Fabrication and micro-photoluminescence study of CdMnTe diluted magnetic quantum dots

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Abstract. We report the growth of self assembled CdMnTe diluted magnetic quantum dots by molecular beam epitaxy. The Mn content within the dots can be efficiently controlled by the growth conditions. The presence of magnetic Mn ions in the zero-dimensional structures results in a strong enhancement of their spin related properties, in the giant Zeeman splitting of excitonic levels, in particular. The insight into these magnetic properties is obtained by means of micro-photoluminescence measurements at an external magnetic field. We study the evolution of several photoluminescence lines related to the emission from individual quantum dots at an external magnetic field. We determine an approximate number of magnetic ions inside the dots and the sizes of the dots by comparing these dependences to the model calculations.

1. Introduction

The presence of an even small amount of transition metal ions within semiconductor quantum dots (QDs) has a great impact on spin related properties of carriers which are confined inside these structures. This is due to a strong sp-d exchange coupling between the carriers and magnetic ions, which is already well known from studies of bulk semiconductors containing magnetic ions, the diluted magnetic semiconductors (for overview see, e.g.,[1]). The most important features of these materials are related to the presence of a giant Zeeman splitting of energy levels the value of which depends on the concentration of magnetic ions and can be even two orders of magnitude larger than in the same semiconductors without magnetic ions. Similar effects as in bulk crystals can be also observed in diluted magnetic quantum dots despite of the fact that the carriers are very strongly localized in these structures and interact only with a finite and relatively small number of Mn ions. The number of magnetic ions inside diluted magnetic QDs is usually of the order of several hundreds per dot [2-4]. There are, however, some reports about CdMnTe QDs containing in average 10 Mn ions per dot [5], or about only one Mn in a single QD [6].
In this work, we show how to control the Mn concentration within the CdTe dots by means of growth conditions, such as the temperature of the Mn effusion cell, its opening time and the number of CdTe monolayers which are doped with Mn. Moreover, we present a method, how to determine the most important parameters responsible for the magnetic properties of the diluted magnetic quantum dots, the number of Mn ions inside the dot and the size of the dot. We achieve this by comparing the magnetic field evolution of the photoluminescence (PL) from an individual QD to the model calculations.

2. Samples and experiment

All samples under consideration are grown in a molecular beam epitaxy system, equipped with Cd, Zn, Mn and Te effusion cells, on 001-GaAs substrates. First, we deposit a 4 µm thick CdTe buffer layer in order to avoid any dislocations originating from the lattice-mismatched GaAs/CdTe interface. The surface of the samples is monitored in situ by the reflection of high energy electron diffraction (RHEED). The main part of the samples consists of 0.7 µm thick Zn0.8Cd0.2Te barrier which is followed by a thin CdTe/CdMnTe/CdTe layer consisting of 6 or 5 monolayers depending on the sample. The manganese ions are added only into 1 or 2 of the central monolayers in very small, precisely defined amounts controlled by monitoring the Mn flux and the opening time of the Mn effusion cell. In this work we focus on the properties of two samples, sample A and sample B, containing Mn amounts that differ in a considerable manner. As estimated from the growth conditions, the Mn content within the dots amounts to 0.04 and 0.003 in sample A and sample B, respectively. After the deposition of the thin CdTe/CdMnTe/CdTe layer, the RHEED pattern still reveals a flat 2D surface, which suggests that the QDs are not formed, yet. The QDs formation process is induced by a method originally introduced for the CdTe/ZnTe system [7], i.e., by covering this strained layer with amorphous tellurium at low substrate temperature and its subsequent thermal desorption. As a result of this treatment, the RHEED image changes from 2D to 3D character which is a typical feature for the formation of self-assembled 3D islands on the surface. In the last step, the structures are capped with 100 nm Zn0.8Cd0.2Te.

The formation of self-assembled QDs is confirmed by the atomic force microscope images (AFM), where uncapped QDs are measured in air immediately after the sample is taken out of the MBE chamber, Figure 1.

**Figure 1.** AFM image of uncapped self-assembled CdMnTe quantum dots

From that imaging we obtain a direct insight into the morphology of bare dots. They are typically lens-like shaped with in-plane diameters ranging from 10 to 40 nm and heights from 2 to 14 nm, whereas the height/diameter ratio ranges from 1 : 3 to 1 : 5. The sheet density of the dots is estimated...
to be $5 \times 10^9$ cm$^{-2}$. Moreover, the sizes of the dots and their density do not depend significantly on the Mn content in the Mn concentration range under consideration, which is consistent with results reported in [8].

The high spatial resolution photoluminescence (microluminescence) measurements are performed at an external magnetic field up to 7T applied perpendicular to the growth axis of the sample. The sample is immersed in liquid helium at constant temperature of 2 K. The photoluminescence signal passes through an analyzer of circular polarization and is detected by a system consisting of a 0.7 m monochromator equipped with a 1200 grooves/mm grating connected to a CCD camera. In this configuration, we may change the detected circular polarization by reversing the direction of the magnetic field. In order to obtain a high spatial resolution of the photoluminescence we focus the size of the excitation spot down to 1 µm in an immersion reflection objective, so that we excite only about 50 quantum dots at the same time. Moreover, we use the non-resonant excitation with a frequency doubled YAG laser (532 nm).

