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# Photoluminescence of ZnSe/$Zn_{1-x}Cd_xSe$ strained superlattices under hydrostatic pressure

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**Abstract**

A study of the photoluminescence (PL) of ZnSe/$Zn_{1-x}Cd_xSe$ strained superlattices under hydrostatic pressure (0–2.5 GPa) at room temperature has been performed for the first time. The small sublinear dependence of PL energy with pressure for the heavy-hole exciton of the well layers was observed. The pressure coefficients of the PL peak were obtained by least-squares fits to the experimental data. The linear pressure coefficient obtained by calculation is in good agreement with the experimental one.

*Keywords:* Luminescence; Superlattices; Diamond; Phase transitions

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## 1. Introduction

Recently, wide-gap II–VI semiconductor quantum wells and ZnSe-based superlattices have received much attention because of their potential application in optoelectronic devices in the blue spectral region. In particular, ZnSe/$Zn_{1-x}Cd_xSe$ heterostructures have shown both strong excitonic absorption and low-threshold optically pumped lasing at room temperature. ZnSe/$Zn_{1-x}Cd_xSe$ has been used as the active region of a blue–green diode laser [1]. The optical and electrical properties of this new material have produced much interest in recent years. Photoluminescence under hydrostatic pressure is a powerful tool for the investigations of electronic structures of semiconductor materials. Photoluminescence (PL) studies under pressure of III–V quantum wells and superlattices have received much attention [2–5]. However, studies of II–VI semiconductor quantum wells and superlattices have received much less. In this paper, the photoluminescence of ZnSe/$Zn_{1-x}Cd_xSe$ at room temperature, under hydrostatic pressures in the range 0–2.5 GPa, is reported and discussed. To our knowledge, there have been no previous studies of the pressure dependence of PL at room temperature of II–VI semiconductor quantum wells and superlattices.

## 2. Experiment

The samples of ZnSe/$Zn_{0.74}Cd_{0.26}Se$ strained-layer superlattices were grown by metal–organic chemical vapour deposition (MOCVD). The substrates were (001)-oriented GaAs. A 1.2 μm thick ZnSe buffer layer was first deposited on the substrates, followed by 150 periods of superlattices. The superlattices consist of 4.0-nm-thick $Zn_{0.74}Cd_{0.26}Se$ well layers, separated by 6.0-nm-thick ZnSe barrier layers. Finally, a 0.3-μm-thick ZnSe cap layer was grown on the top.

The hydrostatic pressure measurements were performed by the diamond anvil cell technique. The GaAs substrate was thinned to about 30 μm and the sample was cut to 150 × 150 $\mu m^2$ squares to be placed in a gasketed diamond anvil cell. A 4:1 methanol–ethanol mixture was used as a pressure medium. The energy shift of the $R_1$ luminescence line from a ruby crystal was used to calibrate the pressure [6].

The PL spectra were excited by the 457.9 nm line of an $Ar^+$ laser. The scattered light was analyzed with a SPEX-1403 double monochromator and detected by a RCA-C31034 cooled photomultiple tube.

## 3. Experimental results

Fig. 1 shows the PL spectra of ZnSe/$Zn_{0.74}Cd_{0.26}Se$ strained superlattices obtained under excitation with the 457.9 nm line of an $Ar^+$ laser at 77 K and room temperature, respectively. The PL spectrum at 77 K exhibited three peaks. The stronger peak $P_2$ is located at 2.569 eV (20732 $cm^{-1}$) and two weaker PL peaks are at 2.660 eV (21472 $cm^{-1}$) and 2.249 eV (18 152 $cm^{-1}$), respectively. With the increase of

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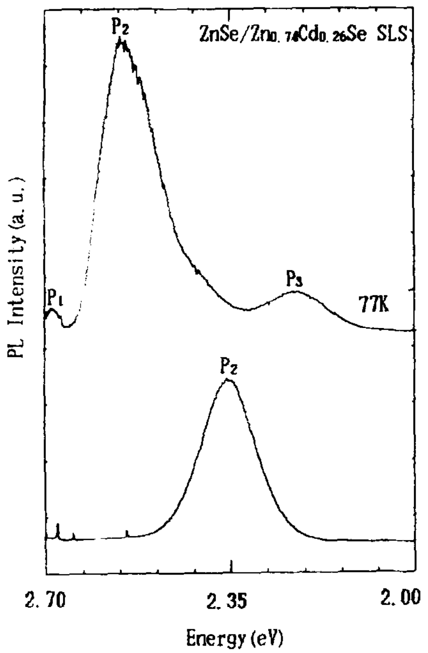

Fig. 1. PL spectra of ZnSe/$Zn_{0.74}Cd_{0.26}Se$ strained superlattices at 77 K and room temperature, respectively.

