# Microphotoluminescence spectroscopy of single nanostructures

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Introduction

1. Semiconductor nanostructures.

Semiconductor nanostructures are nanometer size objects which energy spectrum is quantized due to spatial confinement. They have very interesting in view of both fundamental studies and applications. As artificially fabricated and controlled can provide an experimental test for various quantum-mechanical concepts (from an energy quantization to a quantum electrodynamics phenomena) simultaneously offering improvements of semiconductor devices performance, especially those for optoelectronics or photonics (e.g., lasers, optical amplifiers, single photon sources). For instance, applications in telecommunication systems requires efficient light sources emitting at 1.3µm and 1.55µm – minimal absorption bands and dispersion for optical fibers. Obtaining specific emission/absorption wavelength has become an important issue and resulted in intense research concerning band gap engineering and nanostructures shape and geometry. Many factors influence the band gap energy: material system (structure/substrate), composition of complex compounds and strain. Additionally the size effect influences the energy spectrum significantly becoming the main factor of tuning the electronic and emission properties. A very dynamical development in this area was possible mainly due to the technological progress in growth techniques enabling monolayer thickness precision and nanometer size/shape control and obtaining high material quality (low defect concentration). The most precise ones have epitaxial character - Fig. 1 (e.g., MBE – molecular beam epitaxy or MOCVD – metalo-organic chemical vapour deposition) and exploit the self-assembly mechanism - Fig. 2 (see also Ref. [1] for more details).

![Fig. 1 Subsequent growth (deposition) of crystal materials with different lattice constants (GaAs and InGaAs) – first pseudomorphically – with lattice constant adjustment (strained) and afterwards accompanied by defects (relaxed).](image)

The advantages of self-assembled systems (exhibiting also different degrees of self-organization) are: relative fabrication simplicity, low fabrication costs (with respect to mass production potential) and broad range of available materials,
sizes and geometries. On the other hand the shape and surface density of nanostructures cannot be fully controlled using this method (the objects are self-formed and hence their properties always random to some extent). Additionally, the system is by definition always strained and hence sensitive to defects creation (the growth conditions need to be well known and precisely pre-calibrated).

Fig. 2 Three different growth modes of while a material of different lattice parameter than the substrate is deposited (depending on the strain, i.e. lattice constants difference).

The most characteristic feature is a nonuniformity within the ensemble of such nanostructures. However, this is also a drawback as every structure is in that sense unique but can be turned into an advantage in microphotoluminescence (μPL) investigations as the emission from different objects is spectrally resolved (the emission energy scales with nanostructure size).

In general there are two approaches to nanostructures fabrication: top-down - Fig. 3 (reducing size of macroscopic structures by etching, lithography or electrical definition) and bottom-up (creating them by manipulation of single atoms or molecules).

Fig. 3 Example of top-down approach in nanostructures fabrication – etching a quantum rod out of GaAs/AlGaAs quantum well.

There are many various classes of low-dimensional structures. The most general classification bases on the number of dimensions in which carriers can move freely (are not confined):

- two-dimensional (quantum wells)
- one-dimensional (quantum wires)
- zero-dimensional (quantum dots, rods, rings, discs, posts, dashes, sticks etc.).

Spatial confinement results in different character of density of states (Fig. 4) which determines both the electronic and optical properties.

There are basically two approaches to nanostructures investigations. One of them focuses on the properties of an ensemble of nanostructures by examining the averaged effective response of a whole group of objects in the
number of thousands or even millions. Information gathered that way is sufficient for those applications where the ensemble of structures is employed (as in lasers). Opposed to that is fundamental research (many body physics, excitonic effects) and the applications exploiting single nano-objects (qubits for quantum computation and cryptography, single photon sources, one-electron transistors, micro- and nanolasers, spintronics), where the specific properties of a single nanostructure are more important.

