99/1
	0.2	239.4	40.4	11.0	86/14	96/4
	0.3	349.7	59.4	24.8	86/14	93/7

Table II. Values of V_e, V_{hh}, and V_{lh} and values of V_e/V_{hh} and V_e/V_{lh} in $ZnS_{1-x}Se_x$/ZnS and $Cd_xZn_{1-x}S$/ZnS SQWs.

V_e, V_{hh}, and V_{lh} increase with x because the difference between the bandgaps of $ZnS_{1-x}Se_x$ and ZnS increases with x. V_{hh} is greater than V_{lh} because of the induced compressive strain. In this system, the lattice constant of the $ZnS_{1-x}Se_x$ wells is greater than that of the ZnS barriers. As a result, compressive strain is induced in the $ZnS_{1-x}Se_x$ wells.

We calculate the heavy- and light-hole exciton binding energies both by ignoring [ignoring the second term of V_{PB}, E_{self}, and V_{KT} in eq. (1)] and by considering [using V_{PB} and E_{self} in eq. (1)] the effect of the exciton–LO phonon interaction. Figure 1(a) and (b) show the heavy- and light-hole exciton binding energies calculated both by considering and by ignoring the effect of the exciton–LO phonon interaction in $ZnS_{1-x}Se_x$/ZnS SQWs, respectively, for $x = 0.1$, 0.2, and 0.3.

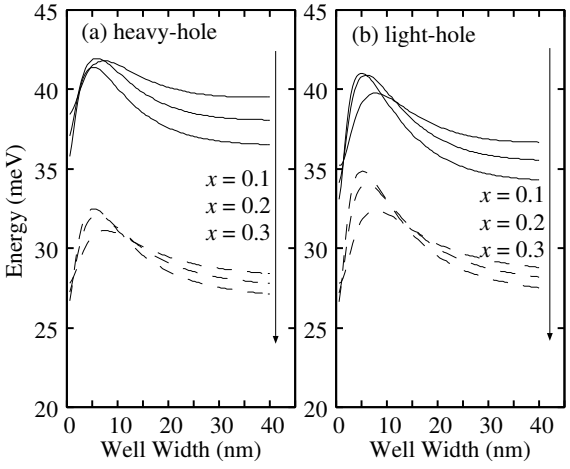

Fig. 1. (a) Heavy-hole and (b) light-hole exciton binding energies calculated by ignoring (broken lines) and by considering (solid lines) the effect of exciton–LO phonon interaction in $ZnS_{1-x}Se_x$/ZnS SQWs as a function of L_w for $x = 0.1$, 0.2, and 0.3.

A comparison of the results of our calculations with the experimental results is indispensable for checking the reliability of our calculations, but the experimental results for the heavy- and light-hole exciton binding energies are not available at present. However, the exciton binding energy calculated using the PB potential of ZnS/ZnMgS QWs shows relatively good agreement with the exciton binding energy measured for narrow ZnS/ZnMgS QWs [4].

The heavy- and light-hole exciton binding energies increase with a decrease in L_w as expected from the decreasing dimension of the exciton wavefunction from a three-dimensional (3D) function to a two-dimensional (2D) function owing to quantum confinement. The shape of the curve illustrating the dependence of the heavy- and light-hole exciton binding energies on L_w is consistent with that reported by Greene *et al.* [7] The changes in the binding energies of the heavy- and light-hole excitons with L_w are essentially similar.

The heavy-hole (light-hole) exciton binding energies calculated by ignoring the effect of the exciton–LO phonon interaction at $L_w = 40$ nm for $x = 0.1$, 0.2, and 0.3 are 28.4, 27.8, and 27.1 meV (28.8, 28.3, and 27.5 meV), respectively. The corresponding bulk heavy-hole (light-hole) exciton binding energies are 24.6, 24.1, and 23.6 meV (31.2, 30.2, and 29.3 meV), respectively, where the heavy-hole (light-hole) exciton Bohr radii are 3.29, 3.36, and 3.44 nm (2.60, 2.68, and 2.77 nm), respectively. Even if L_w is larger than 11 times the exciton Bohr radii, heavy-hole exciton binding energies increase. In contrast, the light-hole exciton binding energies are lower than the bulk exciton binding energies even when L_w is larger than 14 times the exciton Bohr radii. The effect of quantum confinement on the heavy-hole exciton is greater than that on the light-hole exciton because the exciton Bohr radius of the heavy-hole exciton is larger than that of the light-hole exciton.

