

EXCITON PHOTOLUMINESCENCE

https://doi.org/10.1070/QEL16402

Photoluminescence dynamics of direct and indirect excitons in CdTe/ZnTe superlattices with quantum dot layers

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Abstract. **Photoluminescence kinetics is measured for spatially direct and indirect excitons in CdTe quantum dots excited by second harmonic radiation pulses of a picosecond Ti:sapphire laser. The width of a ZnTe barrier layer varied in the range of 2–12 monolayers (MLs). Since the photoluminescence decay curves are not described by a single exponential dependence, two components are analysed – fast and slow, which can be approximated by exponential functions. It is shown that in the samples with a barrier layer width of 12 and 4 MLs, the decay times for the fast component of a direct exciton and an indirect exciton are 0.4 ns and 3 μs, respectively. The long-term component is observed in both spectra. For a direct exciton, the photoluminescence decay time is 6 ns, and for an indirect exciton it is 22 μs. It is found that the recombination times for direct and indirect excitons in a sample with the barrier layer width of 2 MLs are close: in both cases the decay time for the fast component and slow component is 2 and 80 ns, respectively. Taking into account the tensile strain of the ZnTe layer and origin of the quantum well for light holes in this layer it is assumed that electrons in CdTe quantum dots interact with light holes in a ZnTe layer and generate a quasi-direct exciton because electron wave functions penetrate into the barrier.**

Keywords: *photoluminescence, exciton, direct exciton, indirect exciton, wetting layer, quantum dot, recombination time of an exciton, CdTe/ZnTe.*

1. Introduction

3D confinement and the possibility of easy integration into existing semiconductor lasers make quantum dots (QDs) a promising solid-state object for fabricating optoelectronic and quantum-information devices. Quantum dots are especially interesting due to their unique physical properties and possible potential employment in such optoelectronic devices as single-electron transistors, lasers, light emitting diodes and IR photodetectors. Recently, self-organised QDs have been used in new optoelectronic devices such as nano-emitters and single-photon emitters. Understanding the recombination dynamics of charge carriers in QDs is very important, because the performance of these devices is determined by the relaxation kinetics of energy and momentum. Dynamic dependences of photoluminescence (PL) of a QD ensemble are important for understanding the processes of recombination, relaxation and interaction between carriers. Thorough experimental investigations are necessary for the processes of recombination and relaxation from barrier energy states to QD discrete states. However, there is still no clear picture of main recombination processes in CdTe/ZnTe structures with QDs of various sizes. The processes of energy transfer between QDs, generation of radiation by direct and indirect excitons are very important. Of particular interest is the influence of built-in electric fields on the redistribution of charge carriers between QDs and investigation of the influence of the QD size on the time of exciton recombination. Earlier, a reduction of the PL decay time at smaller thickness of the CdTe layer [1] and a strong dependence of the recombination time on the exciton radiation energy in a CdTe QD [2] were found. Similar phenomena were also observed in structures with QDs in InGaN [3].

One more important problem is the comparison of radiative and nonradiative recombination of charge carriers. It is known that the decay of PL observed at high temperatures occurs due to diffusion of carriers, mainly holes, from a QD to a wetting layer or barrier, where radiationless recombination occurs. This process is characterised by an activation energy ΔE.

It is also known that PL time dependences of structures with QDs have two stages: fast and slow. The fast component of PL is related to recombination of 'bright' excitons, whereas the slow component refers to 'dark' excitons [4, 5]. Properties of such complexes depend on the relative orientation of the angular momenta of dimensionally confined charge carriers: an electron and a hole with antiparallel momenta form an optically active bright exciton with a projection of the total angular momentum to the QD growth axis $J_z = \pm 1$, whereas the parallel orientation of the angular momenta results in dark excitons with $J_z = \pm 2$. Due to the absence of an allowed dipole recombination channel, the lifetime of dark excitons may be above microseconds [6]. This time is determined by spin-flip scattering processes with participation of acoustic phonons. As a result of such interactions, dark excitons partially transfer to emitting bright excitons. Dark excitons are often neglected; however, due to their steady nature, dark excitons may adversely affect the properties of QD-based devices. For detecting dark excitons, measurements should be taken in polarised light in a direction normal to the axis of crystal growth.

Finally, radiationless recombination also plays a certain role in QD structures because bright and dark excitons may recombine without emission on impurities and defects in barriers and the wetting layer.