These single object characteristics can be investigated e.g., by microphotoluminescence [2], i.e. studying the emission properties but in very local sense (from a small area of the sample only). The most sophisticated optical method of that kind is near field spectroscopy which allows to overcome the diffraction limit and gives spatial resolution of the order of tens of nanometers. It enables to probe a single nanostructure, but suffers from many limitations making it unsuitable for common characterization. It is, for instance, very demanding with respect to mechanical stability (single nm precision is necessary in all three directions), it bases on very expensive apparatus of AFM (Atomic Force Microscopy) type, and finally allows investigating the objects located very close to the probe (e.g. directly on the surface of a semiconductor wafer). Therefore, the methods based on common optical spectroscopy (some time called “far-field” in contrast to “near-field”) seem to be still a much more practical. They are much less technically demanding, but spatial resolution of which is limited by the diffraction effects.

In this particular exercise we will focus our attention on quasi-zero-dimensional structures, and their most typical representatives – quantum dots (QDs) fabricated by self-assembly. QDs provide the three dimensional confinement for carriers so the energy is fully quantized and in the ideal zero-dimensional case there is no $k$-space (momentum space). The density of states has a discrete delta-like character analogical to that in atoms (reason for calling QDs artificial atoms). Optical transitions in QDs have mainly excitonic character, because carriers are confined in such a small volume that Coulomb
interactions become very important and cause creation of correlated complexes of electrons and holes. These excitonic complexes are much more stable than in bulk materials (their binding energy is much higher). The most common one is a neutral exciton X (electron-hole pair), biexciton XX (two interacting excitons) and charged excitons or trions (composed of three carriers, two of which are the same kind). They can be distinguished in a several ways, e.g., by the dependence of their emission intensity versus the excitation power (linear for exciton or quadratic for biexciton) – see Ref. [4] for reference. If the electronic structure of the QD can be calculated with a good precision the identification might be based on the binding energies of excitonic complexes which determines the relative energetic distance between the respective spectral lines. Another method is to observe the behaviour of the energy levels in magnetic field or perform a polarization resolved measurements (exciton and biexciton lines reveal an energy splitting between two perpendicular linear polarizations due to exciton fine structure - Fig. 5 (e.g. Ref. [3] for more details). Those splittings have opposite signs in the sense that a different polarization is the low-energetic one, whereas trions do not exhibit any splitting. Exciton fine structure results from various spin configurations of electron (+/- 1/2) and heavy hole (+/- 3/2). It consists of states with momentum projection +/-1 – bright states (b,b’– opposite spins of electron and hole (these sates can couple to the electromagnetic filed - allowed transitions) and +/-2 – dark states (d, d’– parallel spins of electron and hole (forbidden transitions). This nominally fourfold degenerate exciton state is in fact (in the real structure) split into four states (levels) of slightly different energy. The degeneracy is lifted due to levels electron-hole exchange interaction and QD shape asymmetry. It is worth noticing, that the particular recombination energies observed in the single-dot experiment can be further modified by the interactions with additional carriers confined in the QD (on higher energy levels) or in the environment (local charge traps e.g., defects, other layers of investigated structure, etc.).

Fig. 5 Schematic representation of the three-level excitonic system together with the exciton fine structure.
2. Experimental technique – basic concepts.

Photoluminescence (PL) is a process of reemitting the light previously absorbed by a medium. In a semiconductor material photons of energy at least equal to the band gap energy excite electron from valence band to the conduction band (PL being the opposite process of releasing the excess electron energy during its transition from the conduction to valence band) or in a quasi-particles picture photogenerate electron-hole pairs that can recombine transferring their energy to a photon. The energy of emitted photon is lower than that of the absorbed photon in a typical non-resonant experiment due to heat dissipation and other relaxation processes. The emission spectroscopy bases on spectral analysis of emitted radiation. Relaxation processes cause that emitted radiation has no memory about the light source it comes from (like polarization or energy of excitation beam) and reflects the band structure of the sample. PL is a very useful technique for studying energy levels of the structure, excitonic complexes, dopants and defects. Like all optical techniques it is non-destructive to the sample. This is a great advantage since makes repeat the experiments possible or characterize/process the sample further.