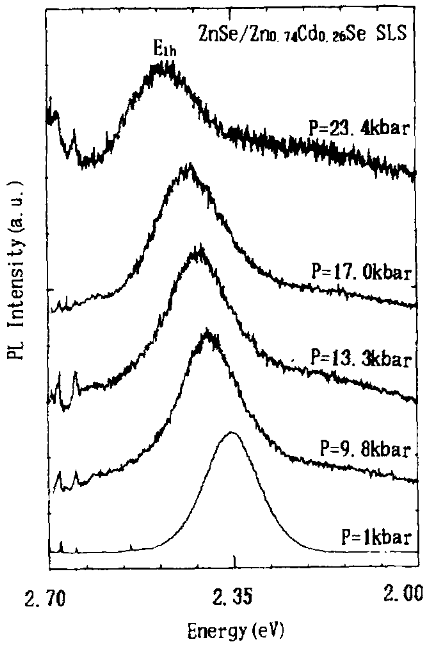

Fig. 2. PL spectra for ZnSe/$Zn_{0.74}Cd_{0.26}Se$ strained superlattices at various pressures and room temperature.

the temperature up to 300 K (room temperature), only the band $P_2$ can be measured and two other peaks disappear, and the emission peak $P_2$ shifts from 2.569 eV (20 732 $cm^{-1}$) to 2.388 eV (19 272 $cm^{-1}$). In II–VI wide-gap superlattices, the enhancement of exciton binding energy and the large oscillator strength make it possible to observe the exciton transition at room temperature [7,8]. Usually, the absorption and luminescence characteristics observed at room temperature in the ZnSe/$Zn_{1-x}Cd_xSe$ quantum wells and superlattices are thought to be due mainly to the $n=1$ HH exciton recombination [7,8], so the emission peak $P_2$ can be attributed to the excitonic transition from the first conduction subband to the $n=1$ heavy hole. By extrapolating for the separation of the heavy hole ($E_{1h}$) and light hole ($E_{1l}$) from the results of Fig. 2 in Ref. [7], we estimate the energy separation of heavy–light holes of approximately 90 meV for the ZnSe/$Zn_{0.74}Cd_{0.26}Se$ superlattices at 77 K [9]. The energy difference between $P_1$ and $P_2$ is about 91 meV. Hence, the PL peak $P_1$ is attributed to the exciton transition from the first conduction subband to the $n=1$ light hole. The origin of the band $P_3$ has not been clear up to now. It is probably ascribed to the recombination of exciton localized at the interface defect or shallow impurities.

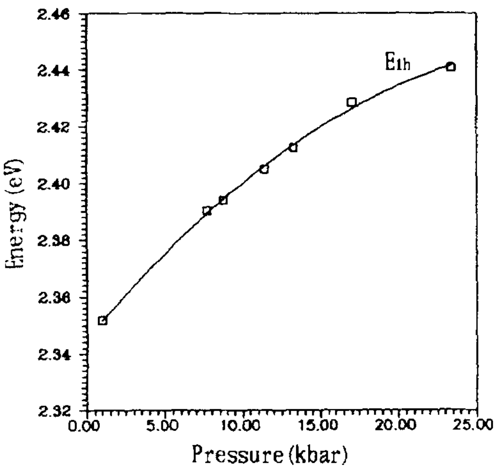

Fig. 3. Energies of the PL peak of ZnSe/$Zn_{0.74}Cd_{0.26}Se$ strained superlattices as a function of pressure.

Fig. 2 shows the photoluminescence of ZnSe/$Zn_{0.74}Cd_{0.26}Se$ strained superlattices under 0–2.5 GPa pressure at room temperature. At room temperature, only $P_2(E_{1h})$ can be observed. The PL peak position shifts towards high energy with increasing pressure, the shape and the linewidth of the peak $P_2$ changes little as the hydrostatic pressure increases. It proves that there is no strain relaxation in the pressure range 0–2.5 GPa.