In the present work, we investigate the kinetics of photoluminescence in CdTe/ZnTe superlattices with CdTe QDs as

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Received 17 April 2017; revision received 13 June 2017
Kvantovaya Elektronika **47** (9) 867–870 (2017)
Translated by N.A. Raspopov

a function of width of ZnTe barriers varied from 12 to 2 monolayers. PL spectra comprise three radiation bands: these are radiation bands of the wetting layer, and direct and indirect excitons [7]. Our task is to study the PL kinetics of direct and spatially indirect excitons as a function of width of ZnTe barriers. We also analyse the activation energy of heavy holes transfer through the potential barrier into a QD.

2. Samples and measurement methods

Three 200-period structures were studied, which comprised layers of self-organising QDs in CdTe/ZnTe grown by the molecular-beam epitaxy on GaAs substrates (100) with a buffer layer CdTe(3 μm)/ZnTe(1.7 μm) [8]. A nominal width of CdTe layers was 3 MLs (1 ML = 3.24 Å), and the widths of ZnTe barrier layers varied from 2 to 12 MLs (1 ML = 3.05 Å).

Study of the sample transverse cross section by high-resolution transmission electron microscopy shows that QDs have the shape of disks with a thickness of 2–3 nm and diameter of 10–20 nm. Self-organising islands in an upper layer are arranged between islands of the lower layer [8]. QDs grow according to the Stranski–Krastanov growth model [8, 9], that is, start the growth on a surface of the wetting layer when the width of the latter is approximately 2 MLs.

Time-resolved measurements were performed by exciting the structures by the pulses of second harmonic radiation of a picosecond Ti:sapphire laser at a wavelength of 400 nm. The repetition rate of laser pulses lowered by an acousto-optical pulse selector to 0.9 MHz (and lower – for long-time range measurements). The radiation passed to a sample at an angle of about 60° with respect to the normal; PL was detected in a reflection geometry in the direction normal to the structure surface. Two lenses were used for collimating PL and focusing it onto an entrance slit of the spectrometer combined with a streak-camera having a single-scan unit. In such a configuration, the streak-camera provided recording spectral-kinetic characteristics of PL in time scales ranging from 1 ns to 1 ms. In addition, the kinetics of weak luminescence of indirect excitons in the structure was recorded without spectral resolution; for this purpose, a low-pass interference filter with a cut-off wavelength of 650 nm was used along with the mirror placed on a spectrometer ring mount instead of one of the gratings. All measurements were taken at a temperature of 5 K; a sample was placed into an optical helium cryostat with temperature control.

Stationary PL spectra were recorded by a SpectraPro2500i spectrograph equipped with a Spec-10 cooled multichannel CCD array; the spectral resolution was 0.05 meV. An argon laser operating at a radiation wavelength of 514.5 nm excited the PL. The power of laser radiation varied from 290 to 800 μW at a laser spot diameter of 200 μm. The measurements were made in a temperature range of 5–85 K.

3. Measurement results and discussion

3.1. Stationary PL of CdTe/ZnTe structures

In PL spectra of CdTe/ZnTe structures with a barrier width of 12 MLs there are three emission bands (Fig. 1a, [7]). The first (high-energy) band with a maximum at an energy of 2.25 eV refers to emission of quantum wells (QW) formed by CdTe wetting layers, the second (E_{max} = 2.05 eV) and third (E_{max} = 1.8 eV) bands are related to luminescence of QDs. According to the interpretation suggested in [10] and our measurements of PL in similar structures with a barrier width of 50 MLs, the second band of 40 meV width at E_{max} = 2.05 eV is determined by exciton recombination in isolated non-interacting QDs when electron and heavy hole forming an exciton are localised in a single QD (direct exciton). The third low-energy band with E_{max} = 1.8 eV is determined by exciton recombination in vertically correlated closely arranged QDs; the width of this band is 270 meV. In this case, the contribution into the recombination is made by electrons and holes localised in spatially separated neighbouring QDs, which form an indirect exciton [11]. The PL time dependence measurements clearly prove the relation of low-energy band to indirect exciton.