One of the limitations of this technique is that it is a probe (in low and intermediate excitation conditions) only of the energetically lowest transition in the system and cannot give information about the whole electronic structure. This is due to the fact that relaxation to the minimum of the conduction band is much faster than the radiative recombination. Emission from higher energy states occurs only in high excitation regime when their occupancy is significant and we deal with a kind of bottleneck or state filling effect – some of the carriers recombine before relaxation (so called hot luminescence) because the lower laying levels to which they could possibly relax are occupied. Other difficulty is proper interpretation of experimental data because of joined response from investigated object and the environment interacting with it. The PL intensity is not straightforward connected to the oscillator strength of the transition and is affected by the kinetics of the relaxation processes. What is more, sometimes the lines broadening makes the analysis and interpretation difficult, i.e. to distinguish between different spectral features which are energetically close.

Standard PL experimental setup requires light source (excitation) and the detection system enabling to analyze emitted radiation. The PL spectra of QDs ensemble has a form of emission band which consists of a sum of individual QD response (Fig. 6), which cannot be resolved due to too many objects emitting at the same time (the spectrum integration time) with very close emission energies casing they are superimposed (Fig. 7). The emission bands are inhomogeneously broadened due to some distribution of dot properties (e.g. their sizes) within the entire ensemble.
Fig. 6 Schematic representation of a QD ensemble spectra origin with red bars denoting the density of states for individual QDs (single dots emission lines). The inset shows the large illumination area (large number of excited/probed QDs).

Fig. 7 Exemplary spectra of a QD ensemble for different excitation power values exhibiting emission from excited states (p-, d-, and f-shell) and the wetting layer (WL).

Some modifications need to be made in the experimental setup in order to measure \( \mu \)PL spectrum. The difference is in the excitation area and so the area of optical response collection - Fig. 8 (for details see next section).

Fig. 8 Influence of the excitation laser spot size, i.e. the size of the illumination/probing area on emission spectra. Emission from individual QDs could be obtained for 2 \( \mu \)m case, i.e. when the spatial resolution became good enough with respect to the surface density of dots.
Due to very low absorption of the QD layer (only partial surface coverage) the sample is non-resonantly excited typically (with photons possessing energies higher than the characteristic transitions in QDs) so the carriers are generated in other parts of the structure and then relax nonradiatively to the QDs – the ground state of the whole system from which the emission takes place. The optical response from a single QD consists of narrow, well-resolved emission lines - Fig. 9 (ground and excited states or different excitonic complexes depending on the number of carriers confined within the QD) with finite line broadening being a sum of natural broadening (originating from Heisenberg uncertainty principle for energy and time), broadening connected with the interaction with the environment changing the emission energy at the timescale of the experiment (Coulomb interaction with other carriers confined in QD or in other parts of the structure via Quantum Confined Stark Effect, interaction with phonons etc.), and finally fluctuation of the experimental conditions within the light collection time.

![Exemplary single QD emission spectra.](image)

Fig. 9 Exemplary single QD emission spectra.

When more than one structure is excited at a time the optical response can still be analyzed as long as the emission energies of QD differ – can be resolved spectrally (as in Fig. 9).

Microphotoluminescence is useful mainly in the investigations of single zero-dimensional objects (called single-dot spectroscopy in general) or in the cases when high excitation power density (provided by the laser beam focusing on the sample surface) is required. Most measurements are carried out at low temperatures. This is motivated by the fact that many different processes become important at elevated temperatures while they stay ‘frozen’ at low temperatures which is important due to fundamental research. It enables to isolate and investigate one physical phenomena at a time and simplify significantly experimental data interpretation. While applications require room temperature performance some of the structures interesting in view of fundamental research provide shallow confinement potential which prevent room temperature emission (the carrier are thermally activated out of the dot so lost for the radiative recombination in there). Also, increasing temperature
causes the spectral line broadening due to the enhanced interaction of the confined excitons with phonons possible overlap of the neighboring lines.

