Journal of Crystal Growth 323 (2011) 380–382

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

# Magneto-optical properties of ZnMnTe/ZnSe quantum dots

W.C. Fan [a], J.T. Ku [a], W.C. Chou [a,*], W.K. Chen [a], W.H. Chang [a], C.S. Yang [b], C.H. Chia [c]

[a] Department of Electrophysics, National Chiao Tung University, HsinChu 30010, Taiwan, ROC
[b] Graduate Institute of Electro-Optical Engineering, Tatung University, Taipei 104, Taiwan, ROC
[c] Department of Applied Physics, National University of Kaohsiung, Kaohsiung 81148, Taiwan, ROC

ARTICLE INFO

Available online 18 November 2010

*Keywords:*
A1. Nanostructures
A3. Molecular beam epitaxy
B1. Nanomaterials
B1. Zinc compounds
B2. Magneto-optic materials
B2. Semiconducting II–VI materials

ABSTRACT

The $\sigma_+$ and $\sigma_-$ circularly polarized time-integrated and time-resolved Photoluminescence (PL) measurements were employed to investigate the carrier spin dynamics of ZnMnTe/ZnSe Quantum Dots (QDs) grown on GaAs substrates by molecular beam epitaxy. The Kohlrausch's stretching exponential function well correlates both the $\sigma_+$ and $\sigma_-$ decay profiles. The measured spin relaxation time is about 23 ns.



## 1. Introduction

Spin dynamics continues to receive attention in current semiconductor research both for their basic materials science interest and for their possible future application in real spintronics devices [1,2]. Semiconductor nanostructures, particularly self-assembled Quantum Dots (QDs), are of great interest in this regard because of the long spin times that could allow control and manipulation of the electron spin [3]. Recently, spin response time of ensemble CdSe/ZnMnSe QD system was studied by the time resolved Photoluminescence (PL) measurements [4]. Nearly, complete spin polarization was observed at 5 K and magnetic field above 1 Tesla (T). However, the CdSe/ZnMnSe QD system has type-I band alignment and fast exciton recombination time. In order to have a QD system of long recombination time and spatially separated electrons and holes for possible spin manipulation, the study of spin dynamics in type-II QD system is urgent. Recently, we have found that type-II Diluted Magnetic Semiconductor (DMS) ZnMnTe QDs can be grown on ZnSe buffer by Stranski–Krastanov mode with wetting layer thickness of about 2 Mono-Layers (MLs) [5]. In current report, the time integrated and time resolved PL measurements with $\sigma_+$ and $\sigma_-$ circular polarization were carried out to investigate the spin dynamics of ZnMnTe/ZnSe QDs. Long radiative recombination time and spin relaxation time were observed.

## 2. Experimental procedure

The sample studied in this paper was grown on GaAs (1 0 0) substrate by MBE system. Prior to the growth procedure, GaAs (1 0 0) substrate was etched in a $H_2O_2$:$NH_4OH$:$H_2O$ (1:5:50) solution for 1 min at room temperature, rinsed in flowing de-ionized water for about 2 min and dried with high purity $N_2$. De-sorption and growth procedures were monitored by the Reflection High Energy Electron Diffraction (RHEED). The effusion cell temperatures of Zn, Mn, Se, and Te were at 294, 695, 178, and 310 °C, respectively. The substrate temperature was fixed at 300 °C. The growth rates for ZnMnTe QDs and ZnSe buffer layer were 0.3 and 0.4 Å/s, respectively. The ZnSe buffer layer included several ML grown by Migration Enhanced Epitaxy (MEE) and a thickness of 50 nm grown by conventional MBE. Immediately after the deposition of ZnSe buffer layer, the alternating supply method of ZnMnTe growth was performed. The alternating supply method for each ZnMnTe growth cycle described as follows: first the surface of ZnSe was exposed to Mn for 5 s, and then exposure to Zn and Te for 5 s alternately with 10 s interruption. The multiple (ZnMnTe/ZnSe) QDs sample has 5 periods with ZnMnTe coverage of 2.6 MLs and the ZnSe spacer thickness is 10 nm. Finally, the 50 nm ZnSe capping layer was grown on the QDs. The magneto-PL spectra were taken in the Faraday geometry. The sample was placed in an optical magnet cryostat and the emitted light was dispersed by a mono-chromator equipped with multichannel charged coupled device. The PL polarization was extracted by using a combination of quarter wave plate and linear polarizer. For the time-resolved PL, the GaN 405 nm pulsed laser diode was used.

