



OPTICAL STUDIES ON EPITAXY FILMS AND SUPERLATTICES OF DILUTED MAGNETIC SEMICONDUCTOR $Zn_{1-x}Mn_xSe$

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$Zn_{1-x}Mn_xSe$ films and $Zn_{1-x}Mn_xSe/ZnSe$ superlattices with different composition x have been grown by molecular beam epitaxy (MBE). Superlattice structure transference from ZnSe as a well to $Zn_{1-x}Mn_xSe$ as a well has been observed for the first time by photoluminescence measurements at small values of x when the temperature increases. It is due to the anomalous behavior of the energy gap at low x in $Zn_{1-x}Mn_xSe$, which forms a bow region and the shape of this bow and the dip in energy gap are dependent strongly on temperature. It has been found by time-resolved photoluminescence spectra that the relaxation time of Mn^{++} ions in excited states in superlattices is much longer than that in thin films. This may be attributed to a low-dimensional scaling effect on the exchange interaction between Mn^{++} ions.

Keywords: A. semiconductors, quantum wells, thin films, D. optical properties, D. electronic band structure

1. Introduction

Diluted magnetic semiconductors (DMS) are new typical semiconductor compounds in which a fraction of the nonmagnetic cations is randomly substituted by magnetic ions. The most extensively studied and thoroughly understood materials of this type are the $A_{1-x}^{II}Mn_xB^{VI}$ alloys. The strong exchange interactions between localized magnetic ions and band electrons (sp-d exchange interaction) and between localized magnetic ions themselves (d-d exchange interaction) in these

materials lead to a series of interesting properties, such as extremely large Zeeman splitting, the giant Faraday effect and the formation of bound magnetic polarons.^[1] The recent development of molecular beam epitaxy (MBE) for II-VI materials allows precisely controlled growth of high-quality DMS, which opens new possibilities for the study of blue-green optical electron devices with DMS-base quantum well structures.^[2,3] Recently, unusual dynamical properties of low-dimensional systems incorporating magnetic spins have been reported.^[4] In this paper we report the results on photolumines-

cence (PL) and time-resolved PL measurements in $Zn_{1-x}Mn_xSe$ epitaxy films and $Zn_{1-x}Mn_xSe/ZnSe$ superlattices with different compositions x . Superlattice structure that transferred from ZnSe as a well to $Zn_{1-x}Mn_xSe$ as a well has been observed for the first time for small values of x when the temperature increases.

2. Experiment

$Zn_{1-x}Mn_xSe$ epitaxy films with different composition were grown directly by MBE on GaAs (100) substrates. The values of x were determined by x-ray diffraction and x-ray energy spectra using a scanning electron microscope. $Zn_{1-x}Mn_xSe/ZnSe$ superlattices with different compositions were grown by MBE on GaAs (100) substrates. Typically, for sample labelled LS-1: the structure consists of a ZnSe buffer layer (~ 500 nm), followed by 30 periods of $Zn_{1-x}Mn_xSe/ZnSe$ (layer width of $Zn_{1-x}Mn_xSe$ = layer width of ZnSe = 30\AA) and with a 30 nm cap layer. The well widths L_W (or barrier widths L_B) of the different samples are 30\AA , 50\AA , and 100\AA .

The reflection spectra of $Zn_{1-x}Mn_xSe$ epitaxy films with different x were carried out at 300 K and 77 K. PL measurements of all samples were excited by N_2 molecular laser at $\lambda=337.1$ nm in a temperature range 20 K–300 K. The excitation of time-resolved PL measurements was provided by a three-harmonic Nd: YAG laser, producing 200 ps pulses with a 10 Hz repetition at 353 nm and the signals were detected by a trigger-controlled streak camera and then computer analysed.

3. Results and Discussion

The energy gap E_g of $Zn_{1-x}Mn_xSe$ as a function of composition x at different temperatures is shown in Fig. 1, where the data at 300 K and 77 K were obtained by reflection spectra measurements from hot wall epilayers and MBE epilayers, respectively. Experimental results show that for the variation of E_g with x there exists an anomalous behavior in the low x region, which forms a bow region and the shape of this bow and the dip in energy are strongly dependent on temperature. The reason for this anomalous behavior is the strong sp-d interaction in $Zn_{1-x}Mn_xSe$

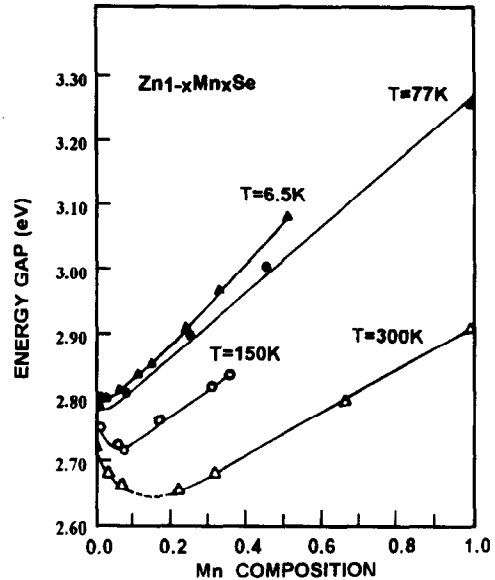


Fig. 1. Energy gap E_g as a function of Mn composition x for $Zn_{1-x}Mn_xSe$ at different temperatures. The data at 77 K and 300 K are from MBE epitaxy films and hot wall epitaxy films respectively using reflection spectra measurements. The data at 6.5 K and 150 K are from ref. 6 and ref. 7 respectively.

