DOI 10.1007/s10946-019-09802-7
Journal of Russian Laser Research, Volume 40, Number 3, May, 2019

SEPARATION OF QUANTUM EMITTERS PRODUCED BY SINGLE DONOR–ACCEPTOR PAIRS UNDER LASER EXCITATION

V. S. Bagaev, V. S. Krivobok, S. I. Chentsov, E. E. Onishchenko, A. A. Pruchkina,* S. N. Nikolaev, M. A. Chernopitssky, and D. M. Litvinov

Lebedev Physical Institute, Russian Academy of Sciences
Leninskii Prospect 53, Moscow 119991, Russia

*Corresponding author e-mail: pruchkina-aa@mail.ru

Abstract

We study features of point emitters in ZnSe-based quantum wells using laser-based spectroscopy with a high spatial resolution. We determine the experimental conditions under which quantum emitters formed by donor-acceptor pairs are observed. We discuss the possibility of studying individual defects forming a donor–acceptor pair using the spectrum of the corresponding quantum emitters.

Keywords: quantum well, microphotoluminescence, donor–acceptor pair, acceptor, ZnSe.

1. Introduction

Spectroscopic techniques operating with integral quantities averaged over a macroscopic ensemble are often ineffective for studying defects in semiconductor heterostructures. The main limitations are associated with a random location of defects with respect to heterointerfaces, as well as the presence of composition fluctuations which determines noticeable inhomogeneous line broadening for any macroscopic ensemble of defects. Typical examples are heterostructures based on the 2–6 compound semiconductors, were point defects can be harmful (e.g., increase the lasing threshold and lead to a degradation of the active medium) as well as beneficial (e.g.. provide intracenter transition for MID IR lasing as in the case of ZnSe:Fe/Cr) for laser applications [1,2]. For a systematic study of defects in such a complex system, a method which enables operations with single objects is desirable to overcome inhomogeneous broadening. Ordinary laser-based microscopy with high spatial resolution allows one to solve this problem but only for low concentrations of defects due to the diffraction limit; see, e.g., [3]. Typically, optical measurements provide a very efficient tool for detailed investigation of single defects but are not suitable for a study of single defects in doped materials.

The approach to overcome this difficulty may, however, be based on the selection of a luminescent pair of two closely spaced defects [4,5]. In this case, the concentration of one of the defects, which plays the role of a "probe," can be chosen so that the possibility of isolating a single object on the scales of optical resolution is conserved. Obviously, this possibility will also be preserved for an interacting pair of the probe-analyzed object (a defect that needs to be investigated). Thus, optical access to a single object can be provided, bypassing the diffraction limit. In the present work, we successfully implement this approach using donor–acceptor pairs (DAPs) in a ZnSe-based quantum well (QW) as an example. We develop a method for observation of isolated quantum emitters formed by donor–acceptor pairs and investigate the properties of such emitters; also we implement the simplest example of defect probing, namely, we determine optically active phonon modes for single acceptors in a quantum well.

Manuscript submitted by the authors in English on May 08, 2019.

2. Experiment

The QW under study consists of a 20 nm thick ZnSe layer placed between the $Zn_{0.84}Mg_{0.16}S_{0.12}Se_{0.88}$ layers with a thickness of 100 nm. This structure was grown by molecular beam epitaxy on a GaAs : Si (001) substrate with electronic conductivity. The QW layer contains background impurities and defects including hydrogen-like Ga_{Zn} donors (caused presumably by Ga diffusion from the substrate) as well as acceptors at a concentration of $\sim 10^{15}$ cm^{-3}. Some of donors and acceptors form DAPs which provide the related luminescence bands in the spectral range of 2.75 – 2.55 eV [5]. The corresponding isolated (quantum) emitters are the main subject of this work.

The measurement of the microphotoluminescence spectra was carried out in reflection geometry at a temperature of 5 K. The QW structure was placed in a helium cryostat and excited by the radiation of a steady-state semiconductor laser operating at a wavelength of 405 nm. The size of the excitation spot was ∼3 mm, and a typical excitation power density was ∼5 mW/cm^2. In our experiments, low excitation density is crucial for visualization of DAP-related quantum emitters. Using cold microlens and a corrective lens, a 20 times magnified luminescence spot was focused on a slit of the grating spectrograph with a dispersion of 1.6 nm/mm. A nitrogen-cooled CCD detector was used for the visualization of luminescence signals. The image obtained on the CCD detector corresponds to a "spectral–spatial" map of the microphotoluminescence [6, 7]. The selected slit width in combination with the pixel size of the CCD detector provided a spectral resolution of not less than 0.04 nm with a spatial resolution of ∼1 μm.

