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# Strain-Induced Electronic States of a CdZnS/ZnS Quantum Well and Its Application to UV Laser Diode

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Strain-induced electronic states and lasing emission properties have been investigated in $Cd_xZn_{1-x}S/ZnS$ quantum wells (x=0.31). Relatively large conduction- and valence-band offsets can be obtained using the model-solid theory : $\Delta E_c$=260 meV and $\Delta E_v$=180 meV. Effective quantum confinement of electrons and holes is suggested in this system and is useful for designing ultraviolet (UV) laser diode. Preliminary calculation of external uniaxial stress effect on the band offset indicates that the energy difference between a heavy-hole in CdZnS and a light-hole in ZnS increases monotonously with increasing stress. The UV stimulated emission was observed in the vicinity of 375 nm under pulsed injection at 30 K.

## 1. INTRODUCTION

Since the first successful reports of II-VI green-blue laser[1] and blue laser[2] diodes, development of II-VI quantum well lasers in the ultraviolet (UV) wavelength (370 - 390 nm) has become the "final target" in the fields of optical storage memory devices.

A great success in the fabrication of UV photodetectors[3,4] and optically pumped lasers[5,6] has been reported on ZnS-based quantum wells which have the largest band-gap energy and exciton-binding energy among II-VI materials. $Cd_xZn_{1-x}S$-based quantum well structures exhibit fundamental absorption edges which can be varied from green to UV[3,4].

The first investigation[5,6] of the UV stimulated laser emission has been done, which lead to the possibility of producing an ultraviolet laser diode from this type of the SLS based on ZnS.

We will report the electronic states of the CdZnS quantum well under external uniaxial strain and ultraviolet stimulated emission of CdZnS/ZnS MQWs under pulsed injection conditions.

## 2. STRAIN-INDUCED ELECTRONIC STATES

### 2.1 Conduction- and valence-band offsets

The CdZnS and ZnS layers are subject to biaxial compressive and tensile strains, respectively, along the <100> direction in the (100) plane. This effect breaks the crystal symmetry from tetrahedral ($T_d$) to tetragonal ($D_{2d}$) and removes the degeneracy of the valence band. This splitting under the $D_{2d}$ distortion results in a significant change in the valence band dispersion on the layer plane. In addition, the hydrostatic component shifts the band gap to a higher or lower energy. The effects of uniaxial strains split the uppermost degenerate valence bands into the heavy-hole and light-hole bands. We used a strain Hamiltonian with a (6x6) secular matrix on the basis of k・p interaction under the condition where the spin-orbit energy is taken into account[7]. The strain-dependent hole dispersion relations to order $k^2$ gives hole energies 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. The heavy-hole ($E_{hh}$) and light-hole ($E_{lh}$) energy are given by following equations, respectively,

$$E_{hh}(k) = H_{hh}(k) + \varepsilon, \qquad \ldots\ldots (1)$$

$$E_{lh}(k) = -\tfrac{1}{2}\Delta_{so}(1+x) + \tfrac{1}{4}(3H_{lh}(k)+H_{hh}(k)) + \tfrac{1}{2}\Delta_{so}(1-2x+9x^2)^{1/2}\{1+(D/\Delta_{so}) \; 1-9x/1-2x+9x^2 + 9/4\,(D/\Delta_{so})^2 \; 1/1-2x+9x^2\}^{1/2}, \qquad \ldots\ldots (2)$$

where $\varepsilon$ is the strain energy described by $[2/3D_u(e_{zz}^{(001)} - e_{xx}^{(001)}]$, $\Delta_{so}$ is the spin-orbit energy and x is given by $\varepsilon/\Delta_{so}$.

The valence-band offset ($\Delta E_{v:hl}$) is here defined by the energy difference between the heavy-hole state (h) in CdZnS and the light-hole state (l) in ZnS without external uniaxial strain. When $k_x=k_y=k_z=0$, $H_{hh}(k)$ and $H_{lh}(k)$ become zero.

The band offsets for the valence and conduction bands between the well and barrier layers are then calculated using following relations[8], respectively,

