Excitation power dependent Coulomb induced recombination dynamics in magnetically doped type-II quantum dots

Steven Tarasek¹, Wu-Ching Chou², Wen-Chung Fan² and Tim Thomay¹

¹ Department of Physics, State University of New York at Buffalo, Buffalo, New York 14260, United States of America
² National Chiao Tung University, 1001 University Road, Hsinchu 30010, Taiwan

E-mail: thomay@buffalo.edu

Keywords: magnetic QD, type II, quantum dot, magnetic polaron, time resolved PL

Abstract

We observe that the wavefunction overlap of the carriers in type-II quantum dots (QDs) can be controlled by magnetic doping and strongly depends on the excitation power density. We study two different II-VI magnetic systems; ZnTe/(Zn, Mn)Se QDs with magnetic dopants in the matrix surrounding the dots, and (Zn, Mn)Te/ZnSe QDs doped in the dot core. Both magnetic systems, regardless of the location of the dopant magnetic ions, show a stark contrast in their emission with high excitation power densities ($P_{ex}$) when compared to nonmagnetic ZnTe/ZnSe QDs. Using time-resolved photoluminescence (TRPL), we observe a saturation in the blue shift for the magnetic systems at a lower $P_{ex}$, while additionally exhibiting a limited lifetime shortening over the entire range of $P_{ex}$, when compared to the nonmagnetic QDs. The results for the two magnetic systems are very similar, showing no dependence on the location of the magnetic impurities. This suggests that the behavior observed is an effect of the magnetic polaron on the band bending in the high $P_{ex}$ regime. The ability to use magnetic ions to quickly saturate the charge concentration and control band bending in QDs could potentially aid in optimizing optoelectronic devices which are sensitive to high charge variations.

1. Introduction

Semiconductor quantum dots (QDs) continue to be of interest due to their potential applications, ranging from LED devices [1] to biomedical imaging research [2]. Specifically the spatially indirect nature of type-II systems have allowed for broad applications, from improved memory cell devices, [3] to increased efficiency in solar cells [4, 5].

A critical aspect of future device engineering is a well developed understanding of the carrier dynamics in these systems [6, 7]. The number of confined carriers present within type-II QDs can be controlled, and this has previously been shown by observing a measurable blue shift in the emission from these systems [8–10]. Changing the number of carriers present leads to a Coulomb-induced effect, culminating in significant alterations to the carrier wavefunctions and confinement potentials [11–14]. As shown by [15] for type-II systems, an increase in carrier concentration will directly lead to an increase in the possible recombination channels; the occupation of the higher energy recombination channels induces a blue shift in the emission, with shorter recombination lifetimes relative to an emission of a lower carrier density excitation.

The presence of dopants has also proven to alter the emission dynamics in QDs. Doping with transition metals such as Mn has led to dual emission in InP/ZnS QDs, including intrinsic and doped emissions which are dependent on dopant concentrations [16]. Additional doping with Cu has allowed for greater control of the dopant emission [17], while the introduction of Ag in doped systems has led to enhanced dual PL emission [18]. Varying dopants and doping concentrations has proven to be a promising platform for the future of solid state light emitting devices.
Doping QDs with magnetic ions has additionally been explored in order to improve spin based memory devices \cite{18, 20} and for potential applications in optoelectronics \cite{21}. The presence of magnetic ions within these structures leads to a localized exchange interaction between the spins of the magnetic dopants and the spins of the photoexcited carriers \cite{22–25}. When doping with several magnetic ions, the resulting behavior allows for the formation of the magnetic polaron \cite{22, 26}. In Mn$^{2+}$ doped systems, the magnetic polaron formation is dominated by the antiferromagnetic exchange between the dopant magnetic spin with the spin of the confined holes \cite{27}. This has previously been demonstrated in Mn$^{2+}$ doped type-II QDs, whether the Mn$^{2+}$ is doped into the QD core or the matrix surrounding the QD \cite{28}. In these same materials, the presence of the magnetic polaron has been shown to have a measurable effect on the exciton recombination for both core and matrix doped QDs \cite{28}. More recently a study of the matrix doped QDs has shown a significant alteration to the hole wavefunction when having multiple hole occupancy in the dot, increasing the confined hole wavefunction penetration into the surrounding matrix \cite{29}.