Fig. 3 shows the effect of pressure on the $E_{1h}$ transition. The line through the data is due to least-squares fits to the function

$$E(p)=E(0)+\alpha p+\beta p^2 \qquad (1)$$

due to its appreciable non-linear behaviour, where $E(0)$ is the zero-pressure transition energy, $\alpha$ is the linear pressure coefficient, and $\beta$ is the non-linear pressure coefficient. By fits to the experimental data, the values of $\alpha$, $\beta$, and $E(0)$ were obtained: $\alpha=67.1$ meV $GPa^{-1}$, $\beta=-12.6$ meV $GPa^{-2}$, and $E(0)=2.345$ eV.

## 4. Calculation and discussion

For ZnSe/$Zn_{0.24}Cd_{0.26}Se$ strained superlattices composed of two component materials, ZnSe with bulk modulus $B_1$ as barrier layers, $Zn_{0.74}Cd_{0.26}Se$ with bulk modulus $B_2$ as well layers, and $B_1' = (dB_1/dp)$, $B_2' = (dB_2/dp)$. According to Murnaghan's equation of state [10], the lattice constant $a(p)$ varies with pressure,

$$a(p) = a(1\ \mathrm{bar})\left(1 + p\frac{B'}{B}\right)^{-1/3B} \tag{2}$$

In the low-pressure limit, Eq. (2) reduces to [11]

$$a(p) = a(1\ \mathrm{bar})\left(1 - \frac{p}{3B}\right) \tag{3}$$

Each component of strain in the superlattices can be decomposed into a hydrostatic and a biaxial component,

$$\bar{\mathrm{E}}_{ij} = \mathrm{E}_{ij}{}^{(h)} + \mathrm{E}_{ij}{}^{(b)} \tag{4}$$

where $\mathrm{E}_{ij}{}^{(h)}$ is the hydrostatic component, which is

$$\begin{aligned}\mathrm{E}_{ij}{}^{(h)}(p) &= \mathrm{E}_{xx}{}^{(h)} = \mathrm{E}_{yy}{}^{(h)} = \mathrm{E}_{zz}{}^{(h)}\\ &= \frac{a(p) - a(1\ \mathrm{bar})}{a(1\ \mathrm{bar})} = -\frac{p}{3B}\end{aligned} \tag{5}$$

where $\mathrm{E}_{ij}{}^{(b)}$ is the in-plane biaxial strain, which is

$$\mathrm{E}^{(b)}(p) = \mathrm{E}_{xx}{}^{(b)} = \mathrm{E}_{yy}{}^{(b)} = \frac{a_{eq}(p) - a(p)}{a(p)} \tag{6}$$

$$\mathrm{E}_{zz}{}^{(b)} = -\frac{2C_{12}}{C_{11}}\mathrm{E}_{xx}{}^{(b)} \tag{7}$$

$a_{eq}$ is the weighted average, in-plane lattice constant for the heterostructure, which is

$$a_{eq}(p) = \frac{(a_1t_1 + a_2t_2)}{(t_1 + t_2)} \tag{8}$$

where $t_1$ is the total thickness of all the ZnSe layers in the SLS, buffer and cap layer. $t_2$ is that for $Zn_{1-x}Cd_xSe$.

By inserting Eq. (3) into Eq. (6), the expression for $\mathrm{E}(p)$ is obtained. If terms are kept only to second order in $p$, the biaxial strain becomes

$$\mathrm{E}^{(b)}(p) = \frac{a_{eq}}{a}\left[1 + \frac{p}{3}\left(\frac{1}{B} - \frac{1}{B_{eq}}\right) + \frac{p^2}{9}\left(\frac{1}{B^2} - \frac{1}{BB_{eq}}\right)\right] - 1 \tag{9}$$

where $B_{eq}$ is the effective bulk modulus, which is

$$\frac{1}{B_{eq}} = \left(2\frac{a_1}{a_{eq}} - 1\right)\frac{t_1}{t_1 + t_2}\frac{1}{B_1} + \left(2\frac{a_2}{a_{eq}} - 1\right)\frac{t_2}{t_1 + t_2}\frac{1}{B_2} \tag{10}$$

Using Eqs. (4)–(9), the fractional change in volume $\Omega$ can be written as

$$\frac{\Delta\Omega}{\Omega} = \bar{\mathrm{E}}_{xx} + \bar{\mathrm{E}}_{yy} + \bar{\mathrm{E}}_{zz} = -\frac{p}{B} + 2\left(1 - \frac{C_{12}}{C_{11}}\right)\mathrm{E}^{(b)}(p) \tag{11}$$

