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Giant Change in the Intensity of Tunneling Afterglow in Excited ZnO Quantum Dots Induced by the Spin Reorientation of Electron–Hole Pairs in Static and Microwave Magnetic Fields

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Long afterglow has been detected in light-excited ZnO quantum dots caused by the spin-dependent tunneling recombination of electron and hole centers. A giant increase in the intensity of afterglow upon a change in the spin orientation of electron and hole centers has been observed under electron paramagnetic resonance conditions, which allowed these centers to be identified.

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In this work, long tunneling afterglow (TA) in ZnO quantum dots (nanocrystals) exposed to short-term irradiation with ultraviolet (UV) light with a quantum energy in the interband absorption region was detected and studied. It was observed at low temperatures for several hours after irradiation was stopped. Previously, long TA was observed only in bulk crystals after x-ray irradiation, and it was induced by tunneling recombination between electron and hole centers generated by x-ray irradiation [1]. The long duration of TA in these systems (up to 20 h after the termination of x-ray irradiation) was due to the long distance between recombining partners. It was shown that TA is a spin-dependent process; therefore, the magnetic quenching of afterglow is observed in strong magnetic fields at low temperatures caused by the spin polarization of electron and hole centers in accordance with the Boltzmann distribution. Based on this effect, it became possible to detect the electron paramagnetic resonance (EPR) of electron and hole centers optically by an increase in the intensity of TA at an instant of EPR due to spin reorientation in one of the recombining partners and, thus, to identify these defects (optically detected magnetic resonance, ODMR) [2].

Electron paramagnetic resonance spectra of electron and hole centers (donors and acceptors) in ZnO quantum dots have recently been studied by the high-frequency electron spin echo (ESE) technique [3–5], and shallow donors and acceptors have been identified in these systems. It has been shown that shallow donors represent interstitial lithium atoms (LiOH has been used in the preparation of nanocrystals) and that acceptors are of two types: (i) deep acceptors conventional for bulk ZnO crystals that represent lithium atoms substituted for zinc atoms Li_{Zn} [6] and zinc vacancies V_{Zn} [7] and (ii) deep acceptors associated with sodium located near the interface. The latter have been identified using electron–nuclear double resonance (ENDOR) [5]. The value of the *g* factor of acceptors associated with sodium has been found by monitoring the EPR signal of exchange-coupled donor–acceptor pairs in small-size ZnO nanocrystals, because the *g* factor of such pairs has been equal to a half-sum of the *g* factors of shallow donors and deep acceptors. Exchange-coupled donor–acceptor pairs with a different type of deep acceptors (Li_{Zn} and V_{Zn}) have not been observed, probably because of the anisotropy of their *g* factors and, consequently, the broadening of EPR lines and a decrease in the intensity of signals. Therefore, the question of whether Li_{Zn} and V_{Zn} acceptors participate in tunneling recombination has remained open.

Before this work, TA was not observed in quantum dots; therefore, we believe that the use of ODMR by tunneling recombination afterglow is the most direct technique for the identification of centers involved in recombination.

As in [3–5], we studied dry powders of free-standing $Zn(OH)_2$-capped ZnO nanocrystals obtained by