In our work, we alter the recombination dynamics of our system through both a Coulomb induced effect as previously done for nonmagnetic type-II QDs \cite{15} and through the presence of magnetic ions as done for low excitation powers in the same material system as used in this work \cite{28}. We use time resolved photoluminescence (TRPL) with a varying excitation power density to show that the blue shift of the emission in type-II QDs is altered through the presence of magnetic ions. We study two doped magnetic QDs, one doped in the dot core and the other in the matrix surrounding the QDs, and present a significant alteration in the high excitation power density behavior between the magnetic systems and their nonmagnetic counterparts.

2. Experiment

The systems studied are epitaxially grown matrix doped ZnTe/Zn,MnSe (M1) and core doped (Zn,Mn)Te/ZnSe (M2) QDs, with a Mn$^{2+}$ doping concentration of 5.2%. Both the matrix and core doped samples were grown with their own ZnTe/ZnSe nonmagnetic reference sample (NM1 and NM2, respectively) during the same growth run to minimize growing variations. All of the QD samples were grown by molecular beam epitaxy (MBE) on a GaAs substrate, with the disk shaped QDs having an average diameter of 20 nm and height of 3 nm \cite{30}. Previous measurements on these same matrix and core doped QDs \cite{28} have demonstrated that while there may have been some diffusion of Mn$^{2+}$, it is still primarily located in the intended dopant position. The hole-Mn magnetic exchange was shown to be higher for the core doped QD versus the matrix doped QD, which was interpreted as the separation between the hole and Mn wavefunction. The TRPL was excited using a pulsed laser system with a wavelength of 400 nm, having a pulse width of <200 fs, a repetition rate of 250 kHz, and an average excitation power density ranging from 0–250 W cm$^{-2}$. The emission was collected using a spectrometer/streak camera system, with a temporal resolution of 30 ps.

3. Results and discussion

TRPL emission dynamics were measured and analyzed for all four samples over a wide range of excitation power densities. The TRPL data shows a clear blue shift depending on the excitation power density. The internal transition for Mn$^{2+}$ of $E_{\text{int}} = 2.2$ eV \cite{22} is higher in energy than the band gap transition in our magnetically doped QDs. This difference in energy leads to the fact that the Mn$^{2+}$ emission does not contribute to the blue shifted TRPL band edge emission in either case. Figures 1(a) and (b) show the TRPL results of the core doped sample M2 (b) and its nonmagnetic counterpart NM2 (a) at $P_{\text{ex}} = 90.0$ W cm$^{-2}$. Gaussian fits of each time slice were used to find the peak energy throughout the duration of the emission, represented by the grey lines in figure 1. Using this, the peak energy at early time ($t = 0$ ns, triangles) and late time ($t = 17$ ns, squares) were found as shown figures 1(a), (b). A direct comparison of the peak energy values for early and late times as a function of $P_{\text{ex}}$ for all samples allows for the major difference between the behavior of doped magnetic QDs versus nonmagnetic QDs to be observed.

Figure 2 shows the peak energy values as a function of $P_{\text{ex}}$ at early/late times for both the matrix doped M1 (a) and the core doped M2 (b), along with their corresponding nonmagnetic references NM1 and NM2. For both samples M1 and M2, there is a distinct difference between the low and high $P_{\text{ex}}$ behavior, separated by the vertical dashed black line at 50 W cm$^{-2}$. In the low $P_{\text{ex}}$ regime for both sets, the emissions of the magnetic and nonmagnetic samples both exhibit a blue shift in their early peak energy. Additionally for low $P_{\text{ex}}$, the energy difference, $\Delta E_{\text{FSAT}} = E(t = 0\text{ns}) - E(t = 17\text{ ns})$, is larger for the magnetic sample in both sample sets. For the high $P_{\text{ex}}$ regime both magnetic samples reach a saturation in the blue shift of their peak energies, changing minimally between 50 W cm$^{-2}$ and the maximum $P_{\text{ex}}$. The saturation in the blue shift is indicated as $E_{\text{FSAT}}$ in figure 2. This is opposed to the behavior of both nonmagnetic references, which continue to blue shift as $P_{\text{ex}}$ is increased.
A three dimensional TRPL spectrum for the nonmagnetic reference sample NM2 at $P_{ex} = 90.0 \text{ W cm}^{-2}$ is shown in figure 1(c). We use this 3D representation of the contour plot in figure 1(a) to emphasize the time evolution of the two different decay processes involved. First we have the fast blue shifted higher energy recombination channel marked by a triangle followed by the fast exponential decay indicated by the cyan line. Second we have the lower energy recombination channel with a significantly slower decay marked by a square at
$\Delta t = 17$ ns. This demonstrates the separation of the fast (higher energy) and slow (lower energy) recombination channels that are present. Due to the Gaussian shape of the emission for each time slice, there is a small contribution from the fast recombination in the lower energy, and vice versa a small contribution from the slow recombination in the higher energy. The PL intensity of these high and low energy recombination channels can be fitted with the sum of two exponentials as a function of time to account for this; one exponential having a lifetime corresponding to the fast recombination, the other with a lifetime corresponding to the slow recombination. The higher energy exponential sum is dominated by the fast recombination, while the lower energy exponential sum is dominated by the slow recombination. Due to this, we attribute the fast (slow) recombination channel lifetime and PL intensity as the fast (slow) component of the high (low) energy exponential sum. The resulting lifetimes and relative PL intensities over the full range of $P_{ex}$ for the fast and slow recombination channels of all samples are shown in Figure 3.