In a PL spectrum of the CdTe/ZnTe structures with a barrier thickness of 2 MLs one can see three emission bands at energies of 2.07, 2 and 1.94 eV (Fig. 1b, [7]). The first band is related to CdTe wetting layers, the other two bands, in our opinion, are related to PL of direct and indirect excitons. A noticeable shift of the maxima of the emission bands of the wetting layer and direct exciton to lower energies at a reduced barrier width is discussed in [7]. In a PL spectrum of the structure with a barrier width of 2 MLs, the low-energy band dominates. We ascribe it to the emission of indirect excitons,

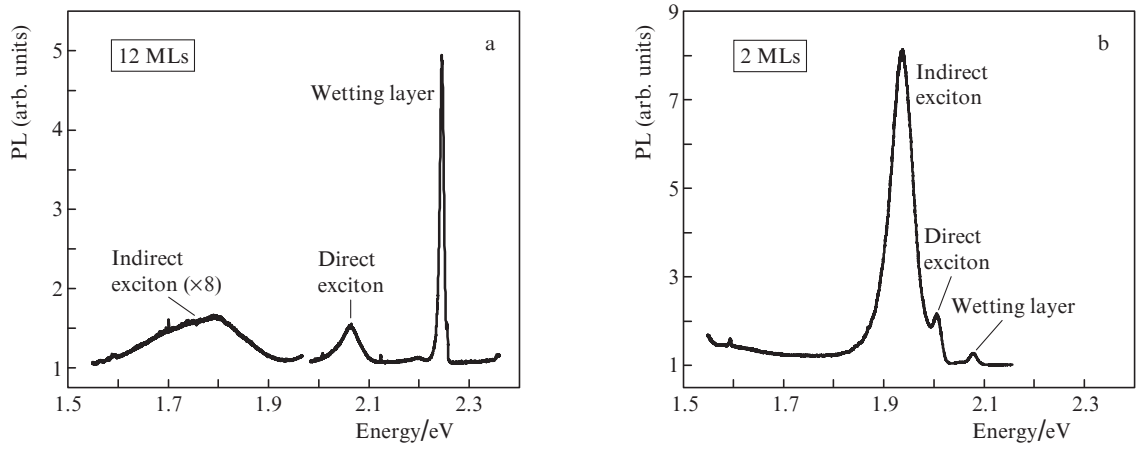

Figure 1. PL spectra of CdTe/ZnTe superlattices with barrier widths of (a) 12 and (b) 2 MLs at T = 5 K and the wavelength of exciting radiation λ_{ex} = 514.5 nm.

although it noticeably differs from a similar band in a structure with a barrier width of 12 MLs. The width of this band is substantially smaller (50 meV), and the integral PL intensity is three times higher than that of indirect excitons in the sample with a barrier width of 12 MLs. At a higher laser radiation power, the maximum of this band shifts to higher energies (the blue shift) by 17 meV, which is an indication of indirect exciton transition [7].

Note that strain of layers plays an important role in the energy structure of CdTe and ZnTe valence bands. Due to a difference in the lattice constants of CdTe and ZnTe, biaxial compressive strain arises in CdTe layers when the width of the ZnTe layer exceeds that of CdTe layer; the latter is 3 MLs in all structures. Under the action of this strain, the valence band splits, and the band of heavy holes shifts up in the energy scale. As a result, the QW is generated in CdTe layers for heavy holes with a potential barrier of ~80 meV. ZnTe layers are not deformed in this case. However, compressive strain in a sample with a barrier width of a ZnTe layer equal to 2 MLs (smaller than the width of CdTe layer) reduces, which lowers the potential barrier of the QW for heavy holes. On the contrary, in the ZnTe layer, tensile strain should arise, which splits the valence band of ZnTe, and the band of light holes shifts up in the energy scale producing QWs for light holes. Tension of the ZnTe layer is confirmed by the fact that the frequency of a ZnTe longitudinal optical phonon in this sample, according to Raman scattering measurements, reduces by 3 cm^{-1} and equals 203 cm^{-1} at a temperature of 300 K.

Thus, the Coulomb bonding arises between an electron in a QD and a light hole in a quantum well of the ZnTe layer. This exciton can be considered quasi-direct because the electron wave functions of neighbouring layers of the QD overlap in the superlattice with such narrow barriers. As will be shown later, this will affect the kinetics of PL.

