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# Donor–acceptor pair luminescence in Zn<sub>0.8</sub>Cd<sub>0.2</sub>Se–ZnSe strained-layer superlattice

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## Abstract

The optical property of a  $Zn_{0.8}Cd_{0.2}Se$ –ZnSe strained-layer superlattice (SLS) has been investigated by making use of photoluminescence and time-resolved spectra. It is found that the donor–acceptor pair (DAP) band shifts towards lower energy with decreasing excitation density and increasing delay time. The luminescence lifetime of the DAP band is slower than that of the exciton luminescence. On the basis of these results the DAP band originates from the radiative recombination of the donor–acceptor pair in  $Zn_{0.8}Cd_{0.2}Se$ –ZnSe SLS. © 1997 Elsevier Science S.A.

Keywords: Organometallic vapour deposition; Superlattices; Optical properties; Surface and interface states

## 1. Introduction

II–VI wide-gap semiconductor quantum well and superlattice structure materials have attracted much attention since Haase et al. [1] observed the blue–green laser in the  $Zn_{0.8}Cd_{0.2}Se$ –ZnSe quantum well laser diode. But most of them concentrate attention on the impurity behavior in the confined layers of p or n types and the excitonic optical property in quantum well and superlattice structures, while the study of impurity behavior in superlattice is limited. In this paper, we report the observation of donor–acceptor (D–A) pair luminescence in undoped  $Zn_{0.8}Cd_{0.2}Se$ –ZnSe strained-layer superlattices (SLS).

#### 2. Experimental details

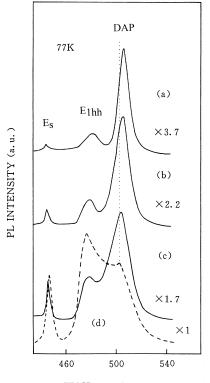
The Zn<sub>0.8</sub>Cd<sub>0.2</sub>Se–ZnSe SLS sample used in this experiment was grown by atmospheric pressure metal organic chemical vapor deposition (AP-MOCVD) at 320 °C. Dimethylzinc (DMZn), dimethylcadmium (DMCd) and H<sub>2</sub>Se were used as the source materials. The sample structure was composed of 120 periods of 7 nm Zn<sub>0.8</sub>Cd<sub>0.2</sub>Se, 7.5 nm ZnSe, with 0.5  $\mu$ m ZnSe cladding and 1.6  $\mu$ m ZnSe buffer layers grown on a GaAs (100) substrate. The photoluminescence (PL) was excited by the 337.1 nm line of a Model UV-24 pulsed  $N_2$  laser. The laser pulse was 10 ns in duration. The spectral distribution of luminescence was carried out using a SPEX 1404 double grating spectrometer with an RCA-C31034 cooled photomultiplier. The luminescence decay and time-resolved spectra (TRS) were measured by a Model 4400 Boxcar Averaging System.

### 3. Results and discussion

Fig. 1 shows PL spectra of the Zn<sub>0.8</sub>Cd<sub>0.2</sub>Se–ZnSe SLS under different excitation densities at 77 K. Three luminescence peaks named E<sub>s</sub>, E<sub>1hh</sub> and donor-acceptor pair (DAP), respectively were observed. The peak positions at the excitation density of 0.08 MW cm<sup>-2</sup> are located at 445.5 nm, 478.8 nm and 505.3 nm, respectively. Among them, the  $E_s$ band is the radiative recombination from exciton-carrier scattering in the ZnSe cladding layer. One of the most interesting aspects concerns the origin of the DAP band. It is found that the DAP and  $E_{1hh}$  bands all shift towards the higher energy with increasing excitation density. In order to get a clear understanding of the origin of DAP band the luminescence decay curves of E<sub>1hh</sub> and DAP bands are shown in Fig. 2. Their recombination lifetimes are 7.5 ns and 11.5 ns, respectively. As the lifetime of DAP band is slower than that of the  $E_{1hh}$  band, it demonstrates that their luminescence mechanisms are different. The TRS can help us to further understand the origin of DAP band. Fig. 3 shows the time dependence

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WAVELENGTH (nm)

Fig. 1. PL spectra of  $Zn_{0.8}Cd_{0.2}$ Se–ZnSe SLS at 77 K under different excitation densities of (a) 0.04 MW cm<sup>-2</sup>, (b) 0.08 MW cm<sup>-2</sup>, (c) 0.2 MW cm<sup>-2</sup> and (d) 0.5 MW cm<sup>-2</sup>.