## 3. Results and discussion

Fig. 1 shows the time integrated PL spectra with $\sigma_+$ and $\sigma_-$ circular polarization at $B=0$ and 5 T for a 2.6 MLs ZnMnTe/ZnSe QDs sample. The large difference in PL intensity between both polarization results from the magnetic field induced spin splitting

* Correspondong author. Tel.: +886 3 571 2121; fax.: +886 3 572 5230.
*E-mail address:* wuchingchou@mail.nctu.edu.tw (W.C. Chou).

0022-0248/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jcrysgro.2010.11.069

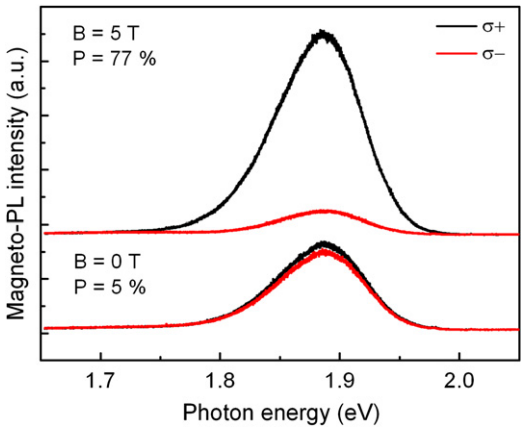


**Fig. 1.** PL spectra with $\sigma_+$ (solid line) and $\sigma_-$ (dashed line) circular polarization of a 2.6 ML multi-QD layers with 10 nm of spacer layer thickness at $B=0$ T and 5 T.

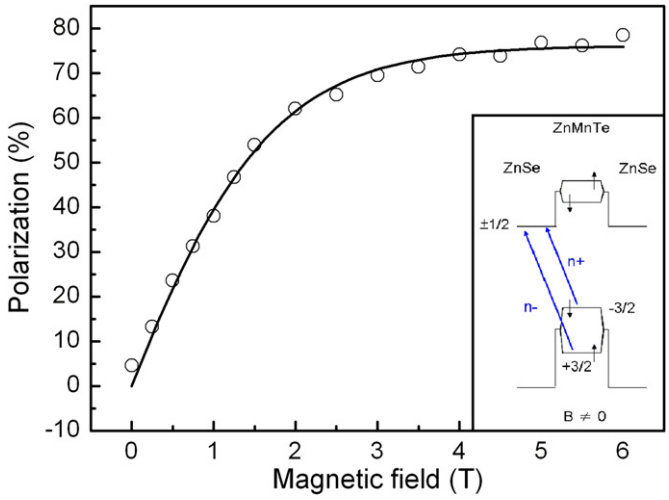


**Fig. 2.** Plot of circular polarization as a function of magnetic field at 10 K (circle). Insert: schematic conduction and heavy-hole band diagram of ZnMnTe/ZnSe quantum dots at $B>0$. The spin splitting in ZnSe is ignored.

of holes in ZnMnTe QDs and electrons in ZnSe matrix. The circular polarization $P=(I_+-I_-)/(I_++I_-)=77\%$ at 5 T, where $I_+$ and $I_-$ are the PL intensities of $\sigma_+$ and $\sigma_-$ circular polarization, respectively. The finite $P$ is unexpected for $B=0$, when there is no expected preferential direction for Mn spin alignment. This non-zero circular polarization at $B=0$ is attributed to the formation of bound magnetic polaron caused by the exchange interaction between the localized holes and Mn 3d levels in the ZnMnTe QDs.

The circular polarization degree $P$ as a function of $B$, obtained from low temperature, is shown in Fig. 2. The $P$ abruptly enhances at low $B$ and gradually saturates at high $B$. The magnetic field dependence follows the Brillouin function, which is a signature of Mn magnetism. Similar results were also observable for other DMS QDs [4,6]. The insert of Fig. 2 shows the splitting of the heavy-hole band and conduction band of ZnMnTe QD at $B>0$ and the allowed transitions for $\sigma_+$ exciton (heavy hole $-\frac{3}{2}$ spin state and electron $-\frac{1}{2}$ spin state) and $\sigma_-$ exciton (heavy hole $+\frac{3}{2}$ spin state and electron $+\frac{1}{2}$ spin state). The light hole spin states are neglected due to the large compressive strain induced heavy-light hole splitting in ZnMnTe QDs and light hole exciton energy is much higher than heavy hole exciton energy. The spin splitting of the conduction electron in ZnSe is also ignored due to very small g factor. Assuming that the exciton recombination time $\tau_R$ for both $\sigma_+$ and $\sigma_-$ exciton are the same. The circular polarization can be described by the two following rate Eqs. (1) and (2) for the heavy-hole excitons of $\sigma_+$ and $\sigma_-$ circular polarization:

