Time resolved photoluminescence measurement of wurtzite InP nanowire

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1 Introduction

InP is a promising material for photonic component for high quantum efficiency and low surface recombination velocity. InP nanowire can exists in both zinc blend and wurtzite but the latter cannot be found in bulk InP materials. Surface states and crystallographic defects affect recombination life time in nanowire system. In this project we are going to use time resolved photoluminescence measurement to determine the carrier life time in wurtzite InP nanowire of different lengths at low temperate (around 4K) using a synchroscan streak camera with a time resolution of 800 fs.

2 Theory

2.1 Wurzite-phase InP nanowire

2.1.1 Crystal structure

Generally, InP can only crystallizes in the zinc-blend structure in bulk. However, it is possible to grow InP nanowire with a wurzite structure. Figure 1 represents the unit cell and the crystal structure of the wurzite-phase InP nanowire.

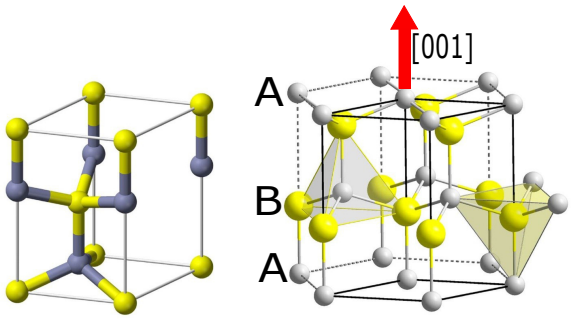

Figure 1: On the right, wurzite-phase InP nanowire unit cell. On the left, wurzite-phase InP nanowire crystal structure.[1]

Wurzite structure is composed of two interpenetrated hexagonal-close-packed lattices. Along the [001] direction, the wurzite lattice is composed of a sequence of stacked hexagonal layers following this pattern: ABABAB...with A corresponding to a In layer and B to a P layer.[2]

2.1.2 Band structure

Figure 2 represents the band structure of the wurzite-phase InP nanowire.
Wurzite-phase InP is a direct band gap semiconductor crystal. As shown in figure 2, due to crystal field and spin-orbital interaction, the valence band is splitted into 3 subbands [2]:

- I^{9v}, also known as heavy hole;

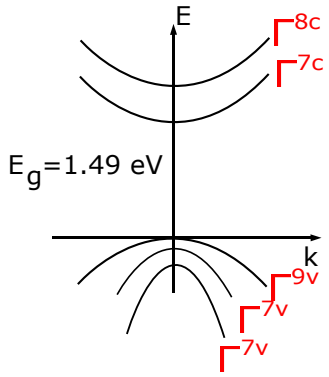

Figure 2: Band strucutre of wurzite-phase InP nanowire.

- Γ_{7v}^{7v}, also known as light hole;
- Γ_{s}^{7v}, also known as split-off band.

The band gap found in the literature at low temperature is approximately 1.49eV.

2.2 Carriers recombination

2.2.1 Photoluminescence process

Electrons and holes are created by the absorption of light. In general, they will rapidly relax respectively to the lowest state available of the conductive band and highest state of the valence band giving off excess energy to the lattice. The electrons will stay there for a certain time called recombination lifetime and then will recombine with holes in the valence band leading to the emission of a photon with the energy corresponding to the band gap. In the case of the laboratory, the bandgap of the wurzite-phase InP nanowire at low temperature is 1.49eV. This mechanism is represented by the red arrow in figure 3

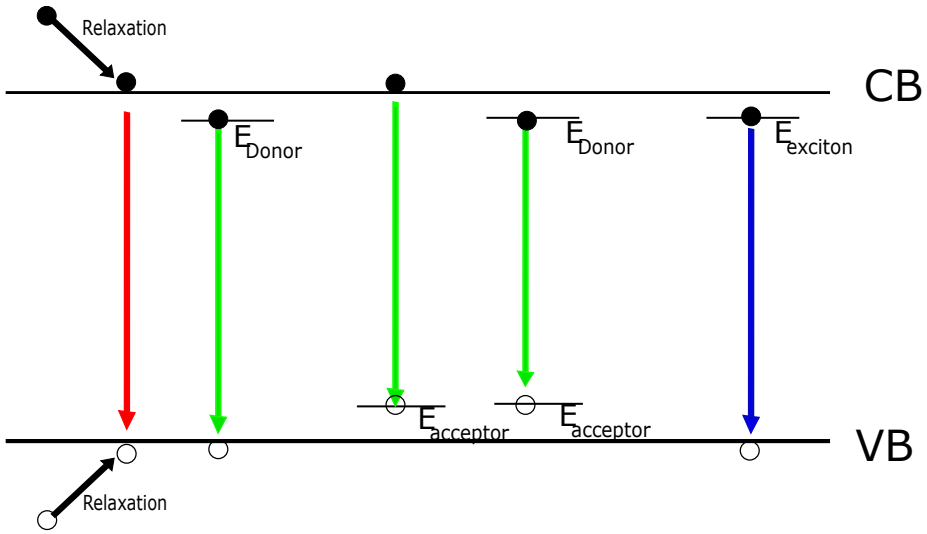

Figure 3: Photoluminescence process