The maximum heavy-hole (light-hole) exciton binding energies calculated by ignoring the effect of the exciton–LO phonon interaction for $x = 0.1$, 0.2, and 0.3 are 31.1, 32.1, and 32.4 meV (32.4, 34.0, and 34.8 meV), respectively; the corresponding LO phonon energies are 42.7, 41.4, and 40.1 meV, respectively. The maximum heavy-

hole (light-hole) exciton binding energy calculated by ignoring the effect of the exciton–LO phonon interaction in QWs is enhanced by a factor of 1.26–1.37 (1.04–1.19); however, the maximum heavy-hole (light-hole) exciton binding energies calculated by ignoring the effect of the exciton–LO phonon interaction are lower than the LO-phonon energies. Despite the fact that the effect of quantum confinement on the heavy-hole exciton is greater than that on the light-hole exciton, the maximum light-hole exciton binding energies are greater than the maximum heavy-hole exciton binding energies. This can be attributed to the fact that the bulk light-hole exciton binding energies are greater than the bulk heavy-hole exciton binding energies.

It is clear from Figure 1(a) [(b)] that the values of heavy-hole (light-hole) exciton binding energy calculated by considering the effect of the exciton–LO phonon interaction are considerably greater than those calculated by ignoring the effect of the exciton–LO phonon interaction. The maximum heavy-hole (light-hole) exciton binding energies calculated by considering the effect of the exciton–LO phonon interaction for $x = 0.1$, 0.2, and 0.3 are 41.8, 41.9, and 41.4 meV (39.8, 40.9, and 41.0 meV), respectively. The maximum heavy-hole (light-hole) exciton binding energy calculated by considering the effect of the exciton–LO phonon interaction in QWs is enhanced by a factor of 1.70–1.75 (1.27–1.40). The factors of the increase in heavy- and light-hole exciton binding energies calculated by both ignoring and considering the effect of the exciton–LO phonon interaction in $ZnS_{1-x}Se_x/ZnS$ SQWs for $x = 0.1$, 0.2, and 0.3 are listed in Table III. The factors of the increase in heavy- and light-hole exciton binding energies calculated by considering the effect of the exciton–LO phonon interaction are greater than those calculated by ignoring the effect of the exciton–LO phonon interaction. The maximum heavy-hole exciton binding energy calculated by considering the effect of the exciton–LO phonon interaction for $x = 0.3$ is lower than that for $x = 0.2$ because the bulk exciton binding energy of $ZnS_{1-x}Se_x$ for $x = 0.3$ is lower than that for $x = 0.2$. The maximum heavy-hole exciton binding energies calculated by considering the effect of the exciton–LO phonon interaction for $x = 0.2$ and 0.3 are greater than the LO-phonon energies; the maximum light-hole exciton binding energy calculated by considering the effect of the exciton–LO phonon interaction for $x = 0.3$ is greater than the LO-phonon energy. The shape of the curve illustrating 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.

QWs	hole	without LO phonon interaction			with LO phonon interaction		
		$x = 0.1$	$x = 0.2$	$x = 0.3$	$x = 0.1$	$x = 0.2$	$x = 0.3$
$ZnS_{1-x}Se_x/ZnS$	heavy	1.26	1.33	1.37	1.70	1.74	1.75
	light	1.04	1.12	1.19	1.27	1.35	1.40
$Cd_xZn_{1-x}S/ZnS$	heavy	1.59	1.82	1.97	1.95	2.18	2.34
	light	1.01	1.16	1.31	1.18	1.33	1.47

Table III. Factors of increase in heavy- and light-hole exciton binding energies for $ZnS_{1-x}Se_x/ZnS$ SQWs and $Cd_xZn_{1-x}S/ZnS$ SQWs.