$$\frac{dn_-}{dt}=G_--\frac{n_-}{\tau_R}+\frac{n_+}{\tau_S}-\frac{n_-e^{-\Delta E/kT}}{\tau_S}, \tag{1}$$

$$\frac{dn_+}{dt}=G_+-\frac{n_+}{\tau_R}-\frac{n_+}{\tau_S}+\frac{n_-e^{-\Delta E/kT}}{\tau_S} \tag{2}$$

where, $n_-$ represents number density of $\sigma_-$ exciton and $n_+$ stands for number density of $\sigma_+$ exciton. $\tau_S$ corresponds to an effective spin relaxation time between the two Zeeman levels. $G_+$ and $G_-$ are generation rates for $\sigma_+$ and $\sigma_-$ exciton, respectively. $kT$ is thermal energy and $\Delta E=g\mu_BB$ is the Zeeman splitting energy between $\sigma_+$ and $\sigma_-$ excitons. g is the effective g factor and $\mu_B$ is the Bohr magneton. For steady state condition, the ratio $\rho=\tau_S/\tau_R$ can be obtained by the experimental data using the following equation:

$$P=\left(\frac{I_+-I_-}{I_++I_-}\right)=\left(\frac{n_+-n_-}{n_++n_-}\right)=\frac{1-e^{\Delta E/kT}}{1+e^{\Delta E/kT}\left(1+\frac{\tau_S}{\tau_R}\right)}. \tag{3}$$

For a very slow spin relaxation ($\tau_S\gg\tau_R$), very large $\rho=\tau_S/\tau_R$ results zero circular polarization. In Fig. 2, $P=77\%$ at 5 T, it results in approximate same order of magnitude for $\tau_S$ and $\tau_R$.

In Fig. 2, the solid line is a fitting curve for the magnetic field dependence of circular polarization $P$ by using Eq. (3) with fitting parameters, g factor and the ratio $\rho=\tau_S/\tau_R$. The best fit to the data yields $\frac{g\mu_B}{kT}=0.94\pm0.03\,(T^{-1})$ and $\tau_S/\tau_R=0.31\pm0.01$. This indicates that the spin relaxation time is about 3 times shorter than the exciton recombination time.

In order to determine $\tau_R$, the decay profiles of time-resolved PL were measured, as shown in Fig. 3. The solid curve is a fit using the Kohlrausch's stretching exponential function

$$I(t)=I_0\,e^{-(t/\tau)^\beta}, \tag{4}$$

where $\tau$ is the exciton radiative recombination time ($\tau_R$), and $\beta$ is the stretching exponential. The solid line fits the experimental data reasonably. Fig. 3 shows a very long decay time of about 76 ns due to the type-II band alignment induced slow exciton recombination. The spin relaxation time is then estimated to be about 23 ns. This spin relaxation time is much longer than other type-I QD systems [4] and could be useful for spin manipulations.

The time-resolved PL spectra were also analyzed by $\sigma_+$ and $\sigma_-$ circular polarization and correlated by the Kohlrausch's stretching exponential function. The resultant data were shown in Fig. 4. The lifetimes of $\sigma_-$ ($\tau_{\sigma-}$) exciton decreases with the increasing magnetic field. On the other hand, the lifetimes of $\sigma_+$ ($\tau_{\sigma+}$) exciton are almost independent of magnetic field. The increasing magnetic field results in the energy splitting of $\sigma_+$ and $\sigma_-$ excitons, it further

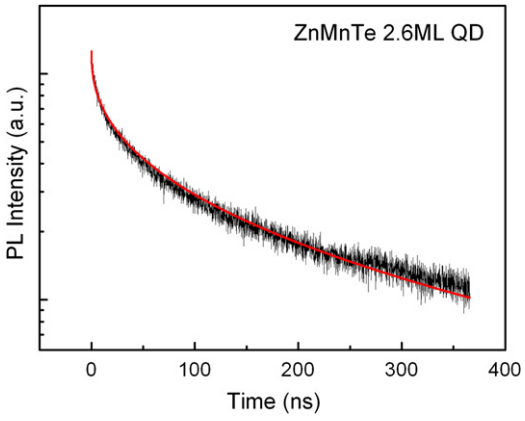


**Fig. 3.** Decay profile of ZnMnTe/ZnSe QDs. The red solid curve is a fit using the Kohlrausch's stretching exponential function described in the text.

