Photoluminescence in analysis of surface and interfaces of Semiconductor nanostructures

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ABSTRACT: The intensity and excitation energy is chosen for different materials to probe different regions and excitations concentrations in the sample. The intensity of the PL signal provides information on the quality of surfaces and interfaces. Also, information on the electronic bands structure and the SC Energy gap can be obtained, as well as thermodynamics quantities such as temperature. For this experiment we just compared the photoluminescence (PL) spectra of AlGaAs/GaAs quantum wells (QWs) with different well widths (100 Å and 85 Å) and InAs/GaAs quantum dots (QD) structures as well as the theoretical aspects were covered. The sample are held in a cryostat and excited by a Helium-Neon laser. The emitted light is then captured by an optical fiber plugged to a spectrometer The optical fibre is plugged to a spectrometer equipped with a CCD detector, driven by a computer allowing us to acquire data. And this was used to avoid interaction between charge carriers and thermally excited phonons, it was used cryogenic temperature around 2k to cool the sample. simply with the theoretical models this experiment allows to collect numerous information about the lowest band to band transition in semiconductor materials and for quantum dots which was the last sample in this study couldn’t be resolved individually.

1. INTRODUCTION

Photoluminescence may be either fluorescence or phosphorescence, or both. Energy can be stored in certain luminescent materials by subjecting them to light or some other exciting agent, and can be released by subsequent illumination of the material with light of certain wavelengths. This type of photoluminescence is called stimulated photoluminescence.\(^1\)

Photoluminescence (PL) is thus the spontaneous emission of light from a material under optical excitation. This light can be collected and analyzed spectrally, spatially and also temporally. In fact, PL spectroscopy gives information only on the low-lying energy levels of the investigated system.\(^2\)

In semiconductor systems, the most common radiative transition is between states in the conduction and valence bands, with the energy difference being known as the band gap. During a PL spectroscopy experiment, excitation is provided by laser light with energy much larger than the optical band gap.\(^3\) The photo-excited carriers consist in electrons and holes, which relax toward their respective band edges and recombine by emitting light at the energy of the band gap. But, radiative transitions in semiconductors may also involve localized defects or impurity levels.\(^4\) In that case, the analysis of the PL spectrum leads to the identification of specific defects or impurities, and the magnitude of the PL signal allows determining their concentration. Finally, higher-energy optical transitions can be studied by means of photoluminescence excitation spectroscopy (PLE).\(^5\) In this latter configuration the detection is fixed on the recombination line of the semiconductor system while the excitation laser energy is tuned. When it matches the energy of an optical transition in the absorption spectrum of the semiconductor, the PL signal increases. PLE is thus analogous to absorption spectroscopy, and identical to it in the specific case where nonradiative relaxation processes are negligible. This technique is often used in the case of semiconductor heterostructures with a low absorption probability, less than 1%, where standard direct absorption spectroscopy is hard to implement. The recombination of the photo-excited carriers can involve
both radiative and nonradioactive processes. The respective rates of radiative and nonradiative recombination can be estimated from a careful analysis of the temperature variation of the PL intensity and PL decay time. In semiconductor systems like quantum wells or quantum dots, the photoluminescence quantum yield is approximately constant up to temperatures of about 50-70K. At higher temperatures nonradiative recombination channels are activated and the PL intensity decreases exponentially. Apart the advantageous simplification of the underlying physics, low temperatures appear unavoidable for the optical study of semiconductor-based nanostructures. The resolution of PL spectra is enhanced when in cryogenic conditions. Indeed, thermal excitation is lowered and therefore the energy of the excited carriers is less exposed to fluctuations due to thermal vibrations.

![Figure 1: Typical experimental set-up for PL measurements.](image1)

We can briefly say photoluminescence process includes three main phases:

1) Excitation: Electrons can absorb energy from external sources, such as lasers, arc-discharge lamps, and tungsten-halogen bulbs, and be promoted to higher energy levels. In this process electron-hole pairs are created.

2) Thermalization: Excited pairs relax towards quasi-thermal equilibrium distributions.

3) Recombination: The energy can subsequently be released, in the form of a lower energy photon, when the electron falls back to the original ground state. This process can occur radiatively or non-radiatively.