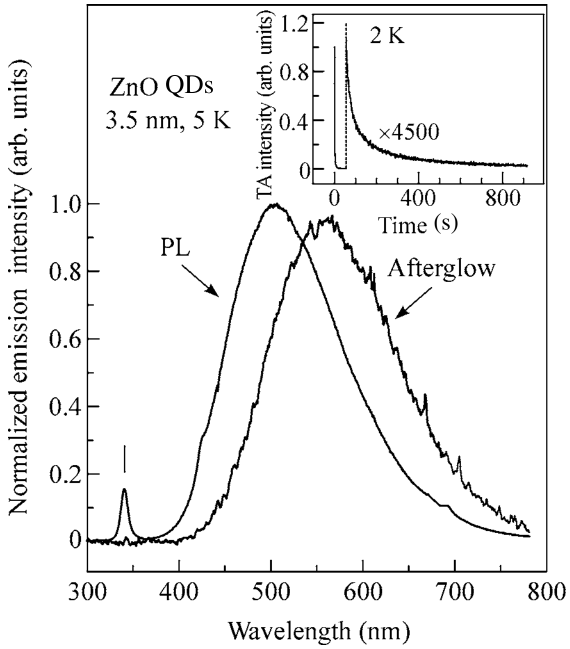

Fig. 1. Tunneling afterglow spectrum recorded for ZnO quantum dots at a temperature of 5 K after short-term irradiation (~5 min) with UV light in the region ~300 nm at the same temperature. The photoluminescence spectrum recorded at 5 K with excitation by ~300 nm radiation is also shown. The vertical line marks the emission of excitons in the photoluminescence spectrum. The time dependence of the intensity of tunneling afterglow in the same sample after short-term irradiation with UV light at 2 K is presented in the inset.

colloid chemistry technique (the sample preparation procedure was described in [3–5]). We studied nanocrystals 3.5 nm in size, and the scatter in their sizes was no more than 10%.

The tunneling afterglow spectrum recorded for ZnO quantum dots 3.5 nm in size at a temperature of 5 K after irradiation with UV light in the interband absorption region (the band gap in a bulk ZnO crystal is 3.3 eV) with a wavelength of ~300 nm at the same temperature is shown in Fig. 1. The photoluminescence (PL) spectrum recorded at 5 K with excitation of ~300 nm is also shown. The vertical line marks the emission of excitons, which is observed only in the photoluminescence spectrum. The TA spectrum was observed in the dark at a low temperature for ~5 h after the termination of UV irradiation. The shape of the spectrum and its intensity remained virtually unchanged in the temperature range 1.5–10 K. The time dependence of the intensity of TA in the same sample after short-term irradiation with UV light at 2 K is presented in the inset in Fig. 1. It is evident that the TA intensity drops by more than three orders of magnitude in the first seconds after the termination of excitation and then slowly decreases for a long time.

It has been found that TA in ZnO quantum dots is a spin-dependent process and that magnetic quenching of TA is observed in strong magnetic fields at low temperatures. The magnetic-field dependence at a temperature of 2 K is presented in Fig. 2 (corrected with regard to the decrease in the TA intensity during the magnetic field sweep). The preferred spin orientations of electron and hole centers in the region of strong magnetic fields due to the Boltzmann distribution are shown conventionally with arrows in the right-hand part of the figure, and the absence of recombination for parallel spins is shown schematically with a double arrow with a cross. The character of quenching corresponds to the recombination of two centers with electron g factors of ~2.0 and spins $S = 1/2$ in accordance with the expression $I = I_0(1 - P_eP_h)$, where I_0 is the TA intensity in a zero magnetic field and P_e and P_h are the spin polarizations of electron and hole centers in the magnetic field. The calculated magnetic-field dependence of the afterglow intensity for the recombination of such an electron–hole pair with electron spins for an electron and a hole $S_e = S_h = 1/2$ and g factors $g_e = 1.965$ and $g_h = 2.003$ is shown with a dashed line. The use of the g factor for holes $g_h = 2.025$ insignificantly changes the calculated dependence (within the limits of the thickness of the dashed line). In the region of magnetic fields of 1.2–1.3 T, a sharp increase in the TA intensity (up to 10%) is observed in the presence of a microwave field (a frequency of 35.2 GHz), while the intensity gradually decreases in the absence of a microwave field, in agree-

