Exciton Binding Energies in ZnSSe/MgSSe Quantum Wells Lattice Matched to GaAs Substrates

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Exciton binding energies in ZnSSe/MgSSe single quantum wells (SQWs) are calculated to study their exciton properties in detail. The heavy-hole exciton binding energies are larger than the light-hole exciton binding energies in narrow wells because the degree of confinement of the heavy-hole excitons is larger than that of the light-hole excitons in these SQWs. The heavy-hole exciton binding and heavy-hole excitonic transition energies calculated for ZnSSe/MgSSe SQWs are comparable to those measured for ZnSe/MgS quantum wells.

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I. INTRODUCTION

The radiative recombination of excitons in ZnO-based quantum wells (QWs) is expected to play an important role in lasing processes [1] because the exciton binding energy in bulk ZnO is very large (59 meV) [2]. Ohtomo *et al.* measured the threshold to be less than 22 kW/cm² for the stimulated emission of excitons at room temperature (RT) in ZnO-based QWs [3].

Monolithically integrated multiwavelength laser diodes (LDs) can be used to reduce the number of optical components in recordable optical media. However, the crystalline structure of AlGaAs-based (AlGaInP-based) semiconductors used in 780-nm (650-nm) LDs differs from that of ZnO-based semiconductors used in blue LDs. Because the crystalline structure of ZnSe is the same as that of AlGaAs (AlGaInP), ZnSe-based blue LDs can be employed in combination with AlGaAs (AlGaInP) LDs for the fabrication of monolithically integrated multiwavelength LDs.

In the case of ZnSe, the bulk exciton binding energy (19 meV) [4] is less than the longitudinal optical (LO)-phonon energy (31 meV) [5]; hence, exciton-LO-phonon scattering can be suppressed in ZnSe-based QWs, in which the exciton binding energy is typically enhanced by a factor of 1.5-2 because of quantum confinement. Therefore, the phenomenon of radiative recombination of excitons has been exploited to enable the use of ZnSe-based QWs in the fabrication of blue LDs. In particular, ZnSe/MgS QWs have been experimentally studied for their use in the fabrication of blue optoelectronic devices [6-8]. Changes in the exciton binding energies with the well width (L_w) have been measured for ZnSe/MgS QWs [9].

In ZnSe-based heteroepitaxial systems, the lattice mismatch between a ZnSe-based epitaxial layer and a GaAs substrate results in a large amount of lattice defects originating from the interface [10, 11]. The lattice defect density has to be reduced to obtain LDs with long life-

FIG. 1: Bandgap energies of II-VI semiconductors as functions of their lattice constants.

times. The ZnSe/MgS QWs have small lattice mismatch of 0.8% and are reasonably lattice matched to GaAs substrates. It was clearly observed from the transmission spectra measured for ZnSe/MgS QWs that the transmission dip consists of the heavy- and light-hole excitons [9]. The strain owing to the lattice mismatch between ZnSe well and MgS barrier splits the uppermost degenerate valence band into heavy- and light-hole bands. On the other hand, in spite of the small lattice mismatch between ZnSe and ZnMgSSe, long-lifetime ZnSe-based LDs could not be achieved [12]. Therefore, we consider that the inhibition in lattice mismatch is important for reducing lattice defect density in ZnSe-based LDs.

The lattice constant of MgSe is larger than that of MgS, whereas the lattice constant of ZnS is smaller than that of ZnSe (Fig. 1). Therefore, the lattice matching between a ZnS_xSe_{1-x} well (or a MgS_{1-y}Se_y barrier) layer and a GaAs substrate is expected to be achieved by adjusting the sulfur (S) (x) [or selenium (Se) (y)] content.

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TABLE I: Physical parameters used in the calculation.

	ZnSe	ZnS	MgSe	MgS
Lattice constant (nm)	0.56681 [15]	0.54093 [15]	0.5964 [16]	0.5615 [17]
Bandgap energy at 4.2 K (eV)	2.82 [18]	3.84 [18]	4.1 [16]	5.4 [17]
Top valence band energy (eV)	-10.56 [19]	-11.84 [19]	-11.0 [19]	-11.93 [19]
Electron effective mass	0.14 [20]	0.28 [20]		
Luttinger parameter γ_1	2.45 [21]	2.54 [20]		
Luttinger parameter γ_2	0.61 [21]	0.75 [20]		
Relative dielectric constant	8.8 [14]	8.6 [22]		
Bowing parameter of ZnSSe	0.63 [23]			
Bowing parameter of MgSSe	0.4911 [23]			