![Figure 2: Photoluminescence schematic. (a) An electron absorbs a photon and is promoted from the valence band to the conduction band. (b) The electrons cools down to the bottom of conduction band. (c) The electrons cool down to the bottom of the conduction band. (c) The electron](image2)
2. THEORETICAL BACKGROUND

Infinite potential well to real quantum well:

Semiconductor materials can be grown either as bulk structures or as superposition of layers of various compositions. The different semiconductor alloys have different characteristic energy band gaps $E_g$. Considering a material A of controlled width $L_z$ (typically a few tens of nanometers) growth along the $z$-axis in between two structures of a material B of higher energy band gap $E_g$, quantum effects can be described. The hetero junction depicted in figure 1 shows the valence and conduction bands of some recombines with the hole resulting in the emission of light with energy $h\nu$.

![Figure 3: Quantum well of GaAs barrier with GeAlAs barriers. The growth axis of such an heterostructure is the $z$-axis. $E_c$, $E_v$, $V_e$ and $V_h$ are respectively the conduction band, valence band, electron potential and hole potential energy.](image)

The objective of our project is to observe the photoluminescence of semiconductor quantum wells with one dimensional confinement of electrons and holes, and measurement the luminescence of individual quantum dots with three dimensional confinement. After a presentation of the experimental aspects of the practical, collected photoluminescence spectra from three SC samples are presented and commented in terms of emission wavelength (photon energy) and spectral characteristics (intensity, line width). These measurements are compared with calculations of the quantum confined energy levels and the expected emission energy from the transitions

$$\left[-\frac{h^2}{2m} \frac{d^2}{dz^2} + V(z)\right] \varphi(z) = E(z)\varphi(z)$$

The potential $V(z)$ is the potential energy that the electrons are subjected to in the heterostructure, and varies along $z$ as the energy gaps of the two different adjoining structures differ. As far as the boundary conditions are concerned, the wave functions as well as their first and second derivatives are taken continuous for all $z$, and $\lim_{z \to \pm \infty} |\varphi(z)|$ is finite. $V(z)$ being constant the exact solutions of equation 1.1 are sums of two plane waves of opposite wave vectors, such that one obtains even and odd states inside and outside the quantum well.\(^9\)
One notes that since $|\varphi(z)|$ should not diverge when $z \to \pm \infty$, $C = D = 0$, and for even states, $B = -E$ and for odd states $B = E$. Applying the boundary conditions at the interfaces $z = \pm L_z/2$, the energy of the bound states satisfies the following implicit equations:

$$
\begin{align*}
&\cos\left(\frac{k_A L_z}{2}\right) = \frac{m_A}{m_A^*} k_A \sin\left(\frac{k_A L_z}{2}\right) \quad \text{for even states} \\
&\cos\left(\frac{k_B L_z}{2}\right) = \frac{m_B}{m_B^*} k_B \sin\left(\frac{k_B L_z}{2}\right) \quad \text{for odd states}
\end{align*}
$$

The case of an infinite quantum well is obtained in the limit $V(z) \to \infty$, which implies $(|z| = \frac{L_z}{2}) = 0$. The discrete values of $k_A$ are in that case given by $k_A l_z = p\pi$ ($p \in \mathbb{N}$). The Quantized energy in an infinite quantum well hence reads:

$$
E_p = \frac{\hbar^2 k^2}{2m^*} = \frac{\hbar^2 \pi^2}{2m^* L_z^2}
$$

The resolution of equation 1.3 consists in finding the energy value $E$ for which the left-hand-side (LHS) and the right-hand-side (RHS) are verified.

Transition energy in real heterostructure:

The couple of equations 1.3 holds also for holes in the valence band. In a view to calculating the bandto-band transition energy of photoluminescence processes. Since the radiative relaxation of PL processes occur only after non-radiative processes which occur faster, one will focus on the lowest transitions, will focus on the transitions between the lowest lying electrons in the conduction band holes of the heavy-hole band. Therefore, the confinement energies derived from the resolution of equations 1.3 will be $E_1$ and $HH_1$.

Table 1.1: Energy gap and effective masses for GaAs and AlAs and intermediate alloy Ga$_{1-x}$Al$_x$As.