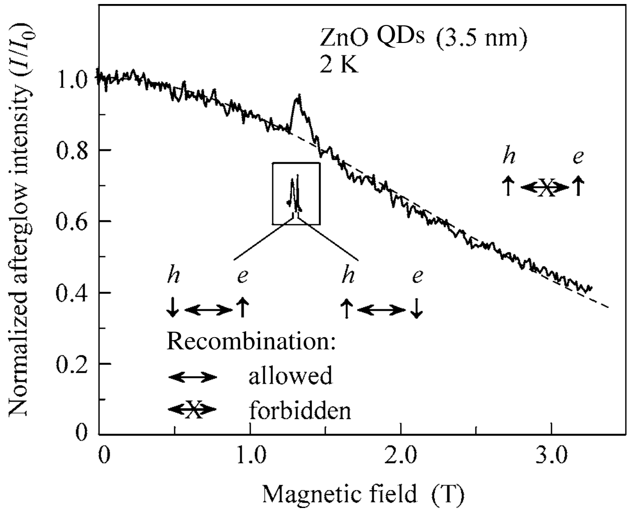

Fig. 2. Magnetic-field dependence of tunneling afterglow in ZnO quantum dots at a temperature of 2 K in the presence of 35.2-GHz microwave field. The dependence of TA in the region of magnetic fields of 1.2–1.3 T at a slow magnetic-field sweep is shown in the inset. The calculated magnetic-field dependence of the TA intensity is shown by the dashed line. The spin orientations of electron (e) and hole (h) centers are shown conventionally by vertical arrows under Boltzmann equilibrium conditions (the upper scheme) and under EPR conditions for electron and hole centers; the double horizontal arrow with a cross schematically shows the recombination process forbidden for the same orientation of spins.

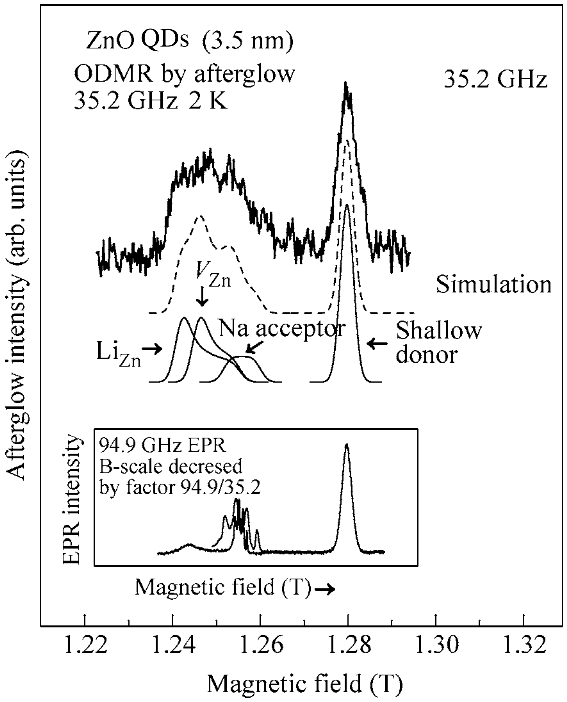

Fig. 3. ODMR signal at a frequency of 35.2 GHz at 2 K recorded by the overall TA spectrum in two hours after the termination of UV excitation. Simulated ODMR spectra of shallow electron centers and three types of hole centers with deep levels are shown below. The EPR spectrum recorded for the same system of quantum dots by the electron spin echo technique at a frequency of 94.9 GHz at 2 K is shown in the inset. The scale of magnetic fields is decreased according to the ratio of frequencies 94.9/35.2.

ment with the theoretical dependence. The dependence recorded at a slow magnetic-field sweep to exclude the effect of relaxation processes on the shape of the resonance signal is shown in the inset. The application of microwave power leads to an increase in the TA intensity in magnetic fields corresponding to EPR transitions for electron (*e*) and hole (*h*) centers due to the reorientation of the electron spin and the switching of the recombination regime. This means that magnetic resonance is detected optically. The effect of recombination switching at the instant of EPR is conventionally shown in Fig. 2 with arrows for hole (on the left-hand side) and electron (on the right-hand side) centers. As a result, the TA intensity at the instant of resonance virtually restores its value (with regard to the decrease in the TA intensity over time). It should be emphasized that the change in afterglow at the instant of resonance can approach 100% for higher frequencies and, correspondingly, strong magnetic fields.