The increases in the maximum heavy- and light-hole exciton binding energies in $ZnS_{1-x}Se_x/ZnS$ SQWs for $x = 0.1$, 0.2, and 0.3 are summarized in Table IV. The maximum heavy-hole (light-hole) exciton binding energy calculated by considering the effect of the exciton–LO phonon interaction decreases with x.

QWs	hole	$x = 0.1$	$x = 0.2$	$x = 0.3$
$ZnS_{1-x}Se_x/ZnS$	heavy	10.7	9.8	9.0
	light	7.4	6.9	6.2
$Cd_xZn_{1-x}S/ZnS$	heavy	8.8	8.9	8.8
	light	5.3	5.0	4.7

Table IV. Increases in maximum heavy- and light-hole exciton binding energies (meV) for $ZnS_{1-x}Se_x/ZnS$ SQWs and $Cd_xZn_{1-x}S/ZnS$ SQWs.

To observe the shape of the curve illustrating the dependence of the heavy- and light-hole exciton binding energies on L_w for narrow wells ($L_w \leq 10$ nm), the heavy-hole exciton binding energies calculated by considering the effect of the exciton–LO phonon interaction for $x = 0.2$ and 0.3 are plotted as shown in Fig. 2 (a); the light-hole exciton binding energy calculated by considering the effect of the exciton–LO phonon interaction for $x = 0.3$ is plotted as shown in Fig. 2 (b). The heavy-hole exciton binding energies calculated by considering the effect of the exciton–LO phonon interaction for $x = 0.2$ and 0.3 are greater than the LO phonon energy of

$ZnS_{1-x}Se_x$ wells when the values of L_w are in the ranges of 3.9–9.0 and 2.7–9.9 nm, respectively. The light-hole exciton binding energy calculated by considering the effect of the exciton–LO phonon interaction in $ZnS_{1-x}Se_x$/ZnS SQWs for $x = 0.3$ is greater than the LO phonon energy of $ZnS_{1-x}Se_x$ well when the value of L_w is in the range of 3.2–8.1 nm. When we consider the effect of the exciton–LO phonon interaction for these ranges of L_w values, the heavy- and light-hole exciton binding energies are comparable to the LO phonon energies of $ZnS_{1-x}Se_x$ wells. However, the difference between the maximum heavy-hole (light-hole) exciton binding energy for $x = 0.3$ and the LO phonon energy is less than 1.5 meV (1.0 meV).

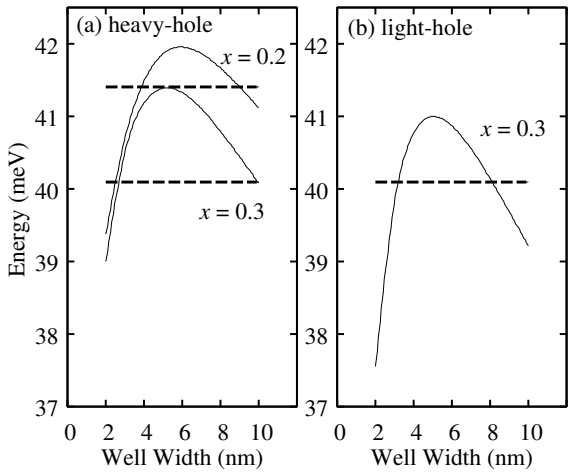

Fig. 2. (a) Heavy-hole ($x = 0.2$ and 0.3) and (b) light-hole ($x = 0.3$) exciton binding energies calculated by considering (solid lines) the effect of exciton–LO phonon interaction in $ZnS_{1-x}Se_x$/ZnS SQWs as a function of L_w. The broken lines indicate the LO-phonon energies.

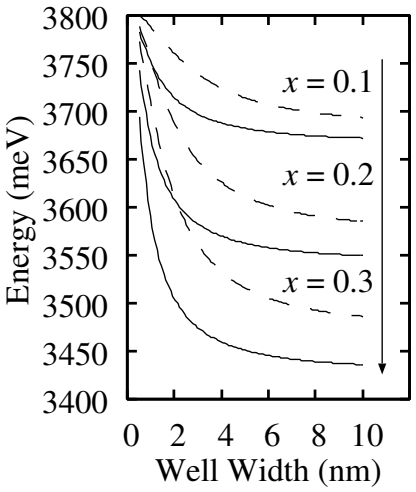

Fig. 3. Heavy-hole (solid lines) and light-hole (broken lines) transition energies calculated by considering the effect of exciton–LO phonon interaction energy in $ZnS_{1-x}Se_x$/ZnS SQWs as a function of L_w for $x = 0.1$, 0.2, and 0.3.