The activation energies ΔE of heavy holes were determined from temperature dependences of PL. For direct excitons in samples with barrier widths of 12, 4 and 2 MLs, these energies are 20.4, 22.6 and ~8.4 meV, respectively. Values of ΔE are determined by heavy hole activation through the effective barrier, which equals the distance between the quantum level and potential barrier boundary, to the wetting layer or to ZnTe barrier layer, where they recombine without emission on impurities and defects. The height of the potential barrier of the QW for heavy holes decreases with decreasing compressive strain in the CdTe layer.

Activation energies ΔE in a sample with a barrier width of 2 MLs are 6.8 and 8.4 meV for the wetting layer and direct exciton, respectively. These facts confirm the reduction of compressive strain and, consequently, the values of QW potential barriers for heavy holes in a QD and in the wetting CdTe layer. The activation energy of an indirect exciton in a sample with a barrier width of 2 MLs is 19.4 meV, which testifies that the activation process in this case is not related to a heavy hole. Note that a PL spectrum of this sample has no wide low-frequency band ($E \approx 1.8$ eV) related to luminescence of indirect excitons, which is present in structures with barrier widths of 4 and 12 MLs. We explain this by the fact that heavy holes in a quantum well of a CdTe QD pass to a QW for light holes of the ZnTe layer, without reaching the nearest QD layer.

3.2. PL kinetics of CdTe/ZnTe structures with barrier widths of 12, 4 and 2 MLs

The PL time dependences of direct and indirect excitons in a sample with a barrier width of 12 MLs are shown in Fig. 2. The fast component of the PL decay for a direct exciton can be described by the exponent that is determined by a recombination time of bright excitons. The slow component can be described by the exponent related to the recombination time of dark excitons converted to bright ones due to scattering [4, 5]. According to Fig. 2a, the decay time of the fast component is $t_1 = 0.4$ ns. The slow component is characterised by the decay time $t_2 = 6$ ns. The decay time of the fast PL component for an indirect exciton is 3 μs, and for the slow component it is 22 μs (Fig. 2b).

In Fig. 3 one can see similar kinetic dependences for the sample with a ZnTe barrier width of 4 MLs. The decay times t_1 and t_2 of the fast and slow PL components for a direct exciton are 0.4 and 4.1 ns, respectively (Fig. 3a). For an indirect exciton, the PL decay time of the fast component is 3 μs, and for the slow component it is 16 μs (Fig. 3b). Obviously, the PL decay times for direct excitons are almost four orders in magnitude less that for indirect excitons. Kinetic characteristics of the fast PL component for direct and indirect excitons in the samples with barrier widths of 4 and 12 MLs are close in

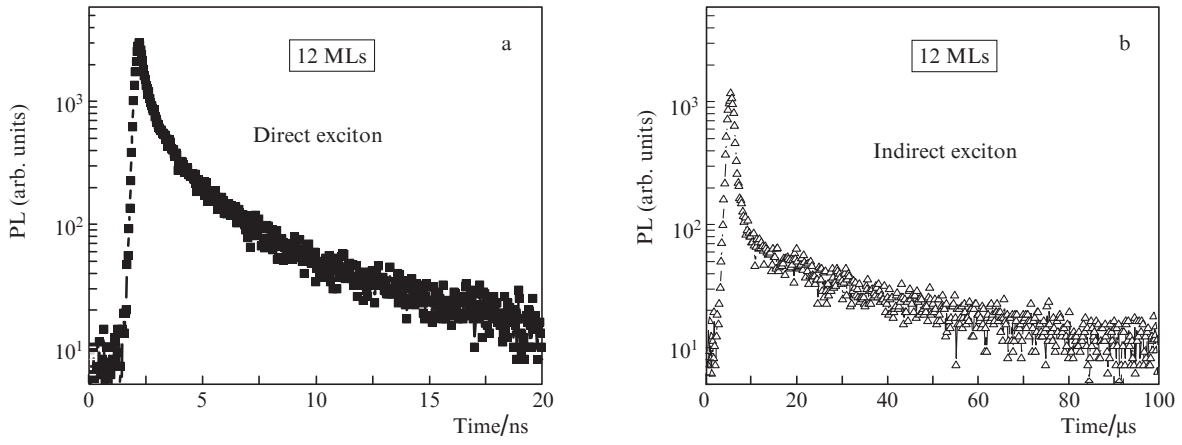

Figure 2. PL kinetics of (a) direct and (b) indirect excitons in the CdTe/ZnTe superlattice with a barrier width of 12 MLs at $T = 5$ K and $\lambda_{ex} = 400$ nm.