3. Observation of Emitters Related to DAP's

Impurity and defect-related emission of the QW under study is qualitatively similar to that of strained ZnSe/GaAs film. Some of the shallow defect levels can be affected by ZnSe/ZnMgSSe interfaces, pushing the levels up, but this effect is negligible for acceptors characterized by a relatively localized ground state in ZnSe. Studies of a single point defect in QWs by the microphotoluminescence technique is difficult due to the fact that even at a defect concentration of $\sim 10^{15}$ cm^{-3} for a QW with a thickness of 20 nm and a characteristic spatial resolution of ∼1 μm, several tens of such objects contribute to the emission spectrum. It excludes a systematic observation of emitters associated with a single impurity atom or single defect. But QW microphotoluminescence can be successfully used to detect radiation from statistically rare objects, such as donor–acceptor pairs, as in the case of bulk semiconductors (for example, Te dimers in ZnSe [4]). Indeed, due to the large (average) spacing of the defects, the probability of DAP formation is relatively low. In particular, for the distances between donor and acceptor $R_{DA} < 10$ nm, this probability is about 0.004. Thus, at an area of ∼8×1 μm size, only one DAP with $R_{DA} < 10$ nm can be found. Such a pair, in contrast to the case of high R_{DA}∼15 – 40 nm, forms an emitter with a high oscillator strength due to noticeable overlapping of the wave functions of acceptor and donor ground states.

Figure 1 a illustrates a CCD image corresponding to a typical "spectral–spatial" map of the microphotoluminescence signal recorded from 1×100 μm spot on the sample surface. The map reveals an ensemble of point emitters, which can be clearly observed against the impurity and defect-related background. The map was obtained at a temperature of 5 K and ∼5 mW/cm^2 excitation power density using an exposure time of 10 s. The characteristic size of emitters is governed by the spatial resolution (∼1 μm) of the experimental setup. At the same time, the emission line half width (∼0.5 meV) is much smaller than the half width of the luminescence line for any known macroscopic ensemble of defects in a ZnSe-based QW. Thus, each sharp emitter in Fig. 1 a corresponds to a single (quantum) object and, consequently,

its emission spectrum is not affected by inhomogeneous broadening. The emitters disappear when the temperature is increased to 15 K (Fig. 1 b), and disappearing or broadening of their narrow emission line is observed when the excitation density increases. It should be noted that, in contrast to free-to-bound transitions [8], rapid quenching with temperature is expected for DAPs due to thermal dissociation of neutral donors [8]. The spectral position of emitters shown in Fig. 1 a as well as the presence of a rather intense phonon replica are typical for the DAP composed of shallow acceptor with the ground state energy ∼80 – 90 meV and a hydrogen-like donor. Luminescence patterns, similar to those presented in Fig. 1, were observed for other types of donor–acceptor pairs in the sample under study.