Dissociation of excitons should be prevented in systems where the difference between the exciton binding energies of the 1s and 2s states is larger than the LO phonon energy [12]. For a more realistic understanding of exciton stability, determining the excited exciton states is necessary. However, doing so is not an easy task. To simplify our calculation, we discuss only the binding energy of the ground exciton state. Further research is necessary to obtain more accurate exciton states by theoretical calculation. Therefore, our result dose not completely describe the whole story of the exciton stability.

B. Exciton transition energies for $ZnS_{1-x}Se_x$/ZnS SQWs

We calculated the heavy- and light-hole exciton transition energies by considering the effect of the exciton–LO phonon energy in $ZnS_{1-x}Se_x$/ZnS SQWs as functions of L_w for $x = 0.1$, 0.2, and 0.3. Figures 3 shows the dependence of the heavy-hole (solid lines) and light-hole (broken lines) exciton transition energies on L_w. The transition energies of the heavy- and light-hole excitons decrease with an increase in L_w because the electron, heavy-hole, and light-hole subband energies decrease with an increase in L_w. The heavy-hole exciton transition energy is lower than the light-hole exciton transition energy because of the induced compressive strain. The changes in the transition energies of the heavy- and light-hole excitons with L_w are essentially similar.

	Experiment [2]	Heavy-hole	Light-hole
$x = 0.32$	3518	3417	3474
$x = 0.38$	3471	3355	3421

Table V. Experimental and theoretically calculated energies of the exciton transition (meV) (heavy- and light-hole). The experimental values were measured using photoluminescence at 4.2 K [2].

For comparison, we calculated the heavy- and light-hole exciton transition energies in $ZnS_{1-x}Se_x$/ZnS SQWs for $x = 0.32$ and 0.38 at $L_w = 8$ nm. The results are listed in Table V.

The transition energies measured by photoluminescence in $ZnS_{1-x}Se_x$/ZnS SQWs for $x = 0.32$ and 0.38 at $L_w = 8$ nm are 3518 and 3471 meV, respectively [2]; the corresponding heavy-hole (light-hole) exciton transition energies calculated by considering the effect of the exciton–LO phonon energy are 3417 and 3355 meV (3474 and 3421 meV), respectively. The transition energies of the heavy- and light-hole excitons decrease with an increase in x because the bandgap energy of $ZnS_{1-x}Se_x$ decreases with an increase in x. The heavy-hole (light-hole) exciton transition energies measured experimentally are considerably greater than those calculated theoretically by us. The discrepancy between the theoretical and the experimental data could be a result of a change in the alloy content. Further research is necessary for a fair comparison of the theoretical results with the experimental results.

C. Effect of quantum confinement on exciton binding energies

To observe the effect of quantum confinement on exciton binding energies, we calculate the heavy- and light-hole exciton binding energies both by considering and by ignoring the effect of the exciton–LO phonon interaction in $Cd_xZn_{1-x}S/ZnS$ SQWs; the image-charge effect is ignored for comparison with the exciton binding energies in $ZnS_{1-x}Se_x/ZnS$ SQWs. The value of V_e in $Cd_xZn_{1-x}S/ZnS$ SQWs is greater than that in $ZnS_{1-x}Se_x/ZnS$ SQWs [9]. Therefore, electrons are strongly confined in well layers. We compare the calculated exciton binding energies in $ZnS_{1-x}Se_x/ZnS$ SQWs with those in $Cd_xZn_{1-x}S/ZnS$ SQWs. The physical parameters used in the calculation of exciton binding energies in $Cd_xZn_{1-x}S/ZnS$ SQWs are listed in ref. [9].

