Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Journal of Crystal Growth 249 (2003) 538–543
JOURNAL OF CRYSTAL GROWTH
www.elsevier.com/locate/jcrysgro

The effects of rapid thermal annealing on the optical properties of $Zn_{1-x}Mn_xSe$ epilayer grown by MOCVD on GaAs substrate

S.L. Lu[a,b,*], J.N. Wang[a], J.S. Huang[b], L.F. Bian[b], D.S. Jiang[b], C.L. Yang[a], J.M. Dai[a], W.K. Ge[a], Y.Q. Wang[a], J.Y. Zhang[c], D.Z. Shen[c]

[a] *Department of Physics, Hong Kong University of Science and Technology, Hong Kong, China*
[b] *Institute of Semiconductors, State Key Laboratory for Superlattices and Microstructures, Chinese Academy of Sciences, Beijing 100083, China*
[c] *Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics, and Physics, Chinese Academy of Sciences, Jilin, China*

Received 14 November 2002; accepted 25 November 2002
Communicated by M. Schieber

Abstract

$Zn_{1-x}Mn_xSe$ thin films with different Mn compositions are grown by metal-organic chemical vapor deposition on GaAs substrate. Good crystallinity of sample is evidenced by X-ray diffraction and rocking-curve measurements. Photoluminescence (PL) properties were carefully studied. A dominant PL peak close to the band edge is observed at low temperature for samples with higher Mn concentration. The temperature-dependent PL and time-resolved photoluminescence show that this emission peak is associated with the recombination of exciton bound to Mn-induced impurity bound states. It is found that rapid thermal annealing can induce reorganization of Mn composition in alloys and significantly reduce the density of impurity induced by Mn incorporation and improve the intrinsic interband transition.

PACS: 81.15.Gh; 78.55.−m; 78.47.+p; 81.40.Ef

Keywords: A1. Photoluminescence; A3. Metalorganic chemical vapor deposition; A3. Epilayer; B2. Semiconducting II–VI materials

1. Introduction

$Zn_{1-x}Mn_xSe$ belongs to a class of materials the so-called diluted magnetic semiconductors (DMS) where their cations in a non-magnetic compound were partially replaced by manganese ions. In these materials, the Mn ion is isovalent with the

*Corresponding author. Institute of Semiconductors, State Key Laboratory for Superlattices and Microstructures, Chinese Academy of Sciences, Beijing 100083, China.
E-mail address: lsljhx@red.semi.ac.cn (S.L. Lu).

0022-0248/03/$ - see front matter
doi:10.1016/S0022-0248(02)02354-0

cation. The random distribution of Mn ions over the cation sublattice leads to important magnetic effects [1]. During the past few years, extensive investigations have been devoted to research on $Zn_{1-x}Mn_xSe$ [2–5]. The recent interests on spintronics stimulate more attention on DMS. Unfortunately, the incorporation of Mn composition in the alloys means larger lattice mismatch which might generate huge number of defect and deteriorate the sample quality [6]. So the optical properties will be greatly affected due to the Mn incorporation. To the best of our knowledge, the research on photoluminescence properties of $Zn_{1-x}Mn_xSe$ epilayers grown by metal-organic chemical vapor deposition (MOCVD) in the absence of external magnetic field is scarce, though wide band gap makes it an appropriate candidate for devices with a response in the blue portion of the visible spectrum.

In current study, $Zn_{1-x}Mn_xSe$ thin films with different Mn compositions are grown by MOCVD on GaAs substrates. Good crystallinity of samples is evidenced by X-ray diffraction and rocking-curve measurements. It is found that a dominant PL peak is observed close to the band edge for the samples with higher Mn composition. The temperature dependence of the PL and time-resolved photoluminescence (TRPL) show that this emission peak is associated with the recombination of exciton bound to Mn-induced impurity bound states. We investigated the PL properties of the sample after its rapid thermal annealing. In comparison with the as-grown sample, the rapid thermal annealing (RTA) can significantly reduce the density of impurity and improve the intrinsic interband transition.