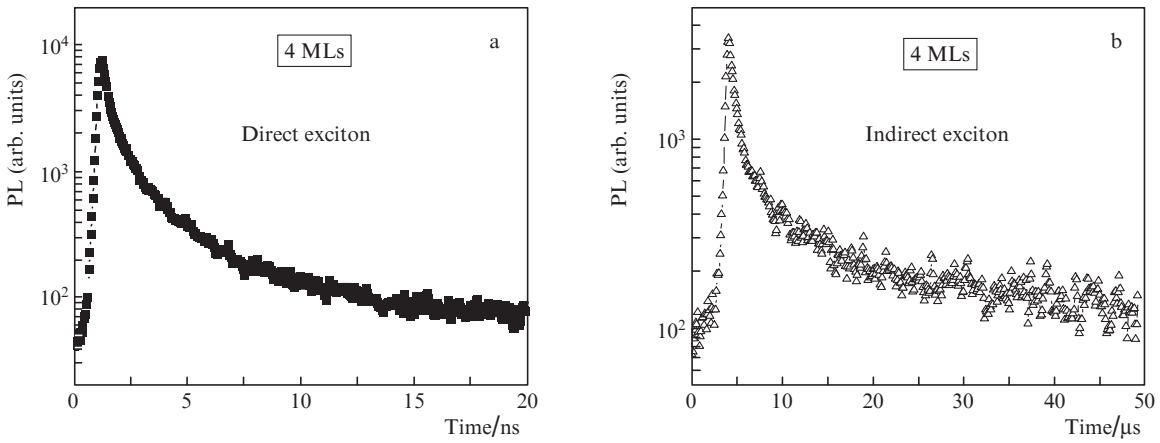

Figure 3. PL kinetics of (a) direct and (b) indirect excitons in the CdTe/ZnTe superlattice with a barrier width of 4 MLs at $T = 5$ K and $\lambda_{ex} = 400$ nm.

value. The slow components of direct and indirect excitons are less in a sample with a barrier width of 4 MLs.

Kinetics of PL in a sample with a barrier width of 2 MLs is presented in Fig. 4. The PL decay times for the fast component of direct and indirect excitons are 2 ns. The decay time t_2 of the PL slow component for both direct and quasi-direct excitons is 80 ns.

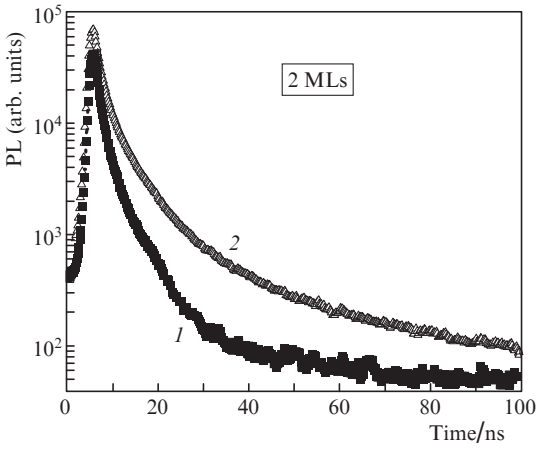

Figure 4. PL kinetics of (*1*) direct and (*2*) quasi-direct excitons in the CdTe/ZnTe superlattice with a barrier layer width of 2 MLs at $T = 5$ K and $\lambda_{ex} = 400$ nm.

4. Conclusion

In samples with barrier widths of 12 and 4 MLs, the PL decay times for the fast component of direct excitons are 0.4 ns; for indirect excitons they are 3 μs. A distinction is found between the recombination times for indirect excitons in samples with a barrier width of 2 MLs and samples with barrier widths of 12 and 4 MLs. In the latter two samples, in which electrons and holes localised in spatially separated neighbouring layers of the QD recombine, the characteristic PL decay times are in the microsecond scale, whereas in the first sample it is several nanoseconds. We suppose that in a sample with a barrier width of 2 MLs, QWs for light holes arise in a ZnTe layer due to tensile strain. Thus, there is an exciton that binds electron in a QD and a light hole in the ZnTe barrier. In view of overlapping wave functions of electrons from neighbouring QD layers, we may speak about the existence of a quasi-direct exciton.

Acknowledgements. The authors are grateful to M.L. Skorikov for participation in the discussion of the results.

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