

## Effect of External Uniaxial Stress on Blue-Green Exciton Emission of CdZnSe Strained-Layer Quantum Wells

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Energy - in-plane wavevector dependent hole dispersion characteristics in Cd<sub>0.2</sub>Zn<sub>0.8</sub>Se strained-layer quantum wells have been investigated using a 6x6 valence band Hamiltonian. In order to estimate an energy splitting between the heavy-hole and light-hole states at k<sub>||</sub>=0 as a function of the well width, we assume the parabolic hole dispersion. In the limit where the spin-orbit energy Δ<sub>so</sub> is larger than the biaxial compressive strain, the strain-dependent mass function approaches to 1. Uniaxial stress experiment along <100> axis was carried out on a green-blue excitonic emission at room temperature in a Cd<sub>0.25</sub>Zn<sub>0.75</sub>Se/ZnS<sub>0.04</sub>Se<sub>0.96</sub> multiple-quantum well and a shift to higher energy and concomitant enhancement in intensity can be observed.

### 1. INTRODUCTION

It is now recognised that strained quantum well (QW) structure is attractive for III-V semiconductor injection lasers because of its flexibility in lasing wavelength design and low threshold current<sup>1, 2)</sup>. Significant progress in widegap II-VI semiconductor quantum wells based on ZnSe has led to a recent successful report of diode lasers operating in the blue-green wavelength region<sup>3)</sup>.

Quantum well in CdZnSe/ZnSe superlattice is compressively strained due to a lattice mismatch of about 1.7% between them. Since Cd<sub>x</sub>Zn<sub>1-x</sub>Se mixed alloy retains the zincblende lattice and a direct bandgap in the composition ranges from x=0.1 to 0.3, all the important optical properties are dependent on the hole energy states near the zone center (Γ<sub>8</sub> symmetry at k=0). In the absence of strain the valence-band maximum in bulk CdZnSe is assumed to be fourfold degenerate states with a character of J=3/2 which leads to complicated dispersion relation. The quantum well band structure lies in the (100) plane perpendicular to the growth direction which brings about a symmetry breaking from T<sub>d</sub> to D<sub>2d</sub>. This yields the same situation as uniaxial stress applied to <100> axis. As a result the biaxial compressive stress splits the degenerate hole band into the heavy-hole and light-hole states and can modify the electronic states and the physical properties such as effective masses and energy levels.

Recently Ahn et al<sup>4)</sup> have calculated the hole band structure in CdZnSe using k · p method in which the conduction and valence bands are decoupled at k<sub>||</sub>=0. They have shown that the light-hole mass is negative at k<sub>||</sub>=0.

In order to investigate the electronic states of the hole bands in the compressively strained CdZnSe quantum wells, we used a (6x6)

Luttinger-Kohn valence band Hamiltonian<sup>5)</sup> including the spin-orbit interaction term H<sub>so</sub>.

This paper describes hole dispersion near k=0 in the CdZnSe quantum well as a function of well width from which the energy separation between the heavy-hole and light-hole is estimated. External uniaxial stress along <100> axis (equivalent to changes of the compressive or tensile stress on the quantum states in the strained layer) is carried out on a blue-green excitonic emission at room temperature of a Cd<sub>0.25</sub>Zn<sub>0.75</sub>Se (30 Å)/ZnS<sub>0.04</sub>Se<sub>0.96</sub> (73 Å) multiple QW.

### 2. HOLE DISPERSION CHARACTERISTICS

We have used a (6x6) secular matrix<sup>5)</sup> derived on the basis of strain (under uniaxial) and k · p interaction. The conduction band is assumed to be parabolic. The strain-dependent hole dispersion relations to order k<sup>2</sup> gives hole energies where basis vectors can be identified with the four components of a J=3/2 angular momentum: heavy hole (hh): |3/2, ±3/2> and light hole (lh): |3/2, ±1/2>, respectively. Each of these eigenvalues are twice Kramers degenerate.