Figure 3 shows a plot of lifetime versus energy for both the matrix (a) and core (b) doped QDs, along with their nonmagnetic counterparts. For all samples, both the fast and slow components of the recombination are plotted for different excitation power densities (red/yellow colorbar for M1 and M2, blue/green colorbar for NM1 and NM2) where their size corresponds to the relative PL intensity of that component. The fast and slow components in all samples exhibit a distinct difference in both lifetime and energy. In both cases, we see a stark contrast between the behavior of the magnetically doped QD compared to the nonmagnetic references. The fast component of all four samples has a constant lifetime $<1$ ns. While the absolute value of the slow component lifetime is different between the magnetic and nonmagnetic QDs, we focus on the change in the slow component lifetime as excitation power increases. A major difference arises in the lifetime shift of the slow component, with the change in lifetime of the nonmagnetic reference QDs, $\Delta \tau_{NM}$, exhibiting a much larger shift compared to the magnetic QDs, $\Delta \tau_{MAG}$. This is observed in Figure 3, with $\Delta \tau_{NM} > \Delta \tau_{MAG}$ for both systems.

Figure 4 shows a conceptual picture of the position of the electron and holes in the energy band diagram and the carrier wavefunctions for the nonmagnetic references (column i), the core doped QD (column ii), and the matrix doped QD (column iii). This is done for three different excitation power densities; the low $P_{ex}$ regime left of the dashed vertical line in Figure 2 (row a), medium $P_{ex}$ at the dashed vertical line (row b), and the high $P_{ex}$ regime right of the dashed vertical line (row c). First we want to discuss the situation visualized in the three
sketches of figure 4 row (a)(including sketches a-i, a-ii, and a-iii). As previously shown, the magnetic polaron formation is dominated by the hole-Mn spin interaction in II–VI systems [22]. This spin interaction reduces the exciton energy, subsequently causing $D_{E_F}$ to be larger for the magnetic QDs when compared to the nonmagnetic references [28]. This difference is indicated in figure 4 as the additional binding energy $E_{MP}$ for both the core (a-ii) and matrix doped (a-iii) QDs. Additionally, previous measurements [28] show a difference in the magnitude of the $E_{MP}$ depending on the location of the Mn, indicated in a-ii and a-iii as $E_{MP}$ for the core doped and $E_{MP}$ for the matrix doped QDs. For low $P_{ex}$, this causes the energy difference $\Delta E_{F} - \Delta S_{MP}$ of both magnetic samples (a-ii and a-iii) to be larger than the energy difference of their nonmagnetic counterparts (a-i). To calculate the $E_{MP}$ for different ensembles of QDs the energy difference of the fast and slow component of the nonmagnetic sample $D_{E_F} - S_{MP}$ is subtracted from the energy difference of the magnetic sample $\Delta E_{F} - \Delta S_{MP}$, since the binding energy effects both temporal components [28]. This situation is indicated in figure 4 row b.

