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Effect of magnetic field on intraionic photoluminescence of (Zn,Co)Se

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ABSTRACT

We report on optical properties of epitaxially grown $Zn_{1-x}Co_xSe$ diluted magnetic semiconductor. Excitonic photoluminescence reveals efficient energy transfer from band carriers to Co^{2+} ions. Magneto-photoluminescence of $^2T_1$–$^4A_2$ intraionic transition of Co^{2+} in ZnSe is evidenced and discussed based on reported magneto-absorption results. Determined values of *g* factors are $g_A = 0.62 \pm 0.09$ and $g_B = 3.71 \pm 0.05$ for optical transitions, and $g_e = -0.8 \pm 0.2$ for the $^2T_1$ excited state of Co^{2+}. Cobalt ion concentration in the sample is determined using both reflection measurements of excitonic giant Zeeman effect and direct magnetometry.

1. Introduction

Possibility of controlling individual spins motivates recent spectroscopic studies of semiconductor structures doped with magnetic ions. For example single ions of transition metals can be manipulated using *s,p-d* exchange interaction [1,2] between magnetic ion and carriers confined in a quantum dot [3]. Such a spin manipulation has been presented for single manganese in CdTe/ZnTe [4,5], InAs/GaAs [6,7], and CdSe/ZnSe [8,9] quantum dots (QD). Moreover coherent oscillations of single 5/2 spin have been demonstrated using a system of single Mn^{2+} ion in a QD [10]. Also a single Co^{2+} spin read-out has been presented using excitonic transitions in a QD CdTe/ZnTe [8,11]. However, there are also other attractive techniques of single spin manipulation which have not yet been applied to systems with individual transition metals [8]. For example single spin of lanthanide ions [12–14] or single N-V centers [15] can be efficiently manipulated using intraionic transitions. Similar sharp intraionic optical transitions can be observed for ions of transitions metals [16,17], e.g. Co^{2+} [18–21] in the ZnSe matrix exhibits sharp spectral line close to 2363 meV [22]. The line was studied firstly using photoconductivity [22,23], zero-field absorption [24], photoluminescence (PL) [25], and finally by magneto-absorption [26,27], which led to identification of this line as related to $^4A_2(F)$–$^4T_2(F)$ intraionic transition of Co^{2+}.

In this paper we present growth, characterization and photoluminescence study of epitaxial (Zn,Co)Se. Excitonic magneto-reflectivity allows determination of cobalt concentration. Excitonic photoluminescence is measured in order to quantify the PL quenching effect related to Co^{2+} ions. Intraionic magneto-photoluminescence is measured in order to confirm results of reported magneto-absorption experiments [26,27], to determine with higher precision characteristic parameters such as *g* factors, and to make a step toward controlling spin of individual cobalt ions using intraionic transitions.

2. Experimental details

The studied sample was grown by molecular beam epitaxy (MBE) on GaAs (100)-oriented substrate followed by 25 nm thick ZnSe buffer and 320 nm thick (Zn,Co)Se layer. High temperature effusion cell with Al_2O_3 crucible was a molecular source of cobalt, similarly as in our previous growth of telluride Co-based diluted magnetic semiconductors (DMS) [28,29,8]. The optical measurements have been performed in a magnet-cryostat at the liquid helium ($T = 1.6$ K). We employ two types of spectroscopic measurements – reflection and photoluminescence, both of them in zero field and in the magnetic field. The halogen lamp was the source of white light in the reflection spectroscopy whereas the semiconductor laser $\lambda = 405$ nm was used to excite photoluminescence. Magnetization measurements have been done at helium temperatures in commercial MPMS XL superconducting quantum interference device (SQUID). Due to very dilute character of the studied layer the adequate experimental code has been strictly followed [30,31].

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3. Sample characterization

To determine cobalt ion concentration we measured magnetooptical effects, which depend on concentration of magnetic ions. Reflectivity spectra were measured for photon energy around the energy gap of ZnSe. In a spectral region close to 2805 meV, we observe a characteristic spectral structure (Fig. 1a), which results from the heavy-hole excitonic transitions [32]. Upon applying external magnetic field the difference in energies of heavy-hole excitonic transitions in two circular polarizations appears. This energy difference is plotted as a function of magnetic field (Fig. 1b). It is a giant Zeeman splitting, which is proportional to the concentration of Co^{2+} ions, x, and which can be described by the equation [2]:

$$\Delta E_{hh} = N_0(\beta-\alpha)x\langle S_z\rangle, \tag{1}$$

where ΔE_{hh} denotes the energy splitting of heave-hole exciton line, $N_0(\beta-\alpha)$ states for the exchange parameter difference and $\langle S_z\rangle$ is a mean value of spin projection of Co^{2+}. Taking $N_0(\beta-\alpha) = 2420 \pm 40$ meV as determined by Liu et al. [32] and describing $\langle S_z\rangle$ by the modified Brillouin function similar to [33,34], concentration of cobalt ions can be found from fitting this function to experimentally observed splitting vs. magnetic field. $\langle S_z\rangle$ is then given by

$$\langle S_z\rangle = SB_S\left(\frac{g_f\mu_B SB}{k_B(T+T_0)}\right), \tag{2}$$

where B_S is the Brillouin function:

$$B_S(y) = \frac{2S+1}{2S}\coth\left(\frac{2S+1}{2S}y\right) - \frac{1}{2S}\coth\left(\frac{1}{2S}y\right). \tag{3}$$