[5] It is suggested that the superlattice structure of $Zn_{1-x}Mn_xSe/ZnSe$ can be transferred from ZnSe as a well to $Zn_{1-x}Mn_xSe$ as a well when the values of x and the temperature are controlled carefully.

Typical PL spectra of $Zn_{1-x}Mn_xSe/ZnSe$ superlattice SL-1 with $x=0.08$, $L_W=L_B=30\text{\AA}$ at different temperatures are shown in Fig. 2. Three PL peaks with different energy positions are observed at 20 K. The strong peak (11 H) at 2.792 eV corresponds to free excitonic recombination from $n=1$, subband of conduction band, to $n=1$, heavy hole subband of valence band, in ZnSe well. The weaker peak at 2.766 eV is assumed to be associated with bound excitonic recombination,^[2] since the energy of this peak is much lower than that of light hole excitons.^[8] The third PL peak at 2.730 eV may be related to impurity emission, which does not shift with temperature increase. When the temperature increase the position of the 11 H excitonic peak has a red shift and the strength of the peak decreases. A new PL peak at 2.741 eV and a weaker one at 2.761 eV have been observed at 150 K (as seen in Fig. 2). The former was assigned to the excitation recombination in

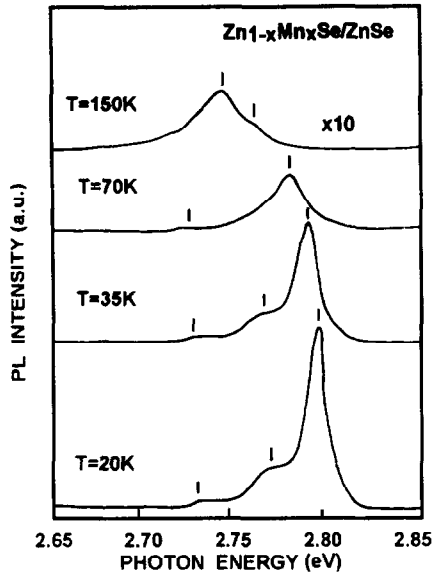


Fig. 2. PL spectra of $\text{Zn}_{1-x}\text{Mn}_x\text{Se}/\text{ZnSe}$ superlattice SL-1 at different temperatures. ($x=0.08$, $L_W=L_B=30\text{\AA}$, with 30 periods)

PL peaks at 20 K : The peak at $E=2.792\text{ eV}$ is due to free excitonic transitions (11 H), and the peak at $E=2.766\text{ eV}$ is due to bound excitonic transitions in the ZnSe well; the peak at $E=2.730\text{ eV}$ is due to transitions associated with impurities.

PL peaks at 150 K: The peak at $E=2.741\text{ eV}$ is due to excitonic transitions in the $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ well and the peak at $E=2.761\text{ eV}$ is due to transitions in the ZnSe barrier.

$\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ well rather than in ZnSe well, since the energy gap of $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ ($x=0.08$) is smaller than that of ZnSe at 150 K (as seen in Fig. 1); The $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ layer has now become a well in $\text{Zn}_{1-x}\text{Mn}_x\text{Se}/\text{ZnSe}$ superlattice structure. The weak peak at 2.761 eV may be related to transitions in the ZnSe barrier. This result shows that the transformation from ZnSe as a well to $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ as a well in $\text{Zn}_{1-x}\text{Mn}_x\text{Se}/\text{ZnSe}$ superlattice with temperature variation has, for the first time, been realized by using the anomalous character of the $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ energy gap at low x .

PL spectra of $\text{Zn}_{1-x}\text{Mn}_x\text{Se}/\text{ZnSe}$ with different x at 20 K are shown in Fig. 3. SL-1 with $x=0.08$ and SL-2 with $x=0.26$. The full width at half-maximum (EWHM) of SL-2 is larger than that of SL-1.