The values of V_e in the $Cd_xZn_{1-x}S/ZnS$ SQWs for x = 0.1, 0.2, and 0.3 are 122.8, 239.4, and 349.7 meV, respectively; [9] the corresponding values of V_{hh} are 20.6, 40.4, and 59.4 meV, respectively; [9] the corresponding values of V_{lh} are 1.5, 11.0, and 24.8 meV, respectively [9]. The values of V_e, V_{hh}, and V_{lh} in $Cd_xZn_{1-x}S/ZnS$ SQWs for x = 0.1, 0.2, and 0.3 are listed in Table II.

The bulk heavy-hole (light-hole) exciton binding energies in $Cd_xZn_{1-x}S/ZnS$ SQWs for x = 0.1, 0.2, and 0.3 are 24.7, 24.3, and 23.8 meV (31.0, 30.0, and 29.0 meV), respectively, where the corresponding heavy-hole (light-hole) exciton Bohr radii are 3.28, 3.32, and 3.37 nm (2.61, 2.69, and 2.78 nm), respectively. The maximum heavy-hole (light-hole) exciton binding energies calculated by ignoring the effect of the exciton–LO phonon interaction in $Cd_xZn_{1-x}S/ZnS$ SQWs for x = 0.1, 0.2, and 0.3 are 39.3, 44.1, and 47.0 meV (31.3, 34.9, and 37.9 meV), respectively; the corresponding LO phonon energies are 43.3, 42.6, and 41.9 meV, respectively. The maximum heavy-hole (light-hole) exciton binding energies calculated by ignoring the effect of the exciton–LO phonon interaction in $Cd_xZn_{1-x}S/ZnS$ SQWs are enhanced by a factor of 1.59–1.97 (1.01–1.31). The factors of increase in heavy- and light-hole exciton binding energies for $Cd_xZn_{1-x}S/ZnS$ SQWs are greater than those for $ZnS_{1-x}Se_x/ZnS$ SQWs. This is because the $Cd_xZn_{1-x}S/ZnS$ SQWs corresponds to strongly confined QWs, which is ascribed to the large V_e. Total band offset for heavy-hole (light-hole) exciton $V_e + V_{hh}$ ($V_e + V_{lh}$) in $Cd_xZn_{1-x}S/ZnS$ SQWs for x = 0.1, 0.2, and 0.3 are 143.4, 279.8, and 409.1 meV (124.3, 250.4, and 374.5 meV), respectively; the corresponding values in $ZnS_{1-x}Se_x/ZnS$ SQWs are 133.7, 258.4, and 374.2 meV (120.8, 231.6, and 332.4 meV), respectively. The values of V_e+V_{hh} (V_e+V_{lh}) in $Cd_xZn_{1-x}S/ZnS$ SQWs for $x = 0.1$, 0.2, and 0.3 are greater than those in $ZnS_{1-x}Se_x/ZnS$ SQWs for x = 0.1, 0.2, and 0.3. The difference between the values of $V_e + V_{hh}$ ($V_e + V_{lh}$) of $Cd_xZn_{1-x}S/ZnS$ SQWs and $ZnS_{1-x}Se_x/ZnS$ SQWs is less than 36 meV (43 meV). The values of the ratio V_e/V_{hh} (V_e/V_{lh}) in $Cd_xZn_{1-x}S/ZnS$ SQWs for x = 0.1, 0.2, and 0.3 are 86/14, 86/14, and 85/15 (99/1, 96/4, and 93/7), respectively; the corresponding values in $ZnS_{1-x}Se_x/ZnS$ SQWs are 29/71, 30/70, and 32/68 (21/79, 23/77, and 23/77), respectively. The values of V_e/V_{hh} and V_e/V_{lh} are listed in Table II. It is clear that the large V_e effectively confines the excitons within the QWs. The maximum heavy-hole (light-hole) exciton binding energies calculated by considering the effect of the exciton–LO phonon interaction in $Cd_xZn_{1-x}S/ZnS$ SQWs for x = 0.1, 0.2, and 0.3 are 48.1, 53.0, and 55.8 meV (36.6, 39.9, and 42.6 meV), respectively. The maximum heavy-hole (light-hole) exciton binding energies calculated by considering the effect of the exciton–LO phonon interaction in $Cd_xZn_{1-x}S/ZnS$ SQWs are enhanced by a factor of 1.95–2.34 (1.18–1.47). The increases in the heavy- and light-hole exciton binding energies are lower than those reported in ref. [9] because we ignored the image-charge effect. Table III lists the factors of increase in heavy- and light-hole exciton binding energies calculated both by ignoring and by considering the effect of the exciton–LO phonon interaction in $Cd_xZn_{1-x}S/ZnS$ SQWs for x = 0.1, 0.2, and 0.3. The factors of increase in the heavy- and light-hole exciton binding energies in $Cd_xZn_{1-x}S/ZnS$ SQWs are greater than those in $ZnS_{1-x}Se_x/ZnS$ SQWs. The increases in the maximum heavy-hole (light-hole) exciton binding energies in $Cd_xZn_{1-x}S/ZnS$ SQWs are 8.8, 8.9, and 8.8 meV (5.3, 5.0, and 4.7 meV), respectively, and these are lower than those in $ZnS_{1-x}Se_x/ZnS$ SQWs. Table IV lists the increases in the maximum heavy-hole and light-hole exciton binding energies in $Cd_xZn_{1-x}S/ZnS$ SQWs for x = 0.1, 0.2, and 0.3. The difference between the increase in the maximum exciton binding energies in $Cd_xZn_{1-x}S/ZnS$ SQWs and in $ZnS_{1-x}Se_x/ZnS$ SQWs is less than 2.0 meV. From the abovementioned findings, the increase in the exciton binding energies is mainly attributable to the quantum confinement due to V_e.