For Co^{2+} ions in ZnSe spin S=3/2 (orbital momentum is quenched) and g factor g_f=2.27 [35]. Next, k_B and μ_B are Boltzmann constant and Bohr magneton respectively, B – value of the magnetic field, T is temperature and T_0 is a phenomenological parameter accounting for antiferromagnetic interactions between Co^{2+} ions. Parameters x and T_0 were fitting parameters of Eq. (1) to the data in Fig. 1b and their values were determined as $x=0.19\pm0.01\%$ and T_0=1.3 K. We note that a similar value of cobalt concentration $x=0.23\pm0.03\%$ was determined from SQUID magnetometry. We conclude therefore that Co concentration is about 0.2%.

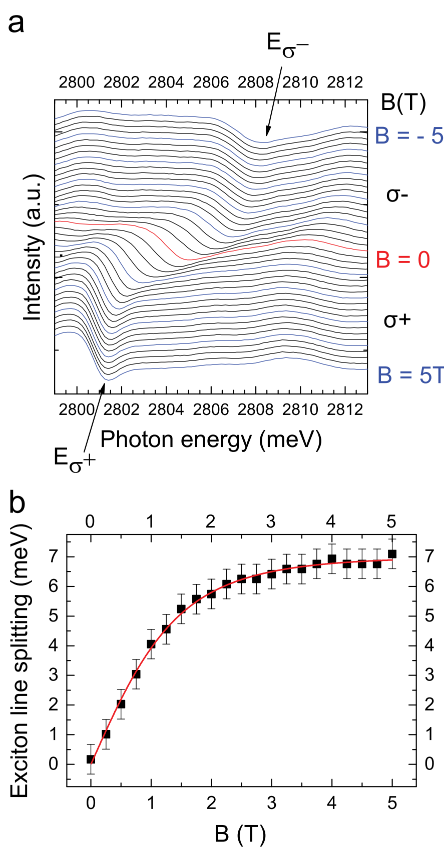

Fig. 1. (Color online) Giant Zeeman effect in (Zn,Co)Se. (a) Excitonic reflectivity spectra in the magnetic field in Faraday configuration performed for (Zn,Co)Se thin film. Arrows and symbols E indicate position of the local minima used for determination of giant Zeeman splitting. Curves for various values of magnetic field are shifted vertically for clarity. (b) Exciton line splitting (squares) as a function of magnetic field with modified Brillouin function fitted (line). Obtained fitting parameters values are Co concentration $x=0.19\pm\ 0.01\%$ and an effective temperature $T_0=1.3\ \pm\ 0.5$ K at T=1.6 K.

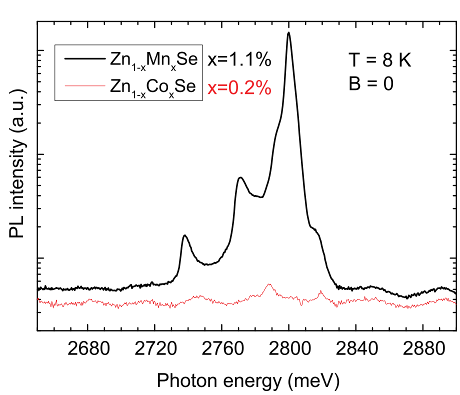

Fig. 2. (Color online) Comparison of the excitonic photoluminescence spectra of the reference MBE grown layer of $Zn_{0.989}Mn_{0.011}Se$ (bold, black curve) and studied (Zn,Co)Se layer (thin, red curve) obtained at identical experimental conditions (the same excitation power, T=8 K, B=0 T). Vertical axis represents signal intensity in logarithmic scale and horizontal axis – energy of photons. Efficient PL quenching due to the presence of cobalt ions is visible.

4. Results

4.1. Excitonic PL

Fig. 2 shows exciton lines observed for two similar samples, (Zn,Co)Se and reference (Zn,Mn)Se, measured in the same experimental conditions, T=8 K and B=0. Photoluminescence intensity of interband transitions is orders of magnitudes lower for (Zn,Co)Se. Despite the fact that magnetic ion concentration is lower in the sample with cobalt ions than in the one with manganese ions, quenching efficiency is higher for (Zn,Co)Se than for (Zn,Mn)Se. Following studies suggest that this fact can be understood as an effective energy transfer from interband to intraionic transitions and this effect is much stronger for Co^{2+} than for Mn^{2+} in the case of ZnSe host semiconductor.

It is interesting to note that the quenching effect due to Co^{2+} is known to be efficient in many structures: bulk ZnS [36], epitaxial layers ZnO [37,38] and CdTe [29], and also colloidal QDs ZnO [39] and CdTe [40]. However, there are also reports on weak or even negligible quenching in ZnTe layers [29] and in CdTe/ZnTe epitaxial QDs containing single Co^{2+} ions [8]. This leads to important question: if very efficient quenching due to Co^{2+} in ZnSe layers reported here, will it result in an efficient quenching of PL in unexplored QDs CdSe/ZnSe, or conversely, quenching due to single cobalt will be negligible even in selenides?