Microphotoluminescence is a diffraction limited technique (the probing area cannot be smaller than a certain size for the given wavelength)\(^*\) and sometimes requires sample preparation to gain spatial resolution sufficient for single-dot investigations. First step can be made during the growth by optimizing growth conditions to obtain low surface density of nanostructures. In this way fewer structures are excited with laser spot of the same size. Dispersion of sizes (emission energies) within the ensemble helps to resolve signal from different structures spectrally. Post growth patterning provide further reduction of excited QDs via defining specific areas with QDs on the sample surface by either using apertures in gold mask or etching mesas (Fig. 10 and Fig. 11). This is also useful if repeating the measurements on specific QDs is necessary.

\[ D = 1.22 \left( \frac{\lambda}{NA \cdot n_{med}} \right) \]

\(^*\) According to the Rayleigh criterion for the diffraction limit the smallest probing area (the smallest spot to which a collimated beam of light can be focused) is: \( D = 1.22(\lambda/NA \cdot n_{med}) \), where \( \lambda \) is the light wavelength, \( NA \) the numerical aperture of the optical element (lens/objective), and \( n_{med} \) is the medium refractive index, which for typical experiments performed in air or vacuum can be put 1.
Experimental setup

1. Scheme.

Fig. 12 Microphotoluminescence setup scheme.

The experimental setup can be divided into functional blocks:
A – cooling
B – excitation
C – imaging
D – detection.

1 – semiconductor laser (non-resonant excitation)
2 – mirror
3 – optical filters – define excitation power
   neutral density – reduce power by a given factor
   scalable – amount of light transmitted through the filter depends on the
   position of beam on its surface
4 – power meter – measures the excitation power after its reduction by the filters
   caution: to measure the power properly one need to choose the proper
   wavelength
5 – cold mirror – selective optical element which reflects short wavelength light
   (excitation beam which is usually visible) simultaneously transmitting the long
   wavelength radiation (emission signal which is very often in the near infrared
   range)
6 – microscope objective (working distance – 20 mm, numerical aperture \( NA = 0.4 \), achromatic with low dispersion) – focuses the excitation beam on the
   sample surface to a spot with a diameter of about 2 \( \mu \text{m} \) (for the excitation
   wavelength of 660 nm, which is typically used)
7 – cryostat – samples are mounted in it (on the cold finger) for cooling process,
   the temperature inside the cryostat is measured by an external controller
8 – liquid helium container – used for low temperature measurements (5K), provides opportunity to measure emission spectra as a function of temperature in a wide temperature range – from liquid helium temperature to room temperature (using the heater built inside the cryostat, on the cold finger), liquid helium is transferred to the cryostat and cools the sample down
9 and 12 – semi-transparent mirrors
10 – lens controlling the expansion of the beam from a broad band light source (11) (e.g. Tungsten halogen lamp), which is then used to illuminate the sample surface for its inspection and monitoring
13 – monitoring camera – provides sample surface image on the television screen (14)
15 – lens focusing the collected PL signal on the entrance slit of the monochromator
16 - monochromator - spectrometer analyzing the radiation and projecting dispersed light onto the detector (17); it is equipped with three gratings enumerated by number of grids per mm; another important parameter of the spectrometer is the size of the entrance slit – smaller slit coincides with better spectral resolution but smaller amount of light reaching the detector;
17 – linear CCD detector (InGaAs or Si – differing in spectral range and sensitivity) – cooled with liquid nitrogen
18 – computer – collecting the spectra and controlling the detection system

Possible additional elements:
- linear polarizers
- filters
- lenses
- mirrors
- depolarizers etc.

Note that the microscope objective (6) is a part of both excitation and detection system – first the laser beam is focused by it and than the emitted radiation is collected through the same path.