2. Experimental procedure

The samples studied here were epitaxial thin films grown by MOCVD on semi-insulating GaAs (1 0 0) substrate at 480°C. The growth was under the pressure of 76 Torr. The Mn composition was 5.8%, 12% and 19%, respectively. The samples were grown under similar conditions. RTA was carried out in a flowing N_2 gas ambient on the sample in a homemade model RTP-300 rapid thermal processor system that was heated by a halogen lamp at a temperature of 650°C for 40 s. X-ray diffraction and rocking curve measurements were performed using Philips PW1825 high-resolution X-ray diffraction system to investigate the sample quality. The PL measurement was performed in a variable-temperature (12–300 K) closed-cycle cryostat under excitation of a 325 nm line of an He–Cd continuous-wave laser. The emission signal was dispersed by a monochrometer and detected by a cooled photomultiplier tube. For the TRPL measurement, a Ti-sapphire mode-locked pulse laser was used as an excitation light source and the time-correlated signal was analyzed by a two-dimensional synchroscan streak camera with an overall resolution of better than 20 ps.

3. Results and discussions

Fig. 1(a) shows the X-ray diffraction spectra of the three samples. As can be seen from the figure, with increasing Mn concentration, the angle distance between the two phases of GaAs and $Zn_{1-x}Mn_xSe$ becomes larger and larger. The rocking curve measurements are shown in Fig. 1(b). The more is the Mn composition is, the weaker is the diffraction intensity. And with increase of the Mn composition, the FWHM becomes wider, with the values of FWHM being 0.107°, 0.207° and 0.31°, respectively. This proves that too much Mn incorporation will degrade the sample quality. The PL measurement also supports this conclusion.

Fig. 2 shows the PL spectra near the band edge of the three samples at 12 K under the same excitation power density. The intensity is normalized in order to get a clear view of the peak position. In the figure, we do not show the emission peak related to the isolated Mn^{2+} transitions which lies at about 2.1 eV [7]. For samples with high Mn concentration, a double-peak characteristic can be seen. Even for samples with 5.8% Mn concentration, a small emission shoulder is also found on the left of the dominant peak. In the case of samples with high Mn concentration, a blue shift of corresponding

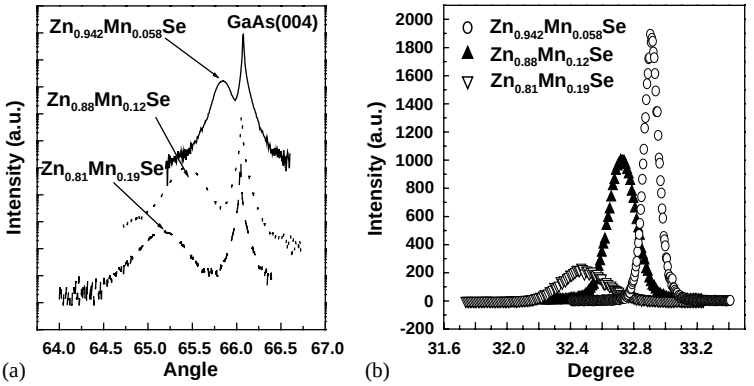

Fig. 1. (a) X-ray diffraction spectra of (0 0 4) reflection and (b) rocking curve spectra of the three samples.

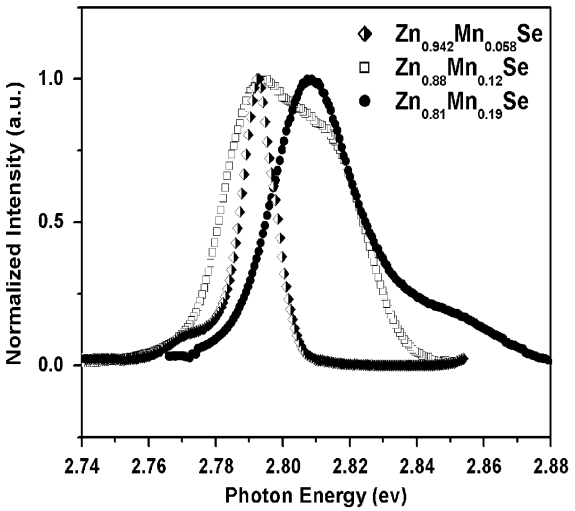

Fig. 2. Normalized PL intensity spectra of the samples at 12 K with a 325 nm laser line excitation.