<table>
<thead>
<tr>
<th></th>
<th>GaAs</th>
<th>Ga$_{1-x}$Al$_x$As</th>
<th>AlAs</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e_g$</td>
<td>1.519+1.3668x+0.2211x$^2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$m_e^*$</td>
<td>0.067</td>
<td>0.67(1-x)+0.13x</td>
<td>0.13</td>
</tr>
<tr>
<td>$m_h$</td>
<td>0.38</td>
<td>0.38(1-x)+0.46x</td>
<td>0.46</td>
</tr>
</tbody>
</table>
The confined electrons and holes being charged particles, they interact together through Coulomb forces. Such interactions give rise to a relative stabilization of these particles in their respective bands, in a bound state called exciton. This quasi-particle have a binding energy $E_{\text{exc}}$. The transition energy of the PL process being the relaxation of the electron-hole pair $(E_1, HH_1)$ within the band gap $(E_{\text{gap}})$, against the corresponding excitonic binding energy $(E_{\text{exc}})$, it hence reads:

$$E_{\text{trans}} = E_{\text{gap}} + E_1 + HH_1 - E_{\text{exc}}$$

3. EXPERIMENTAL SET UP

The sample are held in a cryostat and excited by a Helium-Neon laser. The emitted light is then captured by an optical fibre plugged to a spectrometer.

Cryogenic conditions: the cryostat

As mentioned previously, in order to avoid interaction between charge carriers and thermally excited phonons, the samples are cooled to cryogenic temperatures, at around 2 K. The samples are held in a cryostat which is depicted in figure 4. It consists in two main baths separated by a vacuum tank. The outermost bath is filled with liquid Nitrogen at 77 K. The three samples are maintained by a rotatable holder and immersed in the inner bath which contains liquid Helium at around 4 K. This last boils at 4.2 K, therefore the temperature needs to be even lower to avoid bubbles that can cause light to scatter. Hence the inner part of the cryostat is pumped and the pressure is decreased as well as the temperature, which reaches 2 K. At such a temperature, Helium reaches superfluid phase which ensures no parasitic light scattering.

Exciting and emitted light: optical set-up

The photoluminescence experiment requires an exciting light source as well as a spectrometer, the whole finely adjusted by a set of optical devices such as lenses and polarizer. The optical set-up is shown in figure 5 and consists in a Helium-Neon laser of wavelength $\lambda = 623.8$ nm whose beam is focused by a lens of focal 400 mm onto the selected sample, shining the sample on locally around 100 $\mu$m2. The light from the photoluminescence process is then focused by a lens of focal 240 mm onto an optical fiber. One has first taken precautions of not aligning any reflected light on the collecting lens. The optical fiber is plugged to a spectrometer equipped with a CCD detector, driven by a computer allowing us to acquire data.

Description of the samples

The samples studied during the experiment were of three types. Two quantum Wells (QWL) structures and one quantum wire (QWR) with self-assembled quantum dots (QDs) all along.

The sample C4H12 contains two thick GaAs quantum wells of length $L = 84.16$ Å separated by -- and placed side by side to -- AlAs layers of approximately 10 nm thickness. The sample J211 presents a thin GaAs QWL of length $L = 10$ Å in between two Ga0.7Al0.3As layers. The sample NM133 consists in a collection of GaAs quantum dots (QDs) formed along the free axis of a 10 nm thick quantum wire (QWR), due to the interface thickness fluctuations of ± 1 monolayer (ML) during the epistaxis of the GaAs structure in the V-groove GaAl0.3As structure.
Figure 4: Photograph of the cryostat and a corresponding scheme. The cryostat is approximately 1 meter high and the distances are given indicatively in centimeters in the schematic picture.

Figure 5: The photoluminescence experimental setup

4. MICROPHOTOLUMINESCENCE SET UP:

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.

Micro photoluminescence 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.

Figure 6: Schematic illustration of the idea of patterning: a sample before and after etching process

Figure 7: Example of a SEM image of sample surface with a matrix of micrometer sized structures.
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 \(\mu m\) (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 then the emitted radiation is collected through the same path.

Setup preparation:
- 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, 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).