When $x = 0.06$ and $y = 0.14$, $\text{ZnS}_x\text{Se}_{1-x}/\text{MgS}_{1-y}\text{Se}_y$ single QWs (SQWs) can be lattice matched to GaAs substrates. The bandgap energy of the $\text{MgS}_{0.86}\text{Se}_{0.14}$ layer is larger than that of the $\text{ZnS}_{0.06}\text{Se}_{0.94}$ layer (Fig. 1). The difference between the bandgaps of the $\text{ZnS}_{0.06}\text{Se}_{0.94}$ and $\text{MgS}_{0.86}\text{Se}_{0.14}$ layers is smaller than that of the MgS and ZnSe layers. However, this difference between the two sets of layers is small. It is expected that the exciton binding energies in the $\text{ZnS}_{0.06}\text{Se}_{0.94}/\text{MgS}_{0.86}\text{Se}_{0.14}$ SQWs are comparable to that in the ZnSe/MgS SQWs. The $\text{ZnS}_{0.06}\text{Se}_{0.94}/\text{MgS}_{0.86}\text{Se}_{0.14}$ SQWs are therefore an important candidate for use in the fabrication of blue LDs on GaAs substrates. Estimation of the exciton binding energies in $\text{ZnS}_{0.06}\text{Se}_{0.94}/\text{MgS}_{0.86}\text{Se}_{0.14}$ SQWs is necessary for tuning the optical properties of these QWs for various LD applications.

In this study, we calculate the heavy- and light-hole exciton binding energies as functions of the L_w in $\text{ZnS}_{0.06}\text{Se}_{0.94}/\text{MgS}_{0.86}\text{Se}_{0.14}$ SQWs. We follow a variational approach. Moreover, we calculate the exciton transition energies to achieve appropriate adjustment of the optical bandgap for various applications.

II. CALCULATION METHODS

Greene *et al.* have reported the details of the method for calculating binding energies in QWs [13]. We use a variational method for calculating the exciton binding energies. The exciton Hamiltonian is given by [13]

$$H = -\frac{\hbar^2}{2\mu_{\pm}} \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial}{\partial r} - \frac{\hbar^2}{2m_e^*} \frac{\partial^2}{\partial z_e^2} - \frac{\hbar^2}{2m_{\pm}} \frac{\partial^2}{\partial z_h^2} - \frac{e^2}{\epsilon \sqrt{r^2 + (z_e - z_h)^2}} + V_e(z_e) + V_h(z_h), \quad (1)$$

where $\mu_{\pm}$ is the exciton reduced mass and ϵ , the dielectric constant. $V_e(z_e)$ and $V_h(z_h)$ are the conduction and valence band offsets, respectively. A trial function [14] is given by

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

where $\phi_e(z_e)$ and $\phi_h(z_h)$ are the electron and heavy-hole wave functions, respectively. α and β are variational parameters.

The energy at the bottom of the conduction band in $\text{ZnS}_x\text{Se}_{1-x}$ is calculated by linear interpolation without

using a bowing parameter. On the other hand, the energy at the top of the valence band in $\text{ZnS}_x\text{Se}_{1-x}$ is calculated by linear interpolation using a bowing parameter. In $\text{ZnS}_x\text{Se}_{1-x}$, 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. The energies at the bottom of the conduction band and the top of the valence band in $\text{MgS}_{1-y}\text{Se}_y$ are calculated in the same manner.

The valence band offset is calculated as the difference between the energy at the top of the valence band in the well and that in the barrier. The conduction band offset is calculated as the difference between the energy at the bottom of the conduction band in the well and that in the barrier.

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 calculated as the summation 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 the same manner.

III. RESULTS AND DISCUSSION

The physical parameters used in our calculation are listed in Table I. The parameters pertaining to the alloy material are derived by linear interpolation. The effective masses of heavy and light holes in the z -direction and for the x - y plane are determined in terms of the well-known Luttinger parameters. For simplification of our calculation, the effective masses of electrons, heavy holes, and light holes are assumed to be position independent and equal to the effective masses of those of $\text{ZnS}_{0.06}\text{Se}_{0.94}$. Conduction and valence band offsets are estimated to be 1525 meV and 788 meV, respectively.