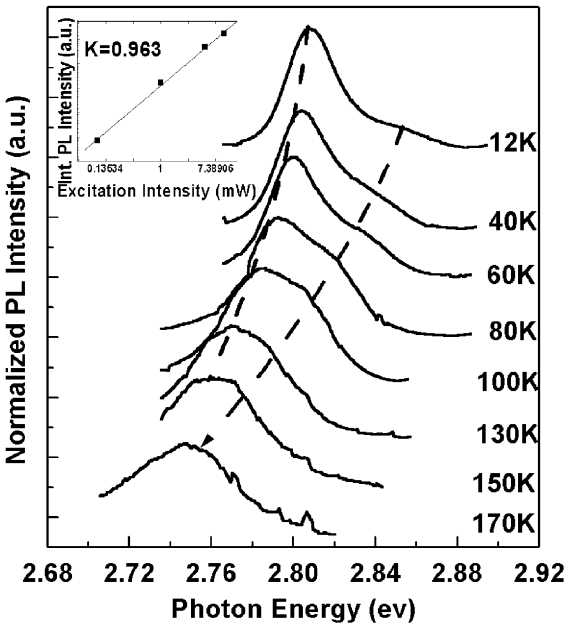

Fig. 3. Temperature dependence of PL intensity for sample with the highest Mn concentration, the inset shows the integrated PL intensity dependence on the excitation power in log scale.

emission peak is clearly seen, as a result of increasing Mn composition.

The temperature-dependent PL of the samples were performed in the experiment. Fig. 3 shows the PL spectra variations with temperature for the highest Mn concentration sample. At lower temperatures, the lower energy peak is dominant. With increase in temperature, the intensities of both peaks drop and the intensity of the two peaks changes relatively. At 150 K, the higher energy peak dominates the emission. With increasing temperature, the red shift of lower energy peak is smaller than that of the higher energy peak. At higher temperature the two peaks approach each other and look like a single one. We assign a higher energy peak to an interband excitonic transition. For lower energy peak, the behavior of its PL quenching with increasing temperature

can be attributed to carrier transfer from exciton bound state to band states and/or non-radiative centers. The inset in Fig. 3 shows the integrated PL intensity dependence on the excitation power in log scale. The rate of slope is obtained by a linear fit of the data points. The exponent value is 0.963, showing an excitonic nature. The temperature dependence of the PL can be evidently explained based on a thermal activation process. At lower temperature, the carriers are most localized to the bound states, resulting in a strong lower energy peak in comparison to higher energy peak. With increase of temperature, the carriers that localized in the bound states were thermally activated into their relevant bands or captured by non-radiative centers. The higher the temperature, the more easily the thermal depopulation process becomes. TRPL spectra also support our above assignments. Fig. 4 shows the decay curves at different photon energies. The curves are displayed in a logarithmic scale and are shifted in the vertical direction for clarity. The inset shows the decay time of PL as a function of monitored emission energy. In the high-energy region, the decay time is

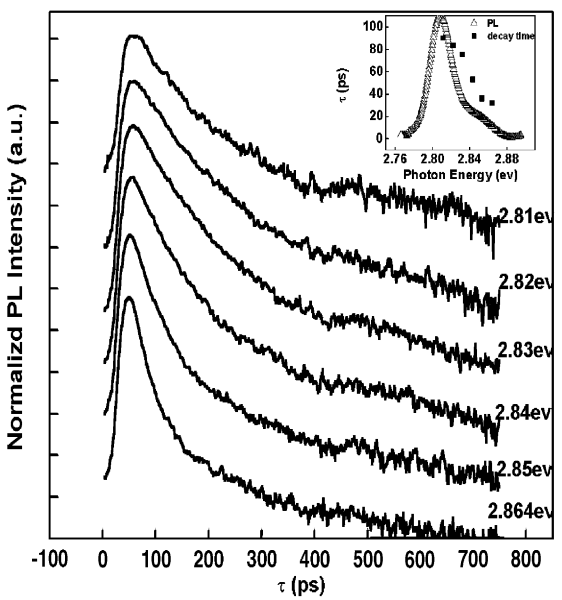

Fig. 4. Decay curves at different photon energies; the inset shows the decay time of PL as a function of monitored emission energy.

almost constant indicating a band edge radiative recombination being dominant. In the low-energy region, with decreasing energy, the decay time increases. This implies that the luminescence is more and more dominated by bound state transitions. Another clue for the existence of bound states is with increasing excitation power density, the lower energy showed a lightly blue shift and saturation, which show the nature of bound states.