$$E_{hh} = -\hbar^2/2m_0 [(k_x^2 + k_y^2) (\gamma_1 - \gamma_2) + k_z^2 (\gamma_1 - 2\gamma_2)] + \epsilon \dots (1)$$

$$E_{lh} = -\hbar^2/2m_0 [(k_x^2 + k_y^2) (\gamma_1 - \gamma_2) + k_z^2 (\gamma_1 - 2\gamma_2)] - 1/2 (\epsilon + \Delta_0) + 1/2 (9\epsilon^2 + \Delta_0^2 - 2\epsilon\Delta_0) \dots (2)$$

and the spin-orbit energy band,

$$E_{s_0} = -\hbar^2/2m_0 [(k_x^2 + k_y^2) \{ \gamma_1 - (1-Z) \gamma_2 \} + k_z^2 \{ \gamma_1 - 2(1-Z) \gamma_2 \}] - 1/2(\varepsilon + \Delta_0) - 1/2(9\varepsilon^2 + \Delta_0^2 - 2\varepsilon \Delta_0) \dots (3)$$

where  $\varepsilon$  is the strain energy  $[2/3D_u(e_{zz}^{(001)} - e_{xx}^{(001)})]$ ,  $\gamma_1$  and  $\gamma_2$  are Luttinger-Kohn parameters,  $k_x$  and  $k_y$  are in-plane wave vectors,  $k_z$  is assumed to the quantisation axis.

We have determined here strain-dependent valence band mass parameter  $Z(x)$  as follows;

$$Z(x) = 1/2 [1 + (1-9x)/(1-2x+9x^2)^{1/2}] \dots (4)$$

$$x = \varepsilon / \Delta_0$$

For the calculation of the band offsets and the dependence of the well width, we used following physical parameters of  $Cd_{0.2}Zn_{0.8}Se$  and  $ZnS_{0.04}Se_{0.96}$  in Table 1.

Table 1 Band parameters used in this study

(1) $Cd_{0.2}Zn_{0.8}Se$ : Lattice constant = 5.75 Å, $C_{11} = 7.42 \times 10^{10} N/m^2$ , $C_{12} = 4.910 \times 10^{10} N/m^2$ , $a_v = 1.65$ eV, $a_c = -4.17$ eV, $b = -1.12$ eV, $E^{top}_v = -10.524$ eV, $E_g = 2.5626$ eV.
(2) $ZnS_{0.04}Se_{0.96}$ : Lattice constant = 5.653 Å, $C_{11} = 8.839 \times 10^{10} N/m^2$ , $C_{12} = 5.071 \times 10^{10} N/m^2$ , $a_v = 1.69$ eV, $a_c = -4.165$ eV, $b = -1.17$ eV, $E^{top}_v = -10.596$ eV, $E_g = 2.8588$ eV.
(3) Luttinger parameters and spin-orbit coupling constant of $CdZnSe$ and $ZnSSe$ same as those in $ZnSe$ : $\gamma_1 = 3.77$ , $\gamma_2 = 1.24$ , $\gamma_3 = 1.67$ , $\Delta_{so} = 0.45$ eV

For example, in the case of the strained-layer superlattice consisting of a 25 Å  $CdZnSe$  well and a 75 Å barrier, the conduction band offset is estimated to be 0.1683 eV and the valence band offset 0.09 eV for the hh state.

Since the biaxial compressive strain for a  $Cd_{0.2}Zn_{0.8}Se/ZnS_{0.04}Se_{0.96}$  QW is estimated to be about 40 meV ( $= |bx \{ C_{11} + 2C_{12} \} / C_{11} x \varepsilon|$ ), the strain-dependent valence band mass parameter approaches to 1. However, as  $x \rightarrow \pm 1$ , the function  $Z(x)$  is significantly modified.

Figure 1 shows the calculated in-plane wavevector dependent  $n=1$  hh and  $n=1$  lh dispersion curves for  $CdZnSe/ZnSSe$  QWs at a constant  $ZnS_{0.04}Se_{0.96}$  barrier width ( $L_b = 75$  Å) as a function of  $Cd_{0.2}Zn_{0.8}Se$  quantum well width (—: 25, ---: 75 and --: 125 Å), where the "zero" denotes the degenerate hole energy in the valence band near  $k=0$  ( $L_w \rightarrow \infty$ ). With increasing the well width, the hh energy ( $E_{hh}$ ) decreases monotonously, while the lh energy ( $E_{lh}$ ) increases. It should be therefore understood that the well width dependence of the lh energy is significant compared to that of the hh energy. It is evident that the hh effective mass becomes lighter with increasing  $|\varepsilon|$ . Since the hole band energies are small compared to both the strain potential and the spin-orbit energy, one can not require the dispersion relation to terms higher than  $k^2$ .