Figure 2 shows heavy- and light-hole exciton binding energies in $\text{ZnS}_{0.06}\text{Se}_{0.94}/\text{MgS}_{0.14}\text{Se}_{0.86}$ SQWs as functions of L_w . For comparison, the heavy- and light-hole exciton binding energies measured for ZnSe/MgS multiple QWs (MQWs) [9] are also plotted. The heavy-hole exciton binding energy measured for a well width of 5 nm is considerably larger than that calculated for $\text{ZnS}_{0.06}\text{Se}_{0.94}/\text{MgS}_{0.14}\text{Se}_{0.86}$ SQWs. The measured heavy-hole exciton binding energies show marked decreases when the value of L_w increases from 5 nm to 10 nm because of a decrease in the quantum confinement effect

FIG. 2: Heavy- and light-hole exciton binding energies calculated for $\text{ZnS}_{0.06}\text{Se}_{0.94}/\text{MgS}_{0.86}\text{Se}_{0.14}$ SQWs as functions of L_w . Solid and dashed curves indicate the plots of heavy- and light-hole exciton binding energies, respectively. The bold line indicates the plot of LO-phonon energy of ZnSe. Open circles indicate the heavy-hole exciton binding energies measured for ZnSe/MgS SQWs reported by Urbaszek *et al.* [9].

on excitons. On the other hand, the heavy-hole exciton binding energy measured for a well width of 10 nm is close to that calculated for $\text{ZnS}_{0.06}\text{Se}_{0.94}/\text{MgS}_{0.14}\text{Se}_{0.86}$ SQWs. The heavy-hole exciton binding energies calculated for $\text{ZnS}_{0.06}\text{Se}_{0.94}/\text{MgS}_{0.14}\text{Se}_{0.86}$ SQWs are comparable to those measured for ZnSe/MgS MQWs [9]. To take a first step in designing ZnSSe/MgSSe QWs, we calculate the exciton binding energy using static dielectric constants for the ZnSSe well and MgSSe barrier. Senger and Bajaj reported that the exciton binding energies calculated for ZnSe/MgS QWs by considering the Pollmann and Büttner (PB) potential are larger than those calculated by ignoring the PB potential [24]. The exciton binding energies calculated for ZnSe/MgS QWs by considering the PB potential agree rather well with those measured for ZnSe/MgS QWs [24]. For simplification of our calculation, we neglect the effect of PB potential in this study. For more realistic understanding of the changes in the exciton binding energies with L_w , the calculation of the exciton binding energy using PB potential is necessary.

With a decrease in the value of L_w , the heavy- and light-hole exciton binding energies increase to reach a maximum value and then decrease rapidly. This is because when the value of L_w decreases, the exciton wave function is compressed in the wells and extends to the barrier region [13]. The shape of the curve representing the dependence of the heavy- and light-hole exciton binding energies on the L_w is consistent with that reported by Greene *et al.* [12]. Changes in the binding energies of the heavy- and light-hole excitons with L_w are essentially similar.

The maximum heavy-hole (light-hole) exciton binding energy is 50.3 meV (47.9 meV). The binding energy of the heavy-hole excitons calculated by neglecting the quantum confinement effect (18.1 meV) is smaller than that of the light-hole excitons calculated by neglecting the quantum confinement effect (20.7 meV). However, the maximum binding energies of the heavy-hole excitons calculated by considering the quantum confinement effect are

FIG. 3: Spatial separation of heavy- and light-hole excitons in the z -direction ($\langle z \rangle$) in $\text{ZnS}_{0.06}\text{Se}_{0.94}/\text{MgS}_{0.86}\text{Se}_{0.14}$ SQWs as functions of L_w . Solid and dashed curves indicate the plots of $\langle z \rangle$ for heavy- and light-hole excitons, respectively.

larger than those of the light-hole excitons calculated under the same consideration. This is because the degree of compression of the exciton wave function for a heavy-hole exciton is larger than that for a light-hole exciton. In order to determine the degree of compression of the exciton wave function, we calculate the dependence of spatial separation of excitons in the z -direction ($\langle z \rangle$) on L_w . $\langle z \rangle$ is given as [25]

$$\langle z \rangle = \langle \varphi | (z_e - z_h)^2 | \varphi \rangle^{1/2}, \quad (3)$$

where φ is the trial function. The calculated results are shown in Fig. 3. $\langle z \rangle$ is minimum at small L_w and increases with L_w . The value of $\langle z \rangle$ for the heavy-hole excitons is smaller than that for the light-hole excitons at the same L_w . The minimum $\langle z \rangle$ for the heavy-hole excitons is smaller than that for the light-hole excitons; hence, the larger degree of compression for the heavy-hole excitons is larger than that for the light-hole excitons.