The next situation we want to discuss is the excitation power dependence of nonmagnetic type-II QDs, as shown in figure 4 column i. This Coulomb induced effect on recombination for nonmagnetic type-II QDs has been previously demonstrated [15], while our nonmagnetic QDs behave as expected. The blue shift, indicated in figure 4 as the increasing magnitude of $E_F$, has been attributed to the opening of higher energy recombination channels as the carrier density is increased, where the number of possible confined hole states in the QD. When increasing the number of photogenerated carriers we increase the number of recombination channels occupied, therefore leading to a time integrated spectral broadening in energy. The occupation of higher energy recombination channels induces a blue shift in the emission with shorter lifetimes relative to the emission of a lower carrier density excitation. The high carrier density also results in a large modification in the carrier wavefunctions, with the hole wavefunctions expanding toward the dot edge due to Coulomb repulsion [29] and the electrons pulled toward the dot edge due to attraction to the holes [15] shown in figure 4 in red(blue) for the hole(electron) wavefunction.

In contrast, the high $P_{ex}$ behavior exhibited in our systems shows a saturation of the blue shift of the fast component only for the magnetic QDs, indicated as $E_{FSAT}$ in figure 2. As displayed in figure 4, $E_{FSAT}$ does not change from b-ii /c-ii to b-iii /c-iii, meaning the fast component shift is saturated throughout the high $P_{ex}$ regime only for the magnetic QDs. In the case of our nonmagnetic QDs, we see a continual blue shift of the fast component represented by the increasing magnitude of $E_F$ from a-ii to a-iii. This goes along with a significant

Figure 4. Schematic of the band diagram for the nonmagnetic references NM1 and NM2 (column (i)), the core doped sample M2 (column(ii)), and the matrix doped sample M1 (column(iii)). This is shown for low(row (a)), medium (row (b)), and high (row(c)) excitation power densities. The red(blue) circles represent the hole(electrons), along with a corresponding sketch of the hole (electron) wavefunction in red(blue).
decrease in lifetime $\Delta \tau_{\text{NM}}$ (blue arrow in figure 3) as discussed previously [15]. On the other hand, the change in lifetime $\Delta \tau_{\text{MAG}}$ (red arrow in figure 3) of both magnetic QDs over the entire range of $P_{\text{ex}}$ are similar to each other and significantly smaller than $\Delta \tau_{\text{NM}}$, due to the saturation behavior. With the core and matrix doped QDs behaving similarly in the high $P_{\text{ex}}$ regime, both experiencing a saturation in their blue shift at the same excitation power density of 50W cm$^{-2}$, the $\Delta E_F$ of both nonmagnetic references eventually exceeds the energy difference of their respective magnetic QDs.

The limited blue shift and saturation behavior exhibited indicates that magnetic impurities have an effect on the alteration to the confinement potential for large excitation power densities. In figure 3, it is shown in both sample sets that both the fast and slow components of the nonmagnetic QDs have a larger PL intensity at higher $P_{\text{ex}}$ compared to the magnetic samples. The lower PL intensity of the magnetic QDs points to a smaller number of excitons compared to the nonmagnetic samples. We assume that the magnetic impurities alter the carrier density compared to the nonmagnetic QDs, effectively decreasing the Coulomb interaction. This is indicated in figure 4 b-iii and c-iii with a reduced confinement potential compared to a-iii, along with the missing carriers indicated by the open red/blue circles. This can additionally lead to the observed smaller absolute lifetimes of the magnetic QDs, as shown in figure 3. With the similar behavior of the core and matrix doped QDs in the high $P_{\text{ex}}$ regime, we attribute this to an effect of the magnetic polaron rather than the location of the magnetic impurities. This approach would point to the influence of the magnetic polaron binding energy on the state distribution of holes within the QD.

4. Conclusions

Our measurements show that the previous work in the low excitation power density regime is reproducible, with the magnetic polaron having a strong effect on the exciton recombination energy [28] as well as the blue shift of the nonmagnetic system with increased pumping power [8]. The difference from current understanding arises in the high excitation power density regime of the magnetic doped systems, where we observe a limited blue shift and shortening of the lifetime in the magnetically doped QDs. The high excitation power results for the core and matrix doped QDs show the same saturation and lifetime shortening, suggesting that this is an effect of the magnetic polaron rather than the location of the magnetic impurities. This extends the possibilities of controlled band bending in type-II systems, where the use of magnetic dopants and excitation power can aid in the design of devices which are sensitive to high charge variations.

Data Availability Statement

The data that support the findings of this study are available upon request from the authors.