3. Results
A typical magnetic field dependence of the micro-PL spectra from sample A and sample B are presented in Figure 2. Despite of a considerably different Mn content within these two samples, the PL spectra show quite similar behaviour. They consist of several relatively sharp lines with the spectral width of the order of 1 meV, whereas their emission energy ranges from 1.7 eV to 2.1 eV. The spectral position of these lines does not change with time, but it depends strongly on the spatial position of the excitation spot. Moreover, when we increase the excitation spot size up to 1 mm we cannot resolve any sharp lines anymore and the PL emission consists only of a smooth and broad emission band. Therefore, we associate the relatively sharp lines with the emission from individual QDs. The emission energy from a particular dot depends on the size of the dot, its chemical composition and strains present in this structure; a large broadening of the PL emission suggests a large distribution of these quantities.

![Figure 2](image)

**Figure 2.** Micro-photoluminescence spectra at various magnetic fields up to 6T from sample 1 (a) and sample (b). Circular polarisation of the spectra proofs that the Mn ions are incorporated within the dots

When we increase the magnetic field, a circular polarization of the PL emission spectrum appears. At about 2 T the emission is almost completely polarized, which is a clear fingerprint of the sp-d exchange interaction between the excitons confined within the dots and magnetic Mn ions and gives us a proof that Mn ions are incorporated inside the QDs.

In our further considerations we will discuss the evolution of several PL-lines from individual QDs at an external magnetic field in the stronger of the two, i.e. $\sigma^+$, circular polarization. In Figure 3a and 3b, we plotted the magnetic field dependencies from two PL lines taken from the low energy part of
the PL emission from sample A and sample B, respectively. Both lines represent, therefore, relatively large quantum dots which differ only by the Mn content. The spectral positions and spectral widths are determined from a fit with a Gaussian at every magnetic field.

Figure 3. Spectral position (upper panel) and spectral width (lower panel) for the PL-line from an individual quantum dot taken from the low energy part of the spectrum of (a) sample A and (b) sample B. Solid line in the upper panel represents a fit with a Brillouin function from which we estimate the Mn content within the studied quantum dot.

Both lines exhibit a qualitatively similar behavior at an external magnetic field. They show a significant redshift of the spectral position, which reflects directly the giant Zeeman splitting of excitonic levels within the dots. The most significant difference between the lines concerns the value of this energy shift. In the case of the QD with a relatively large Mn content (sample A), the energy shift at 6 T amounts to ~30 meV, whereas in the case of sample B with a relatively small Mn concentration - only to 4 meV. The dependence of the spectral position of the PL-lines on the magnetic field can be well fitted with a modified Brillouin function [9]

$$\Delta E(B, T) = \frac{(N_0 \alpha - N_0 \beta)}{2} \cdot x_{\text{Mn}} \cdot S_0 \cdot B_s \cdot \left( \frac{g_{\text{Mn}} \mu_B B}{k_{\text{eff}}} \right)$$

where $\Delta E$ is the energy shift, $N_0 \alpha = 0.22$ eV $N_0 \beta = -0.88$ eV are the s-d and p-d exchange integrals in the bulk material, respectively, $x_{\text{Mn}}$ - the Mn content, $B_s$ - the Brillouin function, $g_{\text{Mn}} = 2$, the Lande factor of the Mn spin, $\mu_B$ – the Bohr magneton, $k$ – the Bolzmann factor, $B$ - magnetic field, $T_{\text{eff}}$ – the effective temperature of the Mn sublattice and $S_0$ - the effective spin of an Mn ion taken from the ref.[9]. $S_0 = 1.57$ and 2.5 were taken for the fits presented in Figure 3a and Figure 3b, respectively. The reduction of the $S_0$ in the case of a relatively large Mn content in the dot reflects the fact that an antiferromagnetic interaction between Mn ions plays then an important role. From these fits we obtain approximate values for the Mn content within the dots, which are 4.3% and 0.3% in the case of the dot from the sample A and sample B, respectively. These values are very close to our expectations basing on the growth parameters. The second fitting parameter, $T_{\text{eff}}$, amounts to 8.4K and 4.9K for the dot with high and low Mn content respectively. The increase of the $T_{\text{eff}}$ with an increasing Mn amount is related to the presence of antiferromagnetic ion-ion exchange interaction, which prevents the Mn from...
being aligned by the external magnetic field [10]. This interaction does not play an important role when the Mn content is very small and the Mn ions are far apart from each other.

The spectral width of the PL lines reflects directly the magnetization fluctuations within the dots [11-13]. The spectral width at 0 T is typically one order of magnitude broader than in non-magnetic quantum dots and decreases with an increasing magnetic field as a result of the alignment of the Mn spins by the external magnetic field. At the highest magnetic fields, which are available, the spectral width of the PL line with relatively low Mn content (Figure 3b) reaches value almost comparable to that of non-magnetic CdTe QDs. This means that we are close to the situation when all Mn ions are aligned by the external magnetic field. In the case of the dot with a higher Mn content, one needs much higher magnetic fields in order to align all Mn ions due to the presence of an ion-ion exchange interaction.