Two evidences can prove that these bound states are associated with the incorporation of Mn in alloy. One is the significant difference in PL for different Mn composition samples. As can be seen from Fig. 2, the relative intensity of the two peaks becomes bigger for more Mn concentration. Another evidence is that a similar behavior of PL with temperature is also found for samples with 12% Mn concentration (not shown). However, the temperature that enables the two peaks to have equal intensity is lower than that of the highest Mn concentration. The fact that a higher Mn composition will lead to a higher transition temperature clearly indicates that the impurity bound states emission is related to Mn incorporation.

The existence of strong bound states will degrade the alloy quality and its long decay time makes it difficult to fabricate high-speed optical-electrical devices. Rapid thermal annealing has been reported to perform on ternary and quaternary alloys to remove non-radiative defects and to enhance optical properties [8–12]. However, for ZnMnSe alloy, until now, as we know, few reports exists on RTA performed on it to improve its optical properties. Here we attempt to perform RTA on the sample to observe its effect on photoluminescence. The sample is the one with the highest Mn concentration. Fig. 5(a) shows the PL for the as-grown and RTA sample at different temperatures, which is represented by the dash line and solid line, respectively. As can be seen from the figure, at 12 K, for RTA sample, the higher energy band edge peak dominates the emission. At 80 K, the bound states-related PL almost disappears and only band edge peak can be found. Compared with as-grown sample, PL related to band edge is enhanced. The temperature-depen-

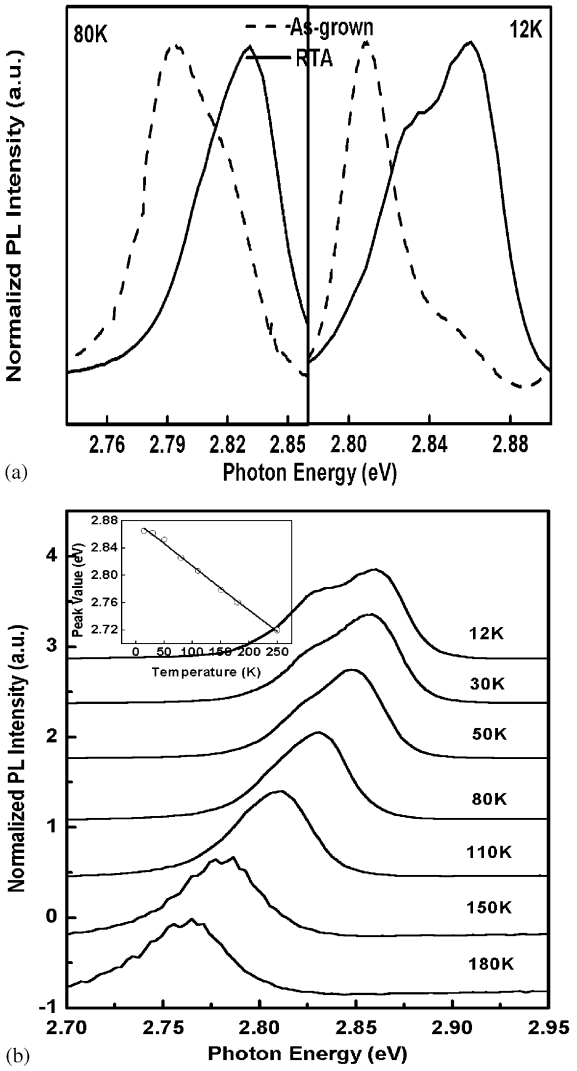

Fig. 5. (a) Comparisons of normalized PL Intensity for the as-grown and RTA sample at different temperature, which is represented by the dashed line and solid line, respectively; and (b) the temperature-dependent PL of RTA sample, the inset shows PL peak energies as a function of temperature (circle points), the solid line is the fitting curve.

dent PL of RTA sample is shown in Fig. 5(b), clearly demonstrating the PL variations with temperature. The inset shows PL peak energies as a function of temperature (circle points). For $Zn_{1-x}Mn_xSe$ alloy, the band gap variation with temperature can not be well fitted using Varshni empirical equation due to the exchange interaction between the Mn^{2+} ion and the band electrons. Bylsma et al. have shown that the x and T dependence of the energy gap, $E_g(x,T)$, can be expressed by [7]

$$E_g(x,T) = E_0 - \frac{\alpha T^2}{T+\beta} = E_0' + dx - \frac{\alpha T^2}{T+\beta} - b\chi T,$$

where E_0' is the energy gap of ZnSe at $T = 0\,K$, d is a constant and χ is magnetic susceptibility. The solid line shown in the inset is fitted using the above function under a given x value. The obtained fitting parameters are $E_0' = 2.79\,eV$, $\alpha = 0.00058\,K^{-1}$, $\beta = 56$ and $b = 1.83(eVcm^3/emu\,K)$, respectively, which is comparable to the literature values. And it also indicates that the higher energy peak in transition is related to the band edge.