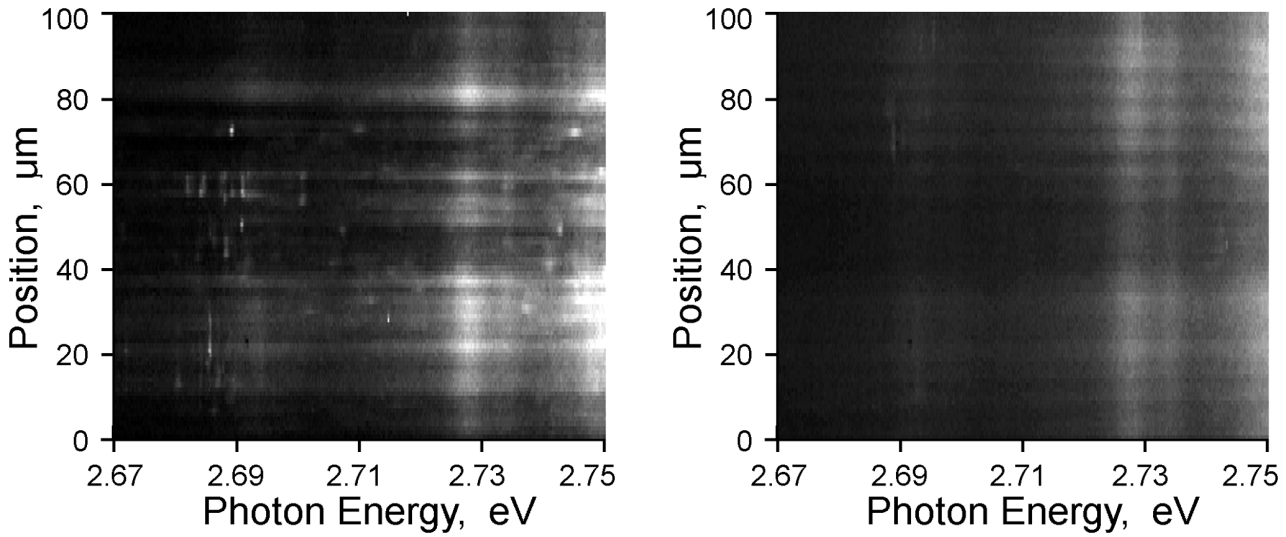

Fig. 1. Spectral–spatial microphotoluminescence maps recorded at a temperature of 5 K (left) and 15 K (right) for a spectral range corresponding to DAPs composed of a shallow acceptor and a hydrogen-like donor. Bright points on the left figure are emitters associated with single DAPs. At 15 K, no single emitters are observed.

4. Fine Structure of Emitter Produced by Single DAP

In the previous work [4] it has been shown that emitters produced by single DAPs reveal a jump-like change in the energy of the emitted photons with time. In [4], the DAP composed of a shallow acceptor and hydrogen-like donors was considered but qualitatively similar behavior is observed for the DAP composed of a deep acceptor and a hydrogen-like donor; see Fig. 2. The beats of spectral position of the zero-phonon emission line over time are apparently typical for any emitters produced by DAPs. These beats are caused by the interaction of the dipole moment of a DAP (in the ground state) with fluctuations of the local electric field. The most likely cause of the restructuring of the electric field near the DAP is a change of charge of defects in its vicinity [4]. For large accumulation times, the described effect leads to the formation of complex spectral structures, the components of which demonstrate anticorrelation. The use of signal accumulation times, which are noticeably shorter than the characteristic times of zero-phonon line jumps, allows us to track the spectral position of the DAP-related lines with time.

To strictly establish that the discussed point sources are indeed single (quantum) emitters, it is necessary to measure correlation functions of the second order – due to the fact that a specific state of an individual defect cannot emit two photons at the same time, a photon antibunching should be observed.

However, an analysis of the pattern of abrupt changes in the luminescence spectra associated with an individual DAP indicates that the emission observed can actually be caused by a single emitter – several components associated with a single DAP are not observed simultaneously.

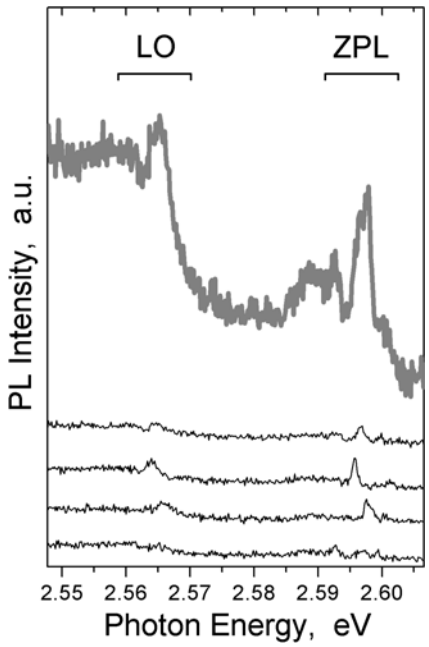

Fig. 2. Emission spectra of a DAP composed of a hydrogen-like donor and deep acceptor recorded using accumulation time of 10 s (black curves at the bottom) and 150 s (gray curve at the top). Here, "ZPL" denotes the zero-phonon line, "LO" is its LO phonon replica, the temperature is 5 K, and the excitation density is 5 mW/cm^2.

Let $\rho(I_1 > I_0)$ be the probability that the emission intensity of the DAP line in one of two positions I_1 exceeds a certain threshold value I_0, $\rho(I_2 > I_0)$ be the probability that the emission intensity of a DAP line at the second position I_2 exceeds the threshold value I_0, and $\rho(I_1 > I_0, I_2 > I_0)$ be the probability that at the same time both I_1 and I_2 exceed I_0. If the lines with intensities I_1 and I_2 are related to independent emitters, the probability that $I_1 > I_0$ and $I_2 > I_0$ simultaneously must be equal to the product of the probabilities $\rho(I_1 > I_0)$ and $\rho(I_2 > I_0)$. If we set the ratio of these probabilities r as

$$r(I_0) = \frac{\rho(I_1 > I_0, I_2 > I_0)}{\rho(I_1 > I_0)\rho(I_2 > I_0)},$$

it should be equal to unity for independent emitters.