Figure 2 shows the energy separation ( $\Delta E = |E_{hh} - E_{lh}|$ ) at  $k_{||} = 0$  of  $Cd_{0.2}Zn_{0.8}Se/ZnS_{0.04}Se_{0.96}$  QWs as a function of well width ( $L_w$ ). In a 25 Å QW,  $\Delta E_{hh-lh}$  is estimated

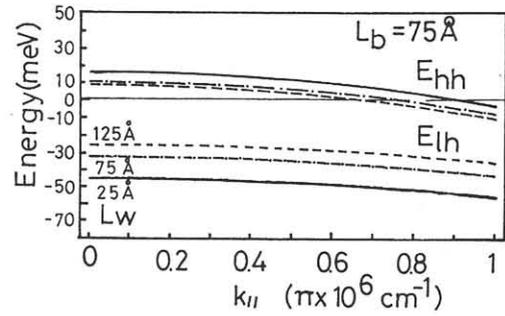


Fig. 1 E-k hole dispersion as a function of  $Cd_{0.2}Zn_{0.8}Se$  well width (—: 25 Å, ---: 75 Å and --: 125 Å).

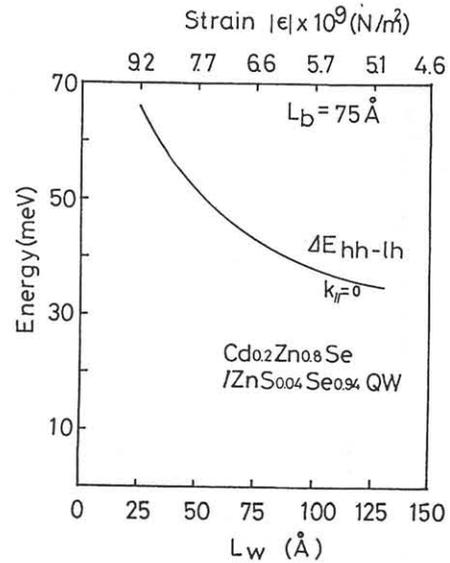


Fig. 2 Energy separation between heavy-hole and light-hole states at a constant  $ZnS_{0.04}Se_{0.96}$  barrier of 75 Å as a function of well width (compressive strain).

to be about 66 meV. With decreasing well width, the  $E_{hh-lh}$  energy is markedly increased due to an increase in the compressive strain as denoted by the upper scale  $|\varepsilon|$  in this figure. An experimental value obtained by Luo et al<sup>6)</sup> is about 55 meV in a  $Cd_{0.2}Zn_{0.8}Se/ZnSe$  single QW ( $L_w = 30$  Å) is in good agreement with the present theoretical one.

Figure 3 shows the energy splitting  $\Delta E_{hh-lh}$  at  $k=0$  of  $Cd_{0.2}Zn_{0.8}Se/ZnS_{0.04}Se_{0.96}$  QWs ( $L_w = 25$  and  $125$  Å) as a function of  $ZnS_{0.04}Se_{0.96}$  barrier layer thickness. For thinner well width, the energy separation becomes large. When  $L_b$  is larger than 75 Å, the  $\Delta E$  separation seems to be saturated as shown in this figure which may imply a result of the strain absorption within the critical thickness.

As shown in Figs. 2 and 3,  $\Delta_{so}$  exceeds the hh and lh energy splitting and as a result the  $k^2$  dependence of the valence band seems valid (eqs. (1) and (2)). People and Spitz<sup>5)</sup> have suggested that in this limit coherent strain

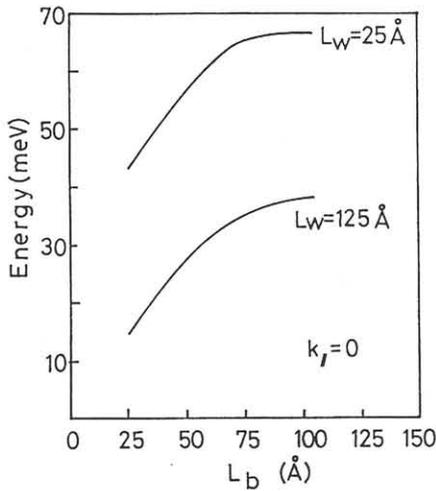


Fig. 3 Energy separation between the heavy-hole and light-hole states for two different well widths ( $L_w=25$  and  $125$  Å) as a function of barrier thickness.

can modify both hh and lh masses, depending both the  $\epsilon$  sign and the magnitude of the tetragonal distortion.