Moreover, to determine the degree of compression of the exciton wave function, the L_w dependence of the probability of finding an exciton inside the well (P) is calculated. P is given as [13]

$$P = \int_0^\infty \int_{-L_w/2}^{L_w/2} \int_{-L_w/2}^{L_w/2} |\varphi|^2 dz_e dz_h r dr. \quad (4)$$

The calculated results are shown in Fig. 4. P increases with L_w and is almost equal to 1. The value of P for the heavy-hole excitons is larger than that for the light-hole excitons at the same L_w . The L_w dependence of P suggests that the degree of confinement of the heavy-hole excitons is larger than that of the light-hole excitons.

When the value of L_w for the $\text{ZnS}_{0.06}\text{Se}_{0.94}/\text{MgS}_{0.14}\text{Se}_{0.86}$ SQWs is in the range of 0.2–8.0 nm (0.2–9.0 nm), the heavy-hole (light-hole) exciton binding energies are all larger than the LO-phonon energy of ZnSe (31 meV) [5]. This indicates that the exciton characteristics are predominant even at RT. The strong interaction between the excitons and LO phonons usually results in the dissociation of the excitons at higher temperatures [9]. Ionization of excitons should be prevented in a system in which all the excitations of the exciton have an energy

FIG. 4: Probability of finding heavy- and light-hole excitons inside the $\text{ZnS}_{0.06}\text{Se}_{0.94}$ well layer (P) as functions of L_w . Solid and dashed curves indicate the plots of P for heavy- and light-hole excitons, respectively.

FIG. 5: Calculated heavy- and light-hole exciton transition energies in $\text{ZnS}_{0.06}\text{Se}_{0.94}/\text{MgS}_{0.86}\text{Se}_{0.14}$ SQWs as functions of L_w . Solid and dashed curves indicate the plots of heavy- and light-hole exciton transition energies, respectively. Open circles indicate the photoluminescence (PL) peak energies measured for ZnSe/MgS SQWs reported by Urbaszek *et al.* [9].

larger than that of the LO phonon [9]. For a more realistic understanding of the exciton stability, the calculation of the excited exciton states is necessary. For simplification of our calculation, we limit our discussion to the binding energy of the ground exciton state; therefore, our result does not provide a complete picture of the exciton stability.

For comparison, we also calculate the heavy- and light-hole exciton transition energies in $\text{ZnS}_{0.06}\text{Se}_{0.94}/\text{MgS}_{0.86}\text{Se}_{0.14}$ SQWs as a function of L_w . The calculated results are plotted in Fig. 5, where open circles indicate the photoluminescence (PL) peak energies measured for ZnSe/MgS SQWs presented in ref. 9. The heavy- and light-hole exciton transition energies calculated by us are larger than the PL peak energies measured for ZnSe/MgS SQWs [9]. This is because the bandgap energy of $\text{ZnS}_{0.06}\text{Se}_{0.94}$ is larger than that of ZnSe. The difference between the calculated and measured values is small.

IV. CONCLUSION

We have calculated the binding energies of heavy- and light-hole excitons in $\text{ZnS}_{0.06}\text{Se}_{0.94}/\text{MgS}_{0.86}\text{Se}_{0.14}$ SQWs. The maximum binding energy of the heavy-hole (light-hole) exciton is 50.3 meV (47.9 meV). The L_w dependence of $\langle z \rangle$ and P suggests that the degree of confinement of the heavy-hole excitons is larger than that of the light-hole excitons. When the value of L_w is in the range of 0.2–8.0 nm (0.2–9.0 nm), the heavy-hole (light-hole) exciton binding energies are all larger than the LO-phonon energy of ZnSe (31 meV). The heavy- and light-hole exciton transition energies calculated for $\text{ZnS}_{0.06}\text{Se}_{0.94}/\text{MgS}_{0.86}\text{Se}_{0.14}$ SQWs are comparable to the PL peak energies measured for ZnSe/MgS QWs. Therefore, $\text{ZnS}_{0.06}\text{Se}_{0.94}/\text{MgS}_{0.86}\text{Se}_{0.14}$ SQWs can possibly be used in the fabrication of blue laser devices using exciton emission at RT.

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