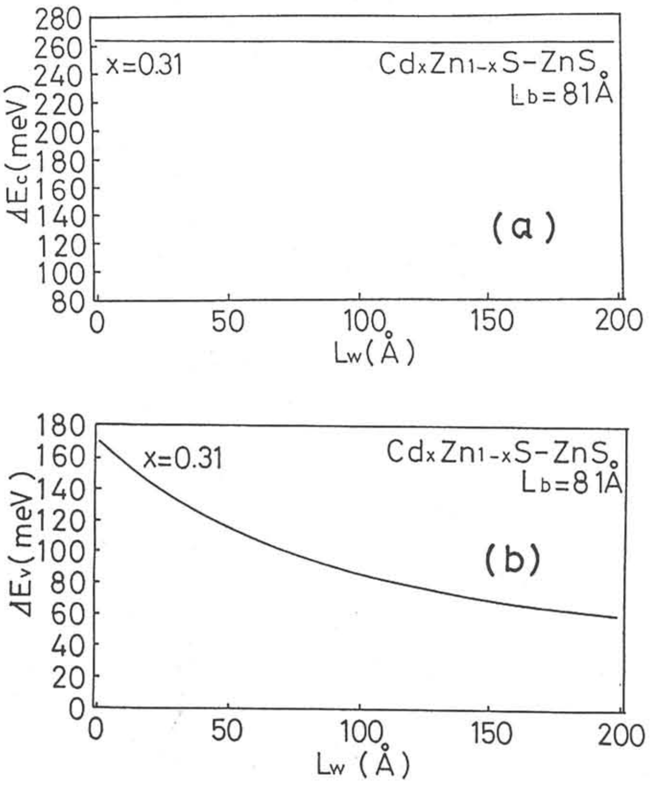


Fig. 1 Band offsets of the conduction band (a) and the valence band (b) in the CdZnS/ZnS system as a function of CdZnS well width with a constant barrier width of 81 Å.

$$\Delta E_c = E_c(b) - E_c(w) \quad \text{..... (3)}$$

$$\Delta E_{vhh} = E_{hh}(w) - E_{lh}(b) \quad \text{..... (4)}$$

where $E_c(b)$ and $E_{lh}(b)$ are the energies of the conduction and light-hole bands of the barrier layer, respectively, and $E_c(w)$ and $E_{hh}(w)$ are the energies of the conduction and heavy-hole bands of the well layer, respectively.

Using the physical parameters listed in ref. 9, the offset values of the conduction ( $\Delta E_c$) and valence ( $\Delta E_v$) band were calculated as a function of CdZnS well width with a constant barrier layer ($L_b$=81 Å) as shown in Figs. 1 (a) and (b), respectively. These results clearly indicate that the band lineup is type I ,and in addition that the quantum confinement of electrons and holes in the alloyed potential well becomes strong with decreasing well width as expected.

## 2.2 Effect of uniaxial stress on the band offsets

When external uniaxial compression is applied parallel to the plane of the quantum well interface between the well and barrier layer, changes in energies of the well layer appear as same as that in the barrier layers. As a result, the changes in energy states of the band offsets [energy difference: $\Delta E_{hh(CdZnS)-hh(ZnS)}$ (heavy-hole in CdZnS and light-hole in ZnS, $\Delta E_{hh(CdZnS)-lh(ZnS)}$ , $\Delta E_{lh(CdZnS)-hh(ZnS)}$ and $\Delta E_{lh(CdZnS)-lh(ZnS)}$) strongly depend on physical parameters such as deformation potential (a, b) and elastic ($C_{ij}$) constants in the well and barrier layers.

The energies of heavy-hole and light-hole bands under uniaxial stress are expressed as follows using eqs. (1) and (2) under the condition of $\Delta_{so} > \varepsilon$, respectively.

$$E_{vhh} = E_{v0hh} + E_H + \varepsilon \quad \text{..... (5)}$$

$$E_{vlh} = E_{v0lh} + E_H - 1/2(\varepsilon + \Delta_{so}) + 1/2(9\varepsilon^2 + \Delta_{so}^2 - 2\varepsilon\Delta_{so}) \quad \text{..... (6)}$$

where $E_{v0hh}$ and $E_{v0lh}$ are the energy of the uppermost valence band in the strained-layer quantum well, $E_H$ is the energy under hydrostatic pressure and described by $a_v(C_{11}-C_{12}/C_{11})$, and $\varepsilon$ is expressed by $b(C_{11}+2C_{12}/C_{11})X$.

Figure 2 shows the changes in energy of four band offsets appearing in the valence band as a function of external uniaxial stress up to 10 kbar. In CdZnS layers containing a large composition of Cd, b becomes large ( CdS:-4.7 eV and ZnS:-0.7 eV) and consequently an abnormal condition such as $\Delta_{so} = \varepsilon$ or $\Delta_{so} < \varepsilon$ can be established around 10 kbar.

With increasing external stress the energy difference in the heavy-hole related band offsets ($E_{hh}$ or $E_{v:hl}$) is monotonically increased as shown in Fig. 2. However, that of the light-hole related band offsets is clearly different from that of heavy-hole related band offsets. The band offset is generally determined by an energy difference between the heavy-hole in CdZnS well and the light-hole in ZnS barrier and is monotonically increased up to 10 kbar (about 6 meV/kbar).