For these superlattices, the valence-band energy and the conduction-band energy vary as

$$\Delta E_v = a_v\left(\frac{\Delta\Omega}{\Omega}\right) + \delta_v\left(\frac{\Delta\Omega}{\Omega}\right)^2 - b(\mathrm{E}_{zz}{}^{(b)} - \mathrm{E}_{xx}{}^{(b)}) \tag{12}$$

$$\Delta E_c = a_c\left(\frac{\Delta\Omega}{\Omega}\right) + \delta_c\left(\frac{\Delta\Omega}{\Omega}\right)^2 \tag{13}$$

where $a_c$ and $a_v$ are conduction-band hydrostatic deformation and valence-band hydrostatic deformation, respectively. $\delta_c$ and $\delta_v$ parameterize the quadratic terms for hydrostatic deformation of conduction-band and valence-band. $b$ is tetragonal deformation.

Using Eqs. (12) and (13) the function of $E_{1h}$ is given by

$$\begin{aligned}E &= E_0 + \Delta E_c - \Delta E_v\\ &= E_0 + (a_c - a_v)\frac{\Delta\Omega}{\Omega}\\ &\quad + (\delta_c - \delta_v)\left(\frac{\Delta\Omega}{\Omega}\right)^2 + b(\mathrm{E}_{zz}{}^{(b)} - \mathrm{E}_{xx}{}^{(b)})\\ &= E_0 - \frac{a_c - a_v}{B}p + [\gamma(a_c - a_v)\\ &\quad - b\eta]\mathrm{E}^{(b)}(p) + (\delta_c - \delta_v)\frac{p^2}{B^2}\end{aligned} \tag{14}$$

where second-order terms, of order $\mathrm{E}p$ and $\mathrm{E}^2$, are small and have been neglected, and

$$\gamma = 2\left(1 - \frac{C_{12}}{C_{11}}\right),\ \eta = \left(1 + 2\frac{C_{12}}{C_{11}}\right).$$

The linear coefficient $\alpha$ is the slope of the pressure dependence of the PL energy. Using Eq. (14), the function of $\alpha$ would be

$$\alpha = -\frac{a_c - a_v}{B} + \frac{a_{eq}}{3a}\left[\frac{1}{B} - \frac{1}{B_{eq}}\right][\gamma(a_c - a_v) - b\eta] \tag{15}$$

The material parameters for ZnSe and $Zn_{1-x}Cd_xSe$ are listed in Table 1.

The linear coefficient by the above calculation is 70.9 meV $GPa^{-1}$ which is in good agreement with the value 67.1 meV $GPa^{-1}$ obtained by experiment.

The effect of pressure on the $E_{1h}$ transition shows the small sublinear dependence of PL energy with pressure, the same as bulk ZnSe [12] and CdSe [13]. Tuchman et al. [12] gave a study of exciton photoluminescence in strained and unstrained ZnSe under hydrostatic pressure, and pointed out that the small sublinear dependence of PL energy with pressure for ZnSe is attributed to the pressure dependence of the bulk modulus. So the small sublinear behaviour in Fig. 3 was also ascribed to the bulk modulus of the superlattices changing with the pressure. In the $Zn_{1-x}Cd_xSe$/ZnSe single quantum wells [9], the effect of pressure on the $E_{1h}$ transition exhibited linear behaviour at 80 K, we note that single quantum well and superlattices have a different effect of pressure on the bulk B because of the difference of structures. Another

Table 1
The parameters used in calculation

| | $a$ (nm) | $a_c - a_v$ (eV) | $b$ (eV) | $C_{11}$ ($10^{-11}$ Pa$^{-1}$) | $C_{12}$ ($10^{-11}$ Pa$^{-1}$) | $B$ (GPa) | $t$ (nm) |
|---|---|---|---|---|---|---|---|
| ZnSe | 0.5669 [a] | −4.37 [b] | −1.2 [b] | 8.26 [b] | 4.98 [b] | 61 [a] | 2400 [d] |
| CdSe | 0.6052 [a] | −3.664 [b] | −0.8 [b] | 6.67 [b] | 4.63 [b] | 53 [a] | |
| $Zn_{0.74}Cd_{0.26}Se$ | 0.5769 [c] | −4.186 [c] | −1.05 [c] | 7.85 [c] | 4.89 [c] | 58.9 [c] | 600 [d] |

[a] Ref. [11].
[b] Ref. [16].
[c] Linearly interpolated from the values of ZnSe and CdSe parameters.
[d] Measured by SEM and X-ray diffraction.

possible explanation was that the transition $E_{1h}$ had different temperature effects at 77 K and room temperature, respectively. The sublinear behaviour was also observed in the $ZnSe/Zn_{1-x}Mn_xSe$ strained superlattices [14].