The fits with a Brillouin function presented in Figure 3 give only very rough estimated values of the Mn content within the dots. They do not take into account, in particular, the finite sizes of the dots. In order to do this we use a model which was originally developed for the description of magnetic polarons within bulk crystals (e.g. [14,15]). The main assumption of this model is that all Mn ions interact equally strongly with the carriers within the dot, and do not interact with Mn ions from outside the dot. This assumption can be made only in the case of a relatively large number of Mn ions within the dots, when we may introduce an average position of Mn ions within the dots. Moreover, we assume that we observe only heavy hole excitons within the dots and light hole excitons are split-off due to strain and a flat general shape of the dot. The Hamiltonian of the magnetic interactions within the dots is given then by the following expression:

$$\hat{H} = \frac{N_{Mn}}{3N_{Mn}} S_{z}^{Mn} + \frac{N_{Mn} S_{z}^{Mn}}{3N_{Mn}} j_{z}^{Mn} + g_{e} \mu_{B} B S_{z}^{e} + g_{s} \mu_{B} B S_{z}^{s} + g_{s h} \mu_{B} B j_{z}$$

(2)

where $N_{Mn}$ is the number of Mn ions within the dot, $S$ the total spin of Mn ions, $s$ the spin of an electron, $S_{z}^{Mn}, j_{z}^{Mn}, S_{z}^{e}$ the projections of the total spin of Mn ions, heavy hole spin, and electron spin on the direction of the magnetic field, respectively, $g_{e} = 1.6$, $g_{s h} \approx 0$ are Lande factors for electron and heavy hole [16], respectively. The density of states in this model is determined by the number of possible Mn spins arrangements which lead to a total spin $S$ and the occupation of these states is given by the Boltzmann distribution. There are only three quantities which are responsible for the magnetic properties of the diluted magnetic QDs: the Mn content, $x_{Mn}$, the effective temperature of Mn sublattice and the number of Mn ions within the dots, $N_{Mn}$, which together with $x_{Mn}$ gives us the information about the size of the dot. $N_{cat} = N_{Mn} / x_{Mn}$ is the approximate number of cation sites, that the particular dot is made of.

Let us consider now three PL lines taken from different parts of the emission spectrum of sample B. A PL-line from the low energy part of the spectrum is shown in Figure 4a and represents relatively large quantum dots. In Figure 4b, the PL-line comes from the central part of the PL-spectrum and represents medium-sized dots, and in Figure 4c, we show a PL line from the high energy part of the spectrum, i.e., from a relatively small QD. The best fits to the spectral position and shape of the dots in terms of the model calculations described above are shown in the right part of Figure 4 and are given by the following fitting parameters. For all three quantum dots, we obtain a very similar Mn content. $x_{Mn} = 0.0038$, 0.0036, 0.0034 for the large, medium sized and small quantum dots, respectively. The effective temperature of Mn sublattice is exactly the same for all the lines, $T_{eff} = 4.9$ K. The only quantity that changes significantly is the number of Mn ions within the dots, $N_{Mn} = 25, 13, 5$ for the large, medium-sized and small QD, respectively. These values correspond to dots built of 6600, 3600 and 1500 cation sites. In order to obtain an impression about the extensions of these dots, we assume that the dots are lens-like shaped with a parabolic curvature with the height to in-plane diameter ratio of 1 : 5. The in-plane diameter of such dots amounts to 18 nm 15 nm and 11 nm, for large, medium-sized and small quantum dot, respectively.
Figure 4. PL lines from individual QDs from sample B (left panel) and model calculations (right panel) (a) relatively large dot, best fit with $x_{\text{Mn}}=0.0038$, $N_{\text{Mn}}=25$, $T_{\text{eff}}=4.9K$ (b) medium sized dot, the best fit with $x_{\text{Mn}}=0.0036$, $N_{\text{Mn}}=13$, $T_{\text{eff}}=4.9K$ (c) small dot, the best fit with $x_{\text{Mn}}=0.0034$, $N_{\text{Mn}}=5$, $T_{\text{eff}}=4.9K$

4. Conclusions
We have developed a method of introducing magnetic Mn ions into self assembled non-magnetic CdTe quantum dots. A big advantage of this approach is the possibility of controlling the average Mn content within the dots by the growth conditions. We have shown that this quantity can vary by at least one order of magnitude. Moreover, the insight to the magnetic properties of individual QDs can be obtained by micro-PL measurements at an external magnetic field, where we observe directly the giant Zeeman splitting of excitonic levels within the dots. The most important quantities responsible for the magnetic properties of diluted magnetic quantum dots, such as the approximate number of Mn ions within the dots and the size of the dots, can be determined by a comparison of the magnetic field evolution of PL-lines from individual QDs to the model calculations.

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