The ODMR signal at a frequency of 35.2 GHz at 2 K recorded by the overall TA spectrum in two hours after the termination of UV excitation is presented in Fig. 3. Shown below are simulated ODMR spectra of shallow electron centers (shallow donors) and three types of hole centers with deep levels (deep acceptors) that were previously discussed in [5]: centers associated with Na atoms localized near the interface, zinc vacancies V_{Zn}, and lithium atoms at zinc positions Li_{Zn}. The overall simulated spectrum is shown with a dashed line. Shallow donors with a *g* factor of 1.965 coinciding with the *g* factor obtained by high-frequency EPR can be detected in the ODMR spectra. At the same time, signals of several types are seen in the low-field part of the spectrum, which belongs to deep acceptors. It seems useful to compare these signals with signals observed by high-frequency EPR. Therefore, the inset presents the EPR spectra recorded for the same system of quantum dots (for ZnO quantum dots 3.5 nm in size after short-term UV irradiation) by the ESE technique at a frequency of 94.9 GHz at 2 K. The scale of magnetic fields is decreased according to the ratio of frequencies 94.9/35.2 in order that the positions of EPR signals be determined by the corresponding *g* factors and the frequency effect be eliminated. Because the hyperfine splitting for surface acceptors associated with sodium (2.4 mT) does not depend on frequency, the real EPR signal for a frequency of 35.2 GHz is shown above. It is evident that there is a correlation between the two procedures of recording EPR spectra; however, the ratios of intensities for various acceptor signals differ significantly. This difference is caused by the difference in the physical principles of detecting EPR underlying these procedures. ODMR is directly associated with the recombination efficiency for defects of a certain type at the instant of detection, while defects remaining in the sample at the instant of detection are observed in the EPR spectrum. It is important to emphasize that the relative intensities of signals of hole centers vary over the time passed after the termination of UV excitation; that is, the proposed procedure allows the entire recombination process to be followed over time.

A weak EPR signal (the change in the PL intensity at the instant of resonance was $\sim 10^{-2}\%$) was observed in the ODMR spectrum recorded by the photoluminescence intensity presented in Fig. 1. The *g* factor of this signal corresponded to exchange-coupled electron–hole pairs composed of a shallow donor and an acceptor of the Li_{Zn} or V_{Zn} type, that is, pairs that were not observed in high-frequency EPR experiments.

The dependence of TA on the spin orientation of electron and hole centers allows the spin–lattice relaxation times T_1 to be measured directly by the decrease in the magnetic resonance signal over time passed after the microwave power was switched off. The time T_1 for electron and hole centers at a temperature of 2 K equals 3–4 s.

The probability of tunneling recombination of electron–hole pairs and, hence, the intensity of tunneling recombination afterglow *I* are rapidly decreasing functions of the distance between recombining partners. The dependence $I(t) \sim C/t$ is fulfilled in bulk materials for large time intervals passed after the termination of (x-ray) excitation [1]. In subsequent studies, it will be of interest to consider specific features of the time dependence of the TA intensity $I(t)$ in quantum dots, that is, under conditions when the distances between recombining partners are spatially confined.

Recombination processes in ZnO quantum dots change under additional weak irradiation with long-wavelength light (red or infrared), leading to the ionization of donors or acceptors and to the appearance of photostimulated luminescence. Previously, we developed a method for detecting the magnetic resonance of excitons and electron–hole pairs in bulk materials by photostimulated luminescence [8], which can be very promising in studying quantum dots.

This work offers new possibilities for studying spin-dependent processes in quantum dots, including studying single quantum dots, because of the high sensitivity of the method due to the absence of exciting light. In addition, the possibility of determining the absolute signs of g factors of recombining partners arises. This is of interest in studying shallow donors, because the sign of their g factors depends on the band structure of the material. The process of dynamic polarization of lattice nuclei in quantum dots can also be studied by methods of detecting magnetic resonance by TA. It seems promising to use the results of this work for the resonance detection of weak high-frequency microwave fields up to the terahertz range. The sensitivity of the method will considerably increase at high microwave frequencies, because the quenching of TA in strong magnetic fields is more significant.

Of special interest is the use of methods developed in this work for studying spin-dependent processes in ZnO quantum dots doped with magnetic ions. Such systems are promising for creating materials for spintronics. In this case, internal magnetic fields created by magnetic ions can lead to anomalous afterglow quenching in these materials.

Thus, long spin-dependent tunneling recombination afterglow is found in ZnO quantum dots excited by short-term UV irradiation. Because of the giant increase in the intensity of tunneling afterglow upon the spin flip in electron and hole centers participating in recombination, these centers were identified by their ODMR spectra. It was shown that recombination involves shallow donors and deep acceptors of two types: (i) deep acceptors conventional for bulk ZnO crystals, namely, lithium atoms substituted for zinc atoms $\mathrm{Li_{Zn}}$ and zinc vacancies V_{Zn}, and (ii) deep acceptors associated with sodium located near the interface.

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