The intensity of the PL signal from the sample was observed to decrease rapidly with pressure. At the pressure of 2.52 GPa, the PL intensity is too weak to measure. The phase transition in ZnSe is 13.7 GPa. The bulk $Zn_{0.74}Cd_{0.26}Se$ shows no structural phase transition at least up to 7 GPa [9]. In the low-pressure region, we can conclude there is no phase transition. So the above effect is unlikely to be caused by a structural phase transition. Another explanation for the decrease in PL intensity might be a conversion from type I to type II in the $ZnSe/Zn_{0.74}Cd_{0.26}Se$ strained superlattices under hydrostatic pressure. In our measured pressure region, the shape and the linewidth of the PL spectra undergo no great change [15], the calculation result of the pressure coefficient is consistent with type I band alignment. So we can rule out the possibility of an indirect level crossing in the $Zn_{0.74}Cd_{0.26}Se$ well as a cause of the loss of intensity. The detailed origin is not clear up to now, maybe it is associated with non-radiation of the $E_{1h}$ transition.

## 5. Conclusions

A study of the PL measurements under hydrostatic pressure on the $ZnSe/Zn_{0.74}Cd_{0.26}Se$ strained superlattices has been performed. This is the first study of the pressure dependence of PL at room temperature in II–VI semiconductor quantum wells and superlattices. The effect of pressure on the $E_{1h}$ transition shows a small sublinear behaviour. The pressure coefficients were obtained by least-squares fits of a computer. The linear coefficient by calculation is in good agreement with that of experiment. A large loss of intensity phenomenon was observed at the low-pressure region. The origin is not clear up to now. Further studies under hydrostatic pressure on similar samples at 77 K are in progress to explain this phenomenon.

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## References

[1] M.A. Haase, J. Qiu, J.M. Depuydt and H. Cheng, *Appl. Phys. Lett., 59* (1991) 1293.

[2] U. Venkateswaran, M. Chandrasekhar, H.R. Chandrasekhar, B.A. Vojak, F.A. Chambers and J.M. Meese, *Phys. Rev. B, 33* (1986) 8416.

[3] G. Li, D. Jiang, H. Han, Z. Wang and K. Ploog, *Phys. Rev. B, 40* (1989) 10 430.

[4] W. Shan, X.M. Fang, D. Li, S. Jiang, S.C. Shen, H.Q. Hou, W. Feng and J.M. Zhou, *Phys. Rev. B, 43* (1991) 14 615.

[5] G.H. Li, B.Z. Zheng, H.X. Han and Z.P. Wang, *Chin. J. Semiconduct., 12* (1984) 177.

[6] J. Wolford and J.A. Bradley, *Solid State Commun., 53* (1985) 1069.

[7] J. Ding, N. Pelekanos, A.V. Nurmikko, H. Luo, N. Samarth and J.K. Furdyna, *Appl. Phys. Lett., 57* (1990) 2885.

[8] J.Y. Zhang, X.W. Fan, B.J. Yang, Z.P. Guan, Y.M. Lu and D.Z. Shen, *J. Cryst. Growth, 138* (1994) 838.

[9] R.J. Thomas, H.R. Chandrasekhar, M. Chandrasekhar, N. Samarth, H. Luo and J. Furdyna, *Phys. Rev. B, 45* (1992) 9505.

[10] F.D. Murnaghan, *Proc. Natl. Acad. Sci., USA, 30* (1994) 244.

[11] Judah A. Tuchman and Irving P. Herman, *Phys. Rev. B, 45* (1992) 11 929.

[12] Judah A. Tuchman, Sangsig Kim, Xhifeng Sui and Irving P. Herman, *Phys. Rev. B, 46* (1992) 13 371.

[13] J.R. Mei and V. Lemos, *Solid State Commun., 52* (1984) 785.

[14] Judah A. Tuchman, Zhifeng Sui, Sangsig Kim and Irving P. Herman, *J. Appl. Phys., 73* (1993) 7730.

[15] Yoichi Yamada, Yasuaki Masumoto, Tsunemasa Taguchi and Kenichi Takermura, *Phys. Rev. B, 44* (1991) 1801.

[16] H.J. Lozykowski and V.K. Shastri, *J. Appl. Phys., 69* (1991) 3235.