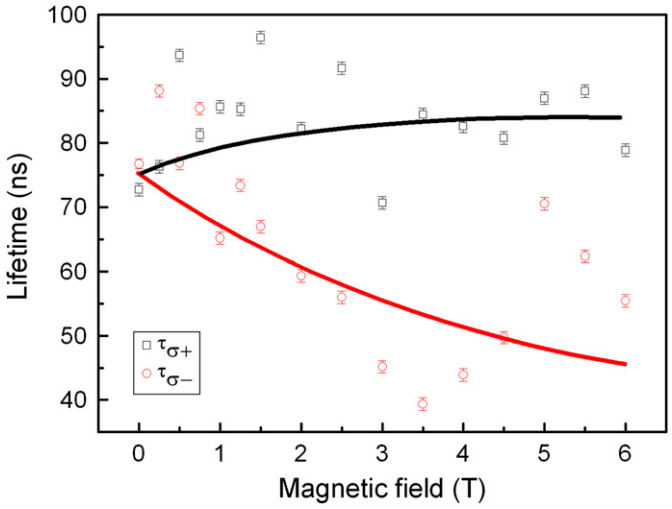


**Fig. 4.** Lifetime as a function of magnetic field. The squares represent $\sigma_+$ and circles stand for $\sigma_-$ circular polarization. The curves are guide to eye.

enhances the spin relaxation from the higher energy $\sigma_-$ excitons to the lower energy $\sigma_+$ excitons. As a result, $\tau_{\sigma-}$ is shorter than $\tau_{\sigma+}$. The lifetime of $\sigma_-$ ($\sigma_+$) excitons is 55 (80) ns at 6 T. The difference between $\tau_{\sigma+}$ and $\tau_{\sigma-}$ is about 25 ns, which is very close to the value obtained by Eq. (3).

## 4. Conclusion

We have investigated the spin dynamics of ZnMnTe/ZnSe QDs. The magnetic field dependence of PL circular polarization degree follows the Brillouin function and evidences the Mn magnetism in ZnMnTe QDs. The Kohlrausch's stretching exponential function well correlates both the $\sigma_+$ and $\sigma_-$ decay profiles. The magnetic field dependence of PL circular polarization degree shows the long spin relaxation time of about 23 ns. The long spin relaxation time could be useful for spin manipulation.

## Acknowledgements

This work was supported by the MOE-ATU and the National Science Council under the Grant no. of NSC 98-2119-M-009-015.

## References

[1] P. Recher, E.V. Sukhorukov, D. Loss, Quantum dot as spin filter and spin memory, Phys. Rev. Lett. 85 (2000) 1962–1965.
[2] K. Chang, K.S. Chan, F.M. Peeters, Spin–polarized tunneling through a diluted magnetic semiconductor quantum dot, Phys. Rev. B 71 (2005) 155309.
[3] S. Mackowski, T.A. Nguyen, H.E. Jackson, L.M. Smith, Exciton spin relaxation time in quantum dots measured by continuous-wave photoluminescence spectroscopy, Appl. Phys. Lett. 83 (2003) 5524–5526.
[4] E. Oh, K.J. Yee, S.M. Soh, J.U. Lee, J.C. Woo, H.S. Jeon, D.S. Kim, S. Lee, J.K. Furdyna, H.C. Ri, H.S. Chany, S.H. Park, Spin polarization of self-assembled CdSe quantum dots in ZnMnSe, Appl. Phys. Lett. 83 (2003) 4604–4606.
[5] M.C. Kuo, J.S. Hsu, J.L. Shen, K.C. Chiu, W.C. Fan, Y.C. Lin, C.H. Chia, W.C. Chou, M. Yasar, R. Mallory, A. Petrou, H. Luo, Growth and optical properties of type-II diluted magnetic semiconductor ZnMnTe/ZnSe quantum dots, Appl. Phys. Lett. 89 (2006) 263111.
[6] S. Mackowski, T. Gurung, T.A. Nguyen, H.E. Jackson, L.M. Smith, G. Karczewski, J. Kossut, Optically induced magnetization of CdMnTe self-assembled quantum dots, Appl. Phys. Lett. 84 (2004) 3337–3339.