- mount the sample into the cryostat, connect and run the turbo pump station (vacuum is required inside the cryostat for thermal isolation of the sample from the outer world), transfer the liquid helium into the cryostat
- cool down the detector – pour liquid nitrogen into the CCD camera dewar caution: the camera controller needs to be on, because the work temperature of the camera is higher than the liquid nitrogen temperature (77K)
• check the optical path of excitation beam and emitted radiation – they should be on the same height coinciding with the height of entrance slit of the monochromator, parallel to the optical table and centrally illuminating all optical elements in-between, first without mirrors 9, 12 and lens 15 by reflecting the excitation beam from a mirror positioned in front of the cryostat
• add previously removed elements
• open the measurement software (SynerJy icon on the desktop), choose CCD spectra and fill in proper (adequate to investigated structures) central emission wavelength, acquisition time, grating and entrance slit size
• by moving objective 6 in horizontal direction find the position when excitation spot is focused on the sample surface (easier when the laser beam power reduced)
• by moving lens 15 in all three directions find the maximum of the signal from the sample (first using the brighter grating and shorter integration time and afterwards for fine tuning - darker grating and increased acquisition time)

Exemplary measurements

1. Real-space sample surface observation.

a) things to do
• check if mirrors 9 and 12 are in the optical axes
• turn on the TV screen 14 and light source 11
• after turning off the ambient light in the room uncover the monitoring camera 13
• move along the sample surface (Fig. 13) using YZ regulation of the cryostat 7
• using sample surface map (Fig. 14) find patterning of different sizes
• compare their nominal size with the size seen on the screen 14
• check what is the smallest possible size of the patterning you are able to see on the screen 14
b) data analysis  
- describe the sample surface (roughness, patterning, quality)
- try to determine the magnification of the microscope objective
- try to determine the distance between adjacent patterning
- what is the smallest observable size of patterning?

2. Comparison of PL spectra from ensemble of and single quantum objects.

a) things to do – for each sample  
- collect two emission spectra of significantly differing in size sample areas  
  (by changing the size of the focused beam – i.e. by defocusing it accordingly)

b) data analysis  
- point out the differences between those two spectra emphasizing characteristic features of both of them
- analyze observed spectra in terms of emission energies and broadening
- for ensemble-like spectra: compare obtained emission energies with band gaps of different structure layers, try to identify emission from different part of the structure basing on the sample description
- what information about the investigated structures can you deduce from each of the spectra?
- compare emission spectra for different samples from one series and describe the influence of the factor (e.g. QDs layer thickness, composition) differing from sample to sample on emission spectra
3. *Influence of sample patterning on emission spectra.*

a) things to do
- collect emission spectra for each of a sample patterning size using the same excitation power for each measurement (Fig. 15)
- for each patterning size find the proper excitation conditions allowing to resolve single-dot spectra

b) data analysis
- plot and describe the influence of the sample patterning size on emission spectra (as a whole)

![Fig. 15 Exemplary emission spectra from mesas of different sizes but equal excitation power.](image)

4. *Excitonic effects.*

a) things to do
- collect emission spectra for different excitation power values in a wide range in a single dot regime

b) data analysis – for each emission line
- plot a PL intensity as a function of excitation power in a double logarithmic scale
  - caution: remember about subtracting the background signal
- try to identify observed emission lines
5. *Polarization-resolved measurements.*

a) things to do
- add a linear polarizer into the optical axis in front of the monochromator
- measure a PL intensity as a function of polarizer position angle

b) data analysis – for each emission line
caution: all the polarization measurements need to be properly calibrated – the polarization characteristic of the setup need to be taken into account
- plot in a polar coordinates the dependence of photoluminescence intensity as a function of polarizer angle
- describe the state of polarization of emitted light
- define polarization axes and obtain the degree of linear polarization of emitted radiation defined as:

\[ DOP = \frac{I_1 - I_2}{I_1 + I_2}, \]

where \( I_1 \) and \( I_2 \) are PL intensity for two orthogonal polarization axes
- look for a fingerprint of fine structure splitting, determine its magnitude


a) things to do
- define polarization axes as in point 5
- collect emission spectra in two orthogonal polarizations for different excitation powers

b) data analysis – for each emission line
- obtain the degree of linear polarization for every excitation power
- plot and analyze the dependence of degree of linear polarization on excitation power
References