ORCID iDs

Wen-Chung Fan https://orcid.org/0000-0002-3486-9623
Tim Thomay https://orcid.org/0000-0003-2271-6803

References

[1] Caruge M J, Halpert J E, Wood V, Bulović V and Bawendi M G 2008 Nat. Photonics 2 247–50
[2] Reshma V G and Mohanan P V 2019 J. Lumin. 205 287–98
[3] Geller M, Marent A, Nowozin T and Bimberg D 2008 J. Phys. Condens. Matter 20 454202
[4] Laghumavarapu R B, Moscho A, Khoshakhlagh A, El-Emawy M, Lester L F and Huffaker D L 2007 Appl. Phys. Lett. 90 173125
[5] Vyskočil J, Hospodková A, Petříček O, Pangrác J, Zíková M, Oswald J and Vetaška A 2017 J. Cryst. Growth 464 64–8
[6] Madureira J R, de Godoy M P F, Brasil M J S P and Ikawa F 2007 Appl. Phys. Lett. 90 212105
[7] Couto O D D, de Almeida P T, dos Santos G E, Balanta M A G, Andriolo H F, Brum J A, Brasil M J S P, Ikawa F, Liang B L and Huffaker D L 2016 J. Appl. Phys. 120 084305
[8] Klenovský P, Steindl P and Geoffrey D 2017 Sci. Rep. 7 43568
[9] Jo M, Sato M, Miyamura S, Sasakura H, Kumanono H and Suemune I 2012 Nanoscale Res. Lett. 7 654
[10] Tabei-Bayashi J, Liang B L, Laghumavarapu R B, Russian D A, Htoon H, Klimov V, Balakrishnan G, Dawson L R and Huffaker D L 2008 Nanotechnology 19 295704
[11] Gradkowski K, Ochsali T J, Pavarelli N, Williams D P, Huyet G, Liang B and Huffaker D L 2010 Appl. Phys. Lett. 97 091105
[12] Gradkowski K, Ochsali T J, Williams D P, Tabei-Bayashi J, Khoshakhlagh A, Balakrishnan G, O‘Reilly E P, Huyet G, Dawson L R and Huffaker D L 2009 J. Lumin. 129 436–60
[13] Gradkowski K, Ochsali T J, Williams D P, Healy S B, Tabei-Bayashi J, Balakrishnan G, O‘Reilly E P, Huyet G and Huffaker D L 2009 physica Status Solidi (b) 246 752–5
[14] Gradkowski K, Pavarelli N, Ochsali T J, Williams D P, Tabei-Bayashi J, Huyet G, O‘Reilly E P and Huffaker D L 2009 Appl. Phys. Lett. 95 061102
[15] Gradkowski K, Ochalski T J, Pavarelli N, Liu H Y, Tatebayashi J, Williams D P, Mowbray D J, Huyet G and Huffaker D L 2012 Phys. Rev. B 85 035432
[16] Zhang G, Mei S, Wei X, Wei C, Yang W, Zhu J, Zhang W and Guo R 2018 Nanoscale Res. Lett. 13 170
[17] Mei S et al 2019 J. Lumin. 212 264–70
[18] Wei X, Mei S, Zhang G, Su D, Xie F, Zhang W and Guo R 2019 Appl. Surf. Sci. 493 605–12
[19] Gurung T, Mackowski S, Karczewski G, Jackson H E and Smith L M 2008 Appl. Phys. Lett. 93 153114
[20] Kneip M K, Yakovlev D R, Bayer M, Maksimov A A, Tartakovskii I I, Keller D, Ossau W, Molenkamp L W and Waag A 2006 Phys. Rev. B 73 045305
[21] Kobak J et al 2014 Nat. Commun. 5 3191
[22] Furdyna J K 1988 J. Appl. Phys. 64 R29–64
[23] Beaulac R, Schneider L, Archer P I, Bacher G and Gamelin D R 2009 Science 325 973–6
[24] Kudelski A, Lemaitre A, Miard A, Voisin P, Graham T C M, Warburton R J and Krebs O 2007 Phys. Rev. Lett. 99 247209
[25] Qu F and Hawrylak P 2005 Phys. Rev. Lett. 95 217206
[26] Nelson H D, Bradshaw L R, Barrows C J, Vlaskin V A and Gamelin D R 2015 ACS Nano 9 11177–91
[27] Sellers I R et al 2010 Phys. Rev. B 82 195320
[28] Barman B et al 2015 Phys. Rev. B 92 035430
[29] Zhang P et al 2019 The Journal of Physical Chemistry C 123 25934–40
[30] Kuo M C et al 2006 Appl. Phys. Lett. 89 263111