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Antiferromagnetic interaction in coupled CdSe/ZnMnSe quantum dot structures

D. Dagnelund,¹ Q. J. Ren,¹ I. A. Buyanova,¹ A. Murayama,² and W. M. Chen¹

¹*Department of Physics, Chemistry and Biology, Linköping University, S-581 83 Linköping, Sweden*

²*Graduate School of Information Science and Technology, Hokkaido University, Sapporo 060-0814, Japan*

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Spin polarization of nonmagnetic CdSe quantum dots (QDs) coupled to adjacent ZnMnSe diluted magnetic semiconductor (DMS) is investigated by CW and time-resolved magneto-optical spectroscopy under tunable laser excitation. Efficient enhancement in the degree of σ^- circular polarization of photoluminescence from the CdSe QDs is observed under optical excitation at the σ^+ -active exciton state of the DMS. The fact that the enhancement persists much longer than the exciton lifetime of the DMS rules out a role of the DMS excitons. A possible explanation is discussed in terms of antiferromagnetic coupling between the excitons in QDs and aligned Mn ions in DMS. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4739852>]

Physics of spin and spin dynamics in coupled semiconductor nanostructures has gained increasing interest in recent years due to its importance for future spin-functional devices,^{1–3} where the information is encoded in the spin states of electrons. The success of future semiconductor spintronics relies on our ability to achieve efficient spin generation, spin injection and transport, spin manipulation, and spin detection. Semiconductor quantum dots (QDs) are particularly promising for solid-state qubits and spin detection due to their weak spin relaxation^{4–7} and high efficiency of optical transitions, superior to semiconductor systems of a higher dimensionality. Recent results have demonstrated marked progresses towards realization of fast optical manipulation of single spins in QDs (Ref. 8) and optically effected controlled-phase gate between two solid-state qubits.⁹ One way of achieving spin polarized carriers and excitons in QDs is via direct spin injection from an adjacent layer. There are active on-going research efforts^{10–14} in exploring possibilities of diluted magnetic semiconductors (DMS) as spin injectors. An alternative route to obtain spin polarized carriers/excitons in QDs is to explore spin-dependent interlayer coupling. Several observations of antiferromagnetic coupling (AFC) between nonmagnetic CdSe QDs and adjacent layers, including DMS quantum wells (QW),^{15,16} DMS QDs (Refs. 17 and 18), and also nonmagnetic QDs,¹⁹ have been reported in the past years. The suggested underlying physical mechanism¹⁸ in the case of coupling to magnetic layers involves acceleration of exciton spin relaxation in the CdSe QDs due to magnetic coupling to photo-generated carriers in the nearby DMS layer, based on continuous-wave (CW) magneto-photoluminescence (PL) measurements. The possibility of magnetic coupling to Mn ions has so far not been considered.

The aim of the present work is to closely examine and unambiguously identify the role of photo-generated carriers/excitons within the DMS in the AFC effect observed in a coupled system of CdSe QDs and ZnMnSe DMS. This is achieved by two experimental approaches that were not employed in the earlier studies. The first approach is tunable laser spectroscopy, with which the laser photon energy can

be tuned to selectively generate carriers and excitons in the QDs alone, in the DMS or in the non-magnetic ZnSe barrier. This enables us to single out the contribution of the DMS exciton spins to spin polarization of the adjacent QDs. It should be noted that such selective excitation was not available in the earlier studies where optical excitation was undertaken at a fixed energy well above the bandgap energies of both DMS and non-magnetic barriers, such that their contributions to the spin polarization of the QDs could not be individually resolved. The second experimental approach employed in this work is time-resolved magneto-PL. Thanks to different lifetimes between the QDs and the DMS excitons/carriers, transient behavior of the QD spin polarization can shed light on direct involvement of the photo-generated excitons/carriers in the DMS in the observed AFC effect.

The sample structures studied in this work were grown by molecular beam epitaxy on a GaAs (001) substrate. A schematic illustration of the structures is shown in Figure 1(a). The $\text{Zn}_{0.93}\text{Mn}_{0.07}\text{Se}$ DMS layer with a thickness of 100 nm was grown on a ZnSe-buffer layer, followed by a spacer layer of ZnSe. Width of the spacer layer (L_B) was intentionally varied between samples as follows: 10, 5, and 2 nm. Then, three monolayers of CdSe were deposited on the ZnSe spacer, forming self-assembled QDs. The dots were finally capped by a 10 nm-thick ZnSe layer. The dot formation was confirmed by scanning transmission electron microscopy (STEM), STEM-HAADF microscopy (high-angle annular dark field), and μ -PL measurements (not shown here). Figure 1(a) shows a cross-sectional STEM image of the sample with a 2-nm wide ZnSe spacer, where the dark and bright regions indicate the Zn- and Cd-rich areas, respectively. From the image, the radius and height of the QDs can be estimated to be about 5 nm and 2 nm, respectively. By utilizing STEM energy-dispersive x-ray (EDX) spectroscopy, we were able to obtain local chemical information (Figs. 1(c)–1(e)). Cross-sectional profiles of the Mn and Cd content for the $L_B = 2$ nm sample are shown in Figures 1(c) and 1(e), respectively, and their integrated line profiles are displayed in Fig. 1(d). It is clear that the QDs and DMS layers are well defined and separated as intended.