The ratio $r(I_0)$ for the DAP formed by deep acceptor calculated using the experimental data is presented in Fig. 3. If I_0 is below the background emission level, the ratio is equal to 1, but as I_0 increases, it begins to fall sharply, which indicates that these lines are not independent, and there is an anticorrelation for spectral components located at different energies. This evidences in favor of the fact that these lines are caused by the same defect and, accordingly, we actually observe the emission of a single (quantum) source. A qualitatively similar behavior was observed for other types of DAPs.

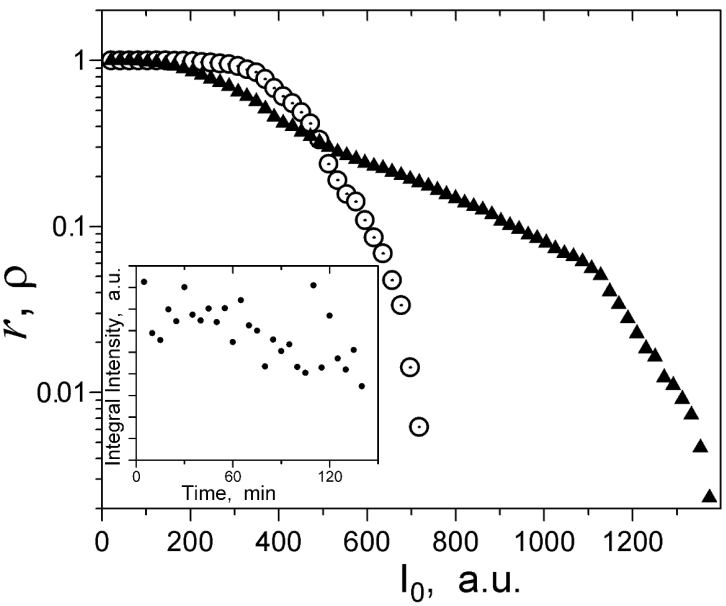

Fig. 3. Anticorrelation of different components corresponding to the ZPL fine structure for DAP-related emitters in Fig. 2. Here, the probability $\rho(I_1 > I_0)$ to detect fluctuating signal exceeding I_0 in a randomly located spectral range of 1 meV (▲), and the coefficient $r = \frac{\rho(I_1>I_0, I_2>I_0)}{\rho(I_1>I_0)\rho(I_2>I_0)}$ associated with the possibility to detect signals exceeding I_0 in two nonoverlapping spectral ranges of 1 meV simultaneously (⊙). Inset shows the integral intensity of the ZPL for DAP over time.

5. Probing of Single Acceptors Using DAP-Related Emitters

Separation of a single emitter formed by DAP provides optical access to each of the two defects constituting it. Below we present en example of "quantum probing" which this access provides – phonon modes coupled to certain single acceptors have been studied via DAP optical spectroscopy. Residual hydrogen-like donors with a Huang–Rhys factor $10^{1.5}-10^2$ times smaller than that for acceptor centers are apparently suitable "quantum probes" for this task. Due to the weak coupling of donors with the ZnSe lattice phonon, replicas of the emitter associated with a given DAP reproduce luminescence-active phonon modes for the single acceptor constituting this DAP. After choosing the appropriate experimental conditions, a large number of spectra were recorded, and only ones with a single peak without any excess spectral components were selected. Steady luminescent background (if any present) was subtracted from the selected spectra; the spectra were shifted to fit the ZPL and were then summed up.

Figure 4 illustrates the final results for the described procedure for DAPs formed by a shallow (E_A∼85 meV, complex defect with Ga or P_{Te} [9,10]), and deep (E_A∼230 meV, a complex formed with the participation of intrinsic point defect [11]) acceptors. Due to the fact that in each case the half width of DAP ZPL did not exceed 0.5 meV, the spectra obtained allowed us to measure LO phonon characteristic energies in the local area of the QW, as well as to study the phonon fine structure associated with the ZnSe/ZnMgSSe interface and/or defect-related local modes.

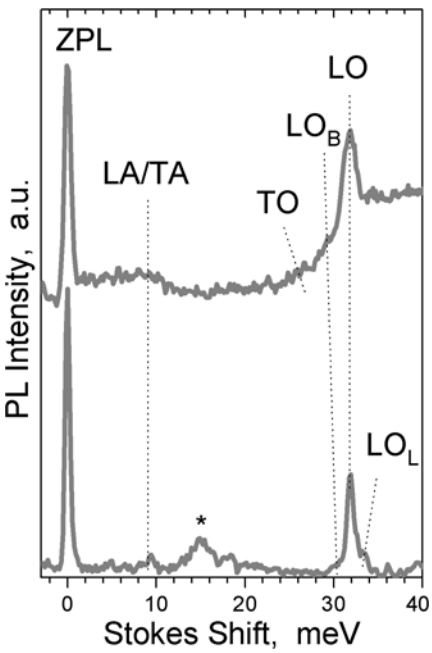

Fig. 4. Emission spectra of individual DAPs composed of a hydrogen-like donor and shallow (bottom curve), as well as deep (upper curve) acceptors. Zero at the abscissa axis corresponds to the spectral position of the zero-phonon line (ZPL). Here, ZnMgSSe LO phonon and local phonon modes are marked by LO_B and LO_L, respectively. Emission of other DAPs is shown by the star.