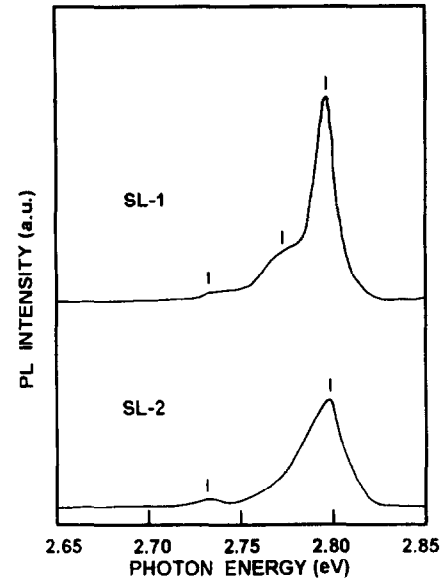


Fig. 3. PL spectra of $\text{Zn}_{1-x}\text{Mn}_x\text{Se}/\text{ZnSe}$ superlattice samples SL-1 ($x=0.08$, $L_W=L_B=30\text{\AA}$) and SL-2 ($x=0.26$, $L_W=L_B=50\text{\AA}$) at 20 K.

Typical time-resolved PL spectra of a 11 H exciton peak at 77 K and 300 K are shown in Fig. 4. (a). The relaxation time of 11 H exciton decreases from 450 ps to 370 ps when the temperature increases from 77 K to 300 K. It may be due to the stronger scattering of Mn^{++} ions in the $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ well layer, because ZnSe as a well at 77 K has been transferred to $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ as a well at 300 K.

The typical time-resolved PL spectra of the Mn^{++} ions intraband transition (${}^4T_1 \rightarrow {}^6A_1$) at 77 K are shown in Fig. 4. (b), where the upper curve corresponds to $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ epitaxy layers and the lower curve corresponds to $\text{Zn}_{1-x}\text{Mn}_x\text{Se}/\text{ZnSe}$ superlattices. The results reveal that the relaxation time of Mn^{++} ions in the excited state in $\text{Zn}_{1-x}\text{Mn}_x\text{Se}/\text{ZnSe}$ superlattices is much longer (1500 PS) than that in $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ thin films (700 ps). This may be due to change in the strength of the spin-exchange interaction between Mn^{++} ions in the low dimensional systems. A detailed study of the low dimensional scaling effect is expected in the near future.

4. Conclusion

We report the results of optical reflection, PL and time-resolved PL spectra on epitaxy layers and super-

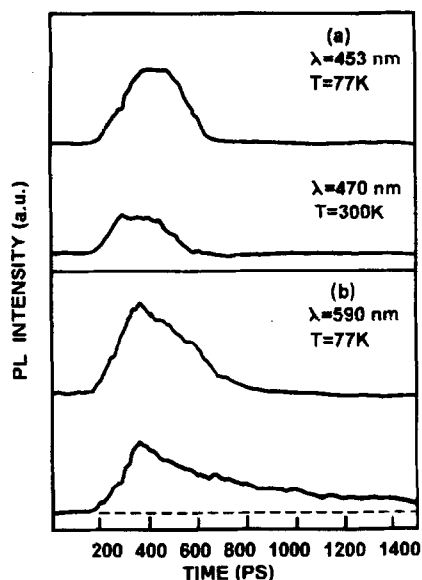


Fig. 4. Time-resolved PL spectra.

- (a) 11 H exciton transitions in $Zn_{1-x}Mn_xSe/ZnSe$ superlattice at 77 K and 300 K.
 (b) Mn^{++} ions excited state transition (${}^4T_1 \rightarrow {}^6A_1$) in $Zn_{1-x}Mn_xSe$ epitaxy layers (upper curve) and $Zn_{1-x}Mn_xSe/ZnSe$ superlattice (lower curve).

lattices in DMS $Zn_{1-x}Mn_xSe$. Superlattice structure transference from ZnSe as a well to $Zn_{1-x}Mn_xSe$ as a well has been observed when the temperature increases. The relaxation time of Mn^{++} ions in $Zn_{1-x}Mn_xSe/ZnSe$ superlattices is much longer than that in $Zn_{1-x}Mn_xSe$ thin films due to a low-dimensional scaling effect on the spin-spin exchange interaction between Mn^{++} ions.

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Reference

1. J. K. Furdyna, *J. Appl. Phys.*, **64**, R29 (1988).
2. N. Hoffman, J. Griesche, W. Heimbrodt, O. Goede and K. Jacobs, *J. Cryst. Growth*, **127**, 347 (1993).
3. B. T. Jonker, H. Abed, L. P. Fu, W. Y. Yu, A. Petrou and J. Warnock, *J. Appl. Phys.*, **75**, 5725 (1994).
4. J. J. Baumberg, D. D. Awschalom and N. Samarth, *J. Appl. Phys.*, **75**, 6199 (1994).
5. J. J. Baumberg, D. D. Awschalom and N. Samarth, *Phys. Rev.*, **B50**, 7689 (1994).
6. R. B. Bylsma, W. M. Becker, J. Kossut, U. Debska and D. Yoderhort, *Phys. Rev.*, **B33**, 8207 (1994).
7. L. Martinez, L. R. Gonzalez and W. Girit, *Phys. Stat. Sol.*, (b) **180**, 267 (1993).
8. F. Krell, A. Schulzgen, F. Hennerger, J. Puls and U. Streller, *Solid-State Electronics*, **37**, 1137 (1994).