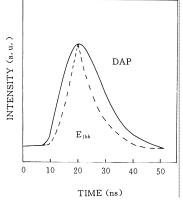


Fig. 2. The averaged normalized luminescence decay curves for  $E_{\rm 1hh}$  (---) and DAP (\_\_\_\_\_) bands in  $Zn_{0.8}Cd_{0.2}Se-ZnSe$  SLS.

of measured PL spectra at 77 K. From Fig. 3 the DAP band shifts towards the lower energy with increasing delay time, while the peak position of  $E_{1hh}$  band undergoes no change with increasing delay time. The  $E_{1hh}$  band should be ascribed to exciton luminescence of the n = 1 heavy hole [2]. It exhibits an intense phase space filling effect of the exciton states with increasing excitation density. Based on previous experiment results in  $Zn_{0.8}Cd_{0.2}Se$ –ZnSe SLS, it indicates that the luminescence behavior of DAP band is just the feature of donor–acceptor (D–A) pair luminescence. It is well known that the energy of photon resulting from D–A pair transition is given by [3]

$$E(r) = E_{\rm g} - (E_{\rm d} + E_{\rm a}) + \frac{e^2}{\epsilon \cdot r}$$
(1)

where  $E_g$  is the energy bandgap,  $E_d$  and  $E_a$  are the donor and acceptor binding energies, respectively,  $\epsilon$  is the dielectric constant, r is the separation between donor and acceptor, and  $e^2/\epsilon \cdot r$  is the Coulomb interaction. As the different intra-pair separations contribute to the luminescence, the optical transition probability of the pair emission W(r) is expressed by [4]

$$W(r) = W_0 \exp\left(\frac{-r}{R_{\rm b}/2}\right) \tag{2}$$

where  $W_0$  is a constant and  $R_b$  is the Bohr radius. From Eq. (2), the transition probability decreases with increasing separation of the D–A pair. Therefore, the distant pair contribution to luminescence becomes larger with increasing delay time. As can be seen in Fig. 3, the luminescence intensity decreases with increasing delay time. According to Eq. (1), the photon energy emitted by a D–A pair decreases with increasing pair separation, i.e. the peak position of DAP band in Fig. 3 shifts towards lower energy with increasing delay time. On the other hand, from Fig. 1, the peak position of DAP band shifts to higher energy with increasing excitation density. This demonstrates that the recombination of the closer D–A pair is dominant. At room temperature, we obtain the same characteristic for DAP band as is obtained in PL spectra of different excitation densities and in TRS at 77 K.

On the basis of the above results and analysis, the DAP band in  $Zn_{0.8}Cd_{0.2}Se$ –ZnSe SLS originates from the radiative recombination of a D–A pair. Why does it occur in the undo-

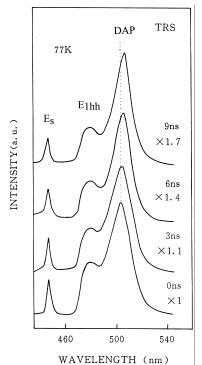


Fig. 3. Time-resolved spectra (TRS) of  $Zn_{0.8}Cd_{0.2}Se$ –ZnSe SLS at 77 K under the excitation density of 0.25 MW cm<sup>-2</sup>.

$$\Delta N = N_1 - N_2 \approx 2Nf \quad N = \frac{4}{a_{1,2}^2}$$
(3)

where *N* is the surface density of chemical bond on either semiconductor which depends only on the lattice constants  $a_{1,2}$  and the particular interface plane. The lattice mismatch *f* between Zn<sub>0.8</sub>Cd<sub>0.2</sub>Se and ZnSe is 1.4%,  $N=1.25 \times 10^{15}$ cm<sup>-2</sup> and  $\Delta N=3.5 \times 10^{13}$  cm<sup>-2</sup>. Because the lattice constant of Zn<sub>0.8</sub>Cd<sub>0.2</sub>Se is larger than that of ZnSe, the dangling bonds are mainly located at the ZnSe side near the interface. It is a capture center which can catch electron from the valence band of Zn<sub>0.8</sub>Cd<sub>0.2</sub>Se. The donor impurity can be introduced by the pollution of cadmium source. As mentioned above, it is reasonable to suggest that the dangling bonds in the interface of Zn<sub>0.8</sub>Cd<sub>0.2</sub>Se–ZnSe SLS should act as the acceptor of the D–A pair. Our earlier work [6] has reported the radiative recombination of D–A pair observed in ZnSe–ZnS SLS based on the same explanation.

#### 4. Conclusion

The luminescence of the DAP band in  $Zn_{0.8}Cd_{0.2}Se$ –ZnSe SLS originates from the radiative recombination of a D–A

pair determined by PL spectra under different excitation densities and TRS with increasing delay time. It suggests that the dangling bonds in the interface of  $Zn_{0.8}Cd_{0.2}Se$ –ZnSe SLS, which can catch electrons, act as the acceptor.

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