As can be seen in Fig. 4, the characteristic LO phonon energy remains approximately the same for each acceptor under consideration and is equal to 31.85±0.05 meV. This value is close to an LO phonon energy of 31.9±0.1 meV, corresponding to the center of the Brillouin zone in bulk ZnSe [12]. Broadening of the LO phonon replica, with respect to ZPL, can be estimated as well. For a shallow acceptor, this broadening is ∼0.1 meV, which is close to the homogeneous broadening caused by a small lifetime of optical phonons. A qualitatively different situation is observed for a deep acceptor – the value of the additional broadening, ∼1.1 meV, is approximately an order of magnitude higher than that for a shallow acceptor. This effect is apparently due to the localization of phonon mode and/or its effective tailing in the quasimomentum space.

Along with the characteristic energy and LO phonon broadening, the data obtained allowed us to analyze the contribution from additional phonon modes. In particular, the short-wave shoulder L_B with ∼30 meV Stokes shift can be identified as a LO phonon in ZnMgSSe barriers. A small high-energy peak observed for the shallow acceptor can be assigned to local phonon modes bound to an acceptor center. The appearance of localized high-frequency phonon modes is an expected effect in the case of a P_{Se} acceptor formed by a relatively light phosphorus impurity. Due to the significant enhancement of electron–phonon coupling, a qualitatively different situation is realized for the deep ac-

ceptor – along with ZnSe and ZnMgSSe LO phonons, the contribution of acoustic (LA/TA) phonons and transverse optical (TO) phonons can be clearly observed.

6. Conclusions

We studied the low-temperature microphotoluminescence of a wide ZnSe-based quantum well under laser excitation in the spectral range corresponding to the emission of shallow defects in ZnSe. We determined the experimental conditions under which quantum emitters formed by donor–acceptor pairs are observed. This type of emitters allows noncontact optical studies of single donors and acceptors in semiconductor heterostructures – a well-known point defect serves as a "quantum probe" providing access to the electronic and phonon subsystems of a complex center. In this paper, the method has been successfully applied to visualize optically active phonon modes coupled to single acceptor centers in ZnSe using hydrogen-like donors as "quantum probes."

Acknowledgments

The work was supported by the Russian Science Foundation under Grant No. 17-72-10265.

References

1. J. Peppers, V. V. Fedorov, and S. B. Mirov, *Opt. Express*, **23**, 4406 (2015).
2. R. Kröger, E. Roventa, A. Gust, et al., *Physica Status Solidi*, **201**, R28 (2004).
3. S. Dhomkar, P. R. Zangara, J. Henshaw, and C. A. Meriles, *Phys. Rev. Lett.*, **120**, 117401 (2018).
4. C. Marcet, R. Andre, and S. Francouer, *Phys. Rev. B.*, **82**, 235309 (2010).
5. V. S. Krivobok, N. Nikolaev, S. I. Chentsov, et al., *JETP Lett.*, **104**, 110 (2016).
6. V. S. Krivobok, S. N. Nikolaev, S. I. Chentsov, et al., *J. Lumin.*, **200**, 240 (2018).
7. A. A. Pruchkina, V. S. Krivobok, S. N. Nikolaev, et al., *J. Russ. Laser Res.*, **39**, 280 (2018).
8. P. J. Dean, B. J. Fitzpatrick, and B. N. Bhargava, *Phys. Rev. B*, **26**, 2016 (1982).
9. G. Neu, E. Tournie, C. Morhain, et al., *Phys. Rev. B*, **6**, 15789 (2000).
10. ISOLDE Collaboration, S. Lany, J. Hamann, et al., *Physica B*, **302**, 114 (2001).
11. Z. Zhu, G. D. Brownlie, G. Horsburgh, et al., *Appl. Phys. Lett.*, **67**, 2167 (1995).
12. D. Nesheva, M. Šćepanović , S. Aškrabić, et al., *Acta Phys. Pol. A*, **116**, 75 (2009).