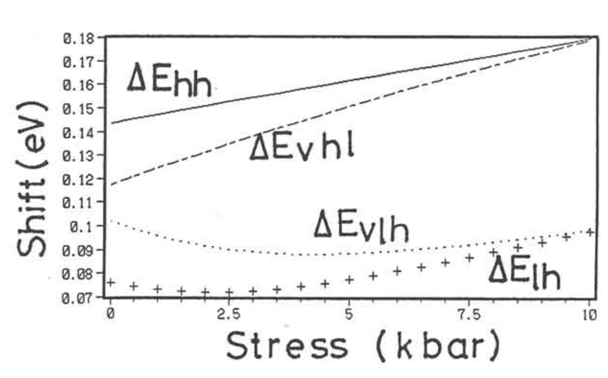


Fig. 2 Changes in the energy difference of the heavy-hole and light-hole related band offsets as a function of external uniaxial stress.

3. SPECTRAL NARROWING and STIMULATED EMISSION

The laser diode (LD) structure with a 1-mm-long resonator was fabricated on a layer of n-type ZnS doped with iodine (ZnS:I ) / (100) $n^+$ GaAs substrate and was based on a window stripe structure with a length of 2000 μm and a stripe width of 15 μm as shown in the insert of Fig. 3. The forward current flow layer was $SiO_2$. The active layer was a MWQ structure consisting of 10 pairs of 41Å undoped CdZnS well layers and 81Å ZnS barrier layers. This MQW structure was embedded in a p-n junction made from ZnS layers doped with Na[10] acceptors and I[11] donors.

Figure 3 shows the stimulated emission spectrum at 30 K from the MQW $Cd_{0.3}Zn_{0.7}S$/ZnS ($L_w$=41Å and $L_b$=81Å) p-n junction diode under a forward bias condition. Typical characteristics of LD with both cleaved facets under pulsed operation at 30 K are shown in this figure. The pulse width and the repetition rate were 300 nsec and 4 Hz, respectively. Spontaneous emission was obtained at 371.5 nm at 8 V and its linewidth was estimated to be about 20 nm.

From the voltage-versus-current characteristics, the built-in voltage for causing stimulated emission was 30 V. Above 30 V, the emission intensity becomes strong and the peak position moves towards the longer-wavelength side (about 40 meV) in comparison with that of spontaneous emission.

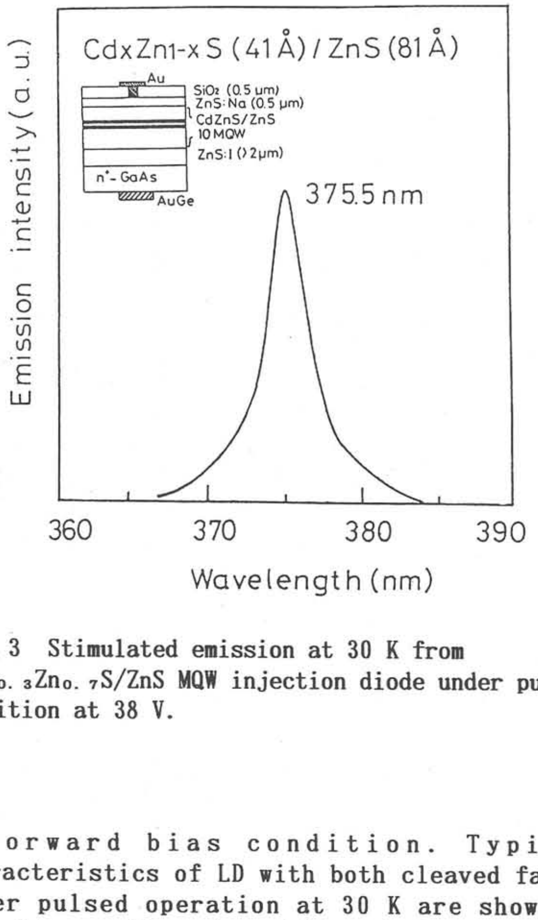


Fig. 3 Stimulated emission at 30 K from a $Cd_{0.3}Zn_{0.7}S$/ZnS MQW injection diode under pulsed condition at 38 V.

The stimulated emission of linewidth less than 3 nm was clearly observed at the wavelength of 375.5 nm above the threshold current of about 6 kA/cm$^2$ at 38 V.

4. CONCLUSIONS

The CdZnS/ZnS strained-layer quantum well is a very promising candidate for UV laser diode in the wide-gap II-VI semiconductors because of the large conduction and valence band offsets. External uniaxial stress can significantly modify the band offsets of the valence band.

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