### 3. UNIAXIAL STRESS EFFECT ON QUANTUM STATES

The  $\text{Cd}_x\text{Zn}_{1-x}\text{Se}/\text{ZnSo}_{.04}\text{Se}_{.96}$  MQW layers were successfully grown on (100) GaAs substrates with a ZnS buffer layer using low-pressure MOCVD method (by Y.Kawakami, May 21 ~ July 12 in 1987).

The  $\text{Cd}_{.25}\text{Zn}_{.75}\text{Se}/\text{ZnSo}_{.04}\text{Se}_{.96}$  MQW produces a single symmetric emission peak in the vicinity of 514 nm having a linewidth of about 45 meV at RT. The origin of the green emission at RT may be due to a relaxation of excitons which consist of a  $n=1$  heavy-hole exciton.

The uniaxial stress applied externally gives us the information on the quantum states similar as the strained-layer QWs<sup>7, 8)</sup>. If uniaxial compression is applied parallel to the plane of the quantum wells, off-diagonal elements of the total Hamiltonian can be non zero even at  $k=0$ .

We tried to carry out the effects of uniaxial stress on excitons in QWs. Figure 4 shows experimental results on the energy shift and the emission intensity ratio between the intensity at zero strain and the intensity of a  $\text{Cd}_{.25}\text{Zn}_{.75}\text{Se}/\text{ZnSo}_{.04}\text{Se}_{.96}$  MQW ( $L_w=30$  Å and  $L_b=73$  Å, 120 periods) applied stress along  $\langle 100 \rangle$  axis at RT. The emission peak shifts towards higher energy with increasing stress<sup>9)</sup> (about 2.5 meV/4kbar). However, the experimentally applied stress is much smaller than the strain being induced by a lattice mismatch. The change in emission intensity under  $\langle 100 \rangle$  axis appears where the intensity  $I_x$  at 4 kbar is about three factors larger than the virgin intensity  $I_0$ . This may be interpreted in terms of an increase in the energy of heavy-hole band ( $1/|E_c - E_{hh}|$ ). However, evidence of the valence subband mixing

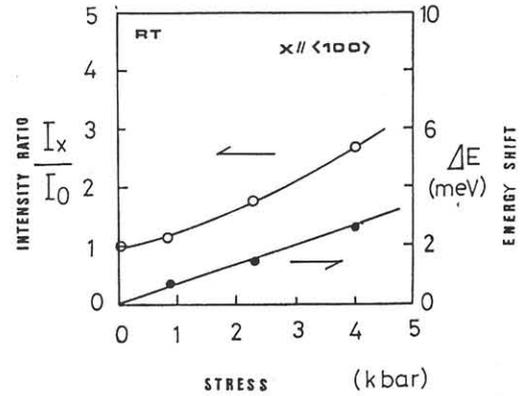


Fig. 4 Changes of the emission peak energy and intensity of blue-green emission in a  $\text{Cd}_{.25}\text{Zn}_{.75}\text{Se}/\text{ZnSo}_{.04}\text{Se}_{.96}$  (120 periods,  $L_w=30$  and  $L_b=73$  Å) MQW at RT as a function of uniaxial stress.

between the hh and lh excitons was not clearly observed at RT.

### 4. CONCLUSION

We have performed the theoretical calculation of E-k hole dispersion relation of the valence band in the strained CdZnSe quantum wells as a function of well width, taking into account of the spin-orbit interaction. The hh and lh energy splitting is smaller than the spin-orbit energy of ZnSe. Uniaxial stress studies give us the information on a blue-green excitonic emission towards higher energy with stress and subsequent increase in emission intensity. It is tentatively suggested that the enhancement of the emission intensity is related to the increase in energy of the hh state which forms excitons.

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