IV. SUMMARY

We study the effect of exciton–LO phonon interaction on the exciton binding energies in $ZnS_{1-x}Se_x/ZnS$ SQWs for values of x in the range of 0.1–0.3. The heavy- and light-hole exciton binding energies increase with the exciton–LO phonon interaction. The increase in the maximum heavy-hole (light-hole) exciton binding energy for $x = 0.1$ is 10.7 meV (7.4 meV). In narrow $ZnS_{1-x}Se_x/ZnS$ SQWs, the heavy-hole exciton binding energy calculated by taking into account the exciton–LO phonon interaction for values of x in the range of 0.2–0.3 exceed the LO phonon energy of $ZnS_{1-x}Se_x$. For narrow wells, the light-hole exciton binding energies calculated by taking into account the effect of LO phonon interaction in $ZnS_{1-x}Se_x/ZnS$ SQWs exceed the LO phonon energy of $ZnS_{1-x}Se_x$ when $x = 0.3$. However, the difference between the maximum heavy-hole (light-hole) exciton binding energy for $x = 0.3$ and the LO phonon energy is less than 1.5 meV (1.0 meV). This QW corresponds to a weakly confining QW, which is ascribed to the small V_e. To increase the exciton binding energy, a larger V_e is required.

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ВПЛИВ ВЗАЄМОДІЇ ЕКСИТОНІВ І ПОЗДОВЖНІХ ОПТИЧНИХ ФОНОНІВ ТА КВАНТОВОГО ОБМЕЖЕННЯ НА ЕНЕРҐІЇ ЗВ'ЯЗКУ ЕКСИТОНА В ОДИНИЧНИХ КВАНТОВИХ ЯМАХ У $ZnS_{1-x}Se_x/ZnS$

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Ми дослідили вплив взаємодії між екситонами й поздовжніми оптичними фононами (ПО) і квантового обмеження на енергії зв'язку екситона в одниничних квантових ямах (ОКЯ) у $ZnS_{1-x}Se_x/ZnS$ для вмісту домішки Se в діапазоні $x = 0.1$–0.3. У вузьких ОКЯ $ZnS_{1-x}Se_x/ZnS$ енергія зв'язку важкої (легкої) дірки, обчислена з урахуванням взаємодії екситонів і ПО фононів для значень у діапазоні 0.2–0.3 (0.3), перевищує енергію ПО фононів у $ZnS_{1-x}Se_x$. Різниця між максимальною енергією зв'язку екситона важкої (легкої) дірки для $x = 0.3$ та енергією ПО фонона менша за 1.5 меВ (1.0 меВ). Отже, в таких ОКЯ характерне слабке квантове обмеження з огляду на малий розрив зони провідності.