5. RESULT

C4H12: two thick quantum wells

Figure 9: Photoluminescence spectrum of C4H12 sample. Exposure time 1 second, detection wave-length 790 ± 8 nm. The maximum of PL intensity is reached for $\lambda = 789.38$ nm that is 1.5706 eV.
The first measurements were done on the C4H12 sample and the corresponding PL spectrum is depicted in figure 9. The main peak at $\lambda = 789.38$ nm is the actual PL response of one of the quantum well contained in the sample, but the small peak at lower energy (i.e. higher wavelength) does not correspond to a second quantum well PL response. It is too narrow to be compared to the main peak, given the structural similarities of the quantum wells. Detection at other ranges of wavelength could have let us observe the spectral response of the second quantum well. Hence the experimental transition energy measured from photoluminescence for sample C4H12 is $E_{\text{trans}} = 1.571$ eV.

This experimental value is compared to the calculation of the transition energy given in Equation 1.5 of section 1.3 on page 4. The energy gap is given by the table 1.1 and the confinement energies of the electron-hole pair computed from the implicit equation 1.3.

**Sample J211: single quantum well**

The second set of measurements is related to the study of sample J211 which consists in a single GaAs quantum well of length $L_z = 10$ Å. The photoluminescence spectra is presented in fig.10. The main PL peak shows a transition energy $E_{\text{trans}} = 1.894$ eV.

![Photoluminescence spectrum of J211 sample.](image)

Figure 10: Photoluminescence spectrum of J211 sample. Exposure time 1 second, detection wavelength $655 \pm 7$ nm. The maximum of PL intensity is reached for $\lambda = 654.63$ nm that is $1.8939$ eV.

J211 is much broader, which suggests a much smaller excited states lifetime. Besides, the Gaussian look of this photoluminescence line reveals some dependency to randomly distributed variables such as thickness fluctuation or impurities. Added to an apparent shift in energy ($\Delta E$), the calculation here shows less agreement with the data, even though systematic errors and inaccuracy from the set-up may still be taken into account.

6. **MEASUREMENT OF QUANTUM DOTS**

The last sample of this series of PL experiment contains randomly distributed InAsGaAs quantum dots along a quantum wire structure. Its PL line is proposed in figure 11. The maximum is reached at an energy $E_{\text{trans}} = 1.3662$ eV. The data treatment has exhibited a better fit when two Gaussian curves were used (instead of one). Indeed, the whole line shows asymmetry with respect to its maximum, where it goes down to its minimum slower at higher wavelength, that is at lower energy. When this ‘shoulder’ at higher wavelength is taken into account for the fitting, best matching is obtained. Fundamentally, the laser source excites thousands of quantum dots and the PL response is
indeed the sum of all the self assembled QDs of various size in the QWR. The laser spot is approximately $100 \, \mu m^2$ and there are $10^{10} - 10^{12} \, \text{QDs/cm}^2$, and:

$$100 \, \mu m^2 = 10^{-8} \, \text{cm}^2$$

that is the excitation of at least $10^3$ quantum dots. Coupled with this great amount of different excitations, localized excitons can form and lead to this homogeneous shifting in energy.

We acquire the data for more than one time to see if there is any peaks due to the cosmic background radiation as detect by the CCD.

In the PL spectrum there may be first 1/2 lines which corresponds to that. The maximum is reached at wavelength of 907.32 nm (1.3662 eV). The energy difference between the different peaks is about 2-4meV. The temperature dependent broadening mechanism may be due to the coupling between localized excitons and acoustic phonons as well as the environment surrounding the QD system.

7. CONCLUSION

In this experiment we have compared the photoluminescence (PL) spectra of AlGaAs/GaAs quantum wells (QWs) with different well widths (100 Å and 85 Å) and InAs/GaAs quantum dots (QD) structures. The corresponding experimental as well as theoretical aspects were covered. The experimental procedures are not extremely demanding except maybe for the required cryogenic temperatures; the rest of the PL set-up consisting essentially in a laser, two lenses and quite of a simple acquiring machinery. Together with relatively simple theoretical models, photoluminescence experiment allows to collect numerous information about the lowest band-to-band transitions in semiconductor materials. The last sample in study consisted in quantum dots that couldn’t be resolved individually. A further study, higher resolved, such as micro photoluminescence experiments, in which the laser source is much more focused on the sample in order to probe a single quantum dot, would essentially give deeper insights of such low-dimensional materials.
References