The mechanism of RTA whichcan enhance the optical properties and remove the non-radiative defects is still a puzzle as different explanations are brought forward [8,12]. For our experiment, the enhancement of intrinsic band edge PL may be attributed to the removal of all kinds of defects during the growth process. The pronounced feature of the reduction of impurity in bound states indicates that the Mn in the alloy tends to distribute more uniformly and many Mn-induced defects are significantly removed, just as expressed in literature [13]. It is noted that although crystallinity of sample is evidenced by X-ray diffraction, however, the random distribution of Mn in the alloy confers it an opportunity to huddle together and induce the alloy disorder. The potential fluctuation induced by alloy disorder forms the lower energy bound states near the band edge. And the bound states will become stronger with increasing Mn concentration, just as the PL comparison of the relative intensity of the two peaks for different Mn composition samples shown in Fig. 2. We think that RTA induces reorganization of Mn inside the alloy and makes an increase in composition uniformity. So the bound states which are induced by Mn incorporation can be significantly diminished. In addition, we have to point out that a slight blue shift of PL can be found compared with the as-grown sample. Same behavior was also found in

GaNAs alloys after RTA. Further study is now in progress.

4. Conclusions

The PL spectra of $Zn_{1-x}Mn_xSe$ epilayers grown by MOCVD were carefully studied. The temperature dependent PL and TRPL show that lower energy emission peak is associated with the recombination of exciton bound to Mn-induced impurity bound states. It is observed that rapid thermal annealing can induce reorganization of Mn composition in alloys and significantly reduce the density of impurity and improve the intrinsic interband transition.

Acknowledgements

The authors would like to thank the financial support of Hong Kong Research Grant Council via grant number—HKUST DAG01/02.SC23.

References

[1] J.K. Furdyna, J. Appl. Phys. 64 (4) (1988) R29.
[2] P.J. Klar, D. Wolverson, J.J. Davies, W. Heimbrodt, M. Happ, Phys. Rev. B 57 (1998) 7103.
[3] N. Dai, H. Luo, et al., Phys. Rev. Lett. 67 (1991) 3824.
[4] A.K. Aora, E.K. Suh, U. Debska, A.K. Ramdas, Phys. Rev. B 37 (1988) 2927.
[5] C.T. Tsai, D.S. Chuu, J.Y. Leou, W.C. Chou, Jpn. J. Appl. Phys. 36 (1997) 4427.
[6] W.C. Chou, C.S. Ro, D.Y. Hong, et al., Chin. J. Phys. 36 (1998) 120.
[7] R.B. Bylsma, W.M. Becker, J. Kossut, U. Debska, Phys. Rev. B 33 (1986) 8207.
[8] L. Grenouillet, C. Bru-Chevallier, et al., J. Appl. Phys. 91 (2002) 5902.
[9] E.V.K. Rao, A. Ougazzaden, Y. Le Bellego, M. Juhel, et al., Appl. Phys. Lett. 72 (1998) 1409.
[10] R. Bhat, C. Caneau, L. Salamanca-Riba, W. Bi, C. Tu, J. Crystal Growth 195 (1998) 427.
[11] D. Kwon, R.J. Kaplar, S.A. Ringel, A.A. Allerman, S.R. Kurtz, E.D. Jones, Appl. Phys. Lett. 74 (1999) 2830.
[12] L.H. Li, Z. Pan, W. Zhang, Y.W. Lin, Z.Q. Zhou, R.H. Wu, J. Appl. Phys. 87 (2000) 245.
[13] Xiaogan Liang, Desheng Jiang, Baoquan Sun, Lifeng Bian, Zhong Pan, Lianhe Li, Ronghan Wu, J. Crystal Growth 243 (2002) 261–266.