FIG. 1. (a) Schematic picture of the studied structures along with an STEM image displaying a close-up of the CdSe QD layer. The bright and dark areas correspond to Cd- and Zn-rich regions, respectively. (c)-(e) Profile of Mn and Cd content across the structure with the 2 nm wide ZnSe barrier. (b) Schematic drawing of the structure aligned with (c)-(e).

Spin polarization properties of the structures were studied by monitoring circularly polarized PL under CW and pulsed excitation by a tunable laser at 2 K and in magnetic fields up to 5 T. In CW measurements, linearly polarized excitation light provided by a dye laser was tuned in the range of 430–460 nm. The resulting PL signal was spectrally resolved by a double grating monochromator and was detected by a photomultiplier tube. Circular polarization degrees of the PL were analyzed by a quarter-wave plate in combination with a linear polarizer. PL excitation (PLE) spectra of the QDs were obtained by monitoring at the peak

position of the QD PL emission while scanning the excitation photon wavelength of the dye laser. Time-resolved PL (TR-PL) measurements were performed using a tunable Ti:sapphire pulsed laser with a repetition rate of 76 MHz and a pulse duration of ~ 2 ps. TR-PL was detected by a streak camera combined with a monochromator. In all measurements, the direction of the propagating light was normal to the sample surface and parallel to the magnetic field for both excitation and detection in a backscattering geometry as shown in Fig. 1(a).

Figure 2(a) shows low temperature CW PL spectra from the structure with $L_B = 10$ nm at 0, 2.5, and 5 T and with excitation energy fixed at 2.88 eV, which is above the bandgap energies of all concerned layers, i.e., the QDs, DMS, and ZnSe spacer. Several emissions can be clearly distinguished. The quantum confined heavy-hole (hh) exciton state in the CdSe QDs gives rise to the PL emission peaking at ~ 2.60 eV, on the lower energy side of the spectra. The observed broad excitonic emission band of the QD ensemble is due to a large variation in the size and also possibly chemical composition of different dots within the sample. The ZnSe and DMS layers both emit at 2.79 eV at 0 T, as expected for the Mn content used.²⁰ In the presence of an external magnetic field, the DMS PL peak undergoes a large red shift in energy by ~ 35 meV at 5 T. This is due to the giant Zeeman splitting of the bright excitonic states of the DMS into two components, leaving the σ^+ active $| -1/2, +3/2 \rangle$ state at the lower energy. Here, $| m_s^e, m_j^h \rangle$ denotes the exciton state consisting of an electron with a magnetic quantum number m_s^e and a hole with m_j^h . The assignment of the exciton state is confirmed by the performed PL polarization measurements (Fig. 2(b)) where strong σ^+ circular polarization is observed for the DMS peak in an applied magnetic field. Here, PL polarization is defined as $P = (I_+ - I_-) / (I_+ + I_-) = (N_+ - N_-) / (N_+ + N_-)$, where $N_{\pm 1}$ is the population of $\sigma^{\pm}$ active $| \mp 1/2, \pm 3/2 \rangle$ exciton states, and $I_{\pm}$ is the intensity of $\sigma^{\pm}$ polarized PL emission. PL from the CdSe QDs and ZnSe layers, on the other hand, becomes σ^-

FIG. 2. (a)-(b) Representative PL and PL polarization spectra obtained at 0, 2.5, and 5 T, under excitation by linearly polarized light at 2.88 eV (430 nm). The PL peak positions of the σ^+ active DMS excitonic emission are indicated by the arrows. (c)-(d) PLE and PL polarization spectra obtained at 0, 2.5, and 5 T by monitoring the QD PL emission at the 2.605 eV (i.e., QD's PL peak position). The PL and PLE peaks related to the σ^+ active DMS exciton state are indicated by the arrows in (a) and (c). All data were obtained at 2 K from the sample with $L_B = 10$ nm, as an example.

polarized at 5 T. This is determined by the ordering of their spin levels that is opposite to that in the DMS, i.e., the σ^- active $|+1/2, -3/2\rangle$ exciton state lies lower in energy due to the Zeeman splitting and is thus favorably populated. In the absence of an external magnetic field, spin degeneracy of the exciton ground state leads to zero circular polarization of the PL from all parts of the structure as expected.

The sizable difference in the bandgap energies of the QDs, the DMS, and the ZnSe spacer in magnetic fields makes the current structures ideal to selectively investigate possible direct effect of photo-generated excitons in the DMS on the polarization properties of the QDs by tuning the excitation photon energy exactly at the excitonic bandgap of the DMS. Representative PLE spectra are displayed in Fig. 2(c), which can be characterized by preferential light absorption within different spatial regions of the structure. Photo-excitation with photon energies below 2.75 eV at 5 T corresponds to selective excitation of the CdSe QDs alone, referred to as quasi-resonant excitation below. The excitonic absorption within the nonmagnetic ZnSe layer gives rise to the PLE peak at ~ 2.8 eV, which at 0 T overlaps with the excitonic absorption of the DMS. The latter undergoes a giant Zeeman splitting in a magnetic field as indicated by the arrows in Fig. 2(c). The observation of the DMS-related excitons in the PLE spectra allows us to accurately determine their spectral positions at different magnetic fields.

The polarization degree of the QDs PL as a function of excitation photon energy is shown in Fig. 2(d). The quasi-resonant excitation provides a direct probe of the intrinsic spin polarization of the QDs, which was found to be approximately -15% at 5 T. When the excitation photon energy was tuned exactly at the σ^+ active DMS excitons state, a significant change of the polarization degree of the QDs PL was detected. Surprisingly, the polarization of the QDs PL becomes further more negative by about -5% at 5 T. This is opposite to what is expected for spin injection from the σ^+ active DMS excitons state to the QDs.^{10–12} This finding unambiguously rules out direct injection of spin polarized carrier/excitons from the DMS as being responsible for the observed change in the QD PL polarization. Instead, it should arise from an anti-parallel spin interaction between the CdSe QDs and the DMS. Anti-parallel interaction has been reported earlier in a number of coupled quantum layer structures,^{15–19} which was suggested to originate from AFC of photo-generated carriers/excitons spins between the QDs and DMS. Up to now, a direct proof for the suggested model is still lacking.

In order to directly determine if the photo-generated excitons in the DMS are indeed directly involved in the observed AFC, we have carried out a detailed investigation of the transient PL properties of the QDs and DMS bearing in mind that their exciton lifetimes are expected to be significantly different. As shown in Fig. 3(a), decay of the σ^+ active DMS exciton at 5 T (Fig. 3(a)) is very fast, dropping by two orders of magnitude within 0.2 ns after the laser pulse. On the other hand, decay of the QD PL is found to be much slower. It is also insensitive to excitation photon energy whether it is below or above the DMS excitonic bandgap, i.e., at 460 nm or 448 nm, except of an overall increase in the PL intensity for the above DMS excitation

FIG. 3. (a) Typical decay curves of the PL intensity detected at the DMS and QD PL peak. For the QDs, decays at two different excitation energies are displayed, i.e., at 460 nm for the quasi-resonant excitation and at 448 nm for the DMS excitation. (b) Transient circular polarization degree of the QD PL under the two different excitation conditions. All data were obtained at 2 K from the sample with $L_B = 10$ nm.

that is in accordance with the PLE results shown in Fig. 2(c). The decay of the QD PL is nonexponential, which can be attributed to contributions from both bright and dark exciton states of the QDs as well as from QDs with different sizes.

The polarization dynamics of the QD PL at 5 T is presented in Fig. 3(b). After the unpolarized laser pulse under the quasi-resonant excitation condition (at 460 nm), the QD PL develops a negative PL polarization as a result of thermalization of excitons from the higher to the lower lying Zeeman level. After about 1 ns, the polarization value starts to saturate at a certain level. The saturation level critically depends on the excitation photon energy. A strong increase in the QD polarization is observed under the excitation at the DMS exciton state, by about -5% as compared with that under the quasi-resonant excitation, in agreement with the results from the CW measurements (see Fig. 2(d)). On the other hand, the decay dynamics of the QD polarization is very similar under both excitation conditions. Most importantly, it is found to be uncorrelated with the decay dynamics of the excitons in the DMS, i.e., the QD polarization continues to grow even after the DMS excitons have vanished. This finding forces us to rule out the exciton spins in the DMS as the source of the AFC between the QDs and the DMS—a model suggested so far in the literature. Otherwise, the AFC effect would have ceased to exist after the lifetime of the DMS excitons that would have led the QD PL polarization returning back to the value under the quasi-resonant excitation.

Besides the DMS exciton spins, spins of the Mn ions in the DMS can also be aligned under the optical excitation at the σ^+ active DMS exciton state at 5 T. As spin dynamics of the Mn ions is known to be relatively slow, in order of 1 μ s in DMS with a similar Mn content,²¹ the spin-polarized Mn ions could effectively maintain their interaction with the QD exciton spins within the lifetime of the QD excitons (i.e., over the 1.5-ns time window in our TR-PL measurements). Therefore, the spin-aligned Mn ions in the DMS can be a plausible source of the enhancement in the QD PL and spin polarization. The involved physical processes must be able to alter the parameters of the QD excitons that determine the QD PL and spin polarization, i.e., lifetime, spin splitting, and spin-relaxation time. The QD exciton lifetime is shown to be independent of excitation energies, see Fig. 3(a), and therefore cannot be responsible for the observed effect. Spin splitting of the QD exciton could be affected by spin interactions between the QD excitons and the Mn ions in the DMS, i.e., an interlayer magnetic coupling between these two spin-polarized ensembles in the applied magnetic field. It has been shown²² that dipolar magnetic interactions can result in strong internal magnetic fields. In our case, this internal magnetic field can increase the spin splitting of the QD excitons leading to the observed increase in the QD PL polarization under the excitation of the DMS when the Mn ions become spin polarized. It is interesting to note that under photo-excitation at and above the bandgap energy of the ZnSe spacer layer that is sandwiched between the QDs and the DMS, the QD polarization enhancement is strongly suppressed as shown in Fig. 2(d). This is despite of the fact that the DMS excitons and also the Mn ions are still spin polarized under such excitation condition, as judging from the strong polarization of the DMS PL emission shown in Fig. 2(b). This suppression could be attributed to efficient screening of the magnetic interaction between the QDs and the DMS by the ZnSe spacer layer. Another physical process that can also in principle affect the QD PL/spin polarization is acceleration of spin-relaxation of the QD excitons in the presence of the Mn ions in the adjacent DMS, provided that an overlap in their wavefunctions or a strong magnetic dipole-dipole interaction ensures efficient spin flip-flops between them. A strong wavefunction overlap seems to be highly unlikely, however, considering the large (10 nm) thickness of the ZnSe spacer, which separates QDs and DMS. Moreover, it is unclear why photo-excitation of the DMS is required here as the spin flip-flop process should remain active even the spins of the Mn ions are not aligned under the quasi-resonant excitation of the QDs, as long as the extent of the wavefunction overlap between the QD excitons and the Mn ions in the DMS is comparable. This model also encounters difficulties to provide an explanation for the observed suppression of the effect under the optical excitation of the ZnSe layer. These experimental facts seem to favor the magnetic coupling between the QD exciton spins and the spin-polarized Mn ions in the DMS, discussed above, as a more plausible model.

We would also like to point out that the observed QD polarization enhancement upon excitation of the DMS is strongly dependent on the ZnSe spacer thickness. The effect completely vanishes as we lower the spacer width from 10 to

5 nm (see Fig. 4). Moreover, with an even thinner spacer (i.e., 2 nm), a decrease of the QD polarization was observed. This observation could indicate that the excitons in the QDs are subject to several counteracting interactions, such as anti-ferromagnetic, ferromagnetic coupling, and spin injection, of which relative importance changes with the spacer thickness. Such dependence on the spacer thickness is somewhat expected, as common magnetic interactions such as magnetic dipolar coupling and exchange interaction are known to be a sensitive function of the separation between two coupled magnetic layers.²² Together with the results from earlier reports,^{17,18} the observed AFC seems to be effective when the spacer thickness is in the range of 5-40 nm.

In conclusion, magneto-optical PL, PLE, and TR-PL measurements were employed for studies of magnetic interactions between the nonmagnetic CdSe QDs and the ZnMnSe DMS QW. PLE has provided strong experimental evidence for an interlayer magnetic interaction when the coupled QDs and DMS are separated by a 10 nm thick ZnSe spacer layer, probably via dipole-dipole antiferromagnetic coupling. From the TR-PL, the magnetic interaction was found to be long-lived (>1.5 ns) and is concluded to occur between the exciton spins in the CdSe QDs and spin-polarized Mn ions in the DMS, not the DMS excitons as commonly suggested in the literature. For the coupled structures with a lower ZnSe spacer thickness, the observed effect vanishes, which indicates decreasing importance of the AFC

FIG. 4. PLE and PL polarization spectra obtained at 2 K and 5 T from the structures with barrier thickness L_B of (a) 10 nm, (b) 5 nm, and (c) 2 nm. Excitation source was linearly polarized and detection window was set at the QD PL peak position for all curves.

in the presence of other competing magnetic interactions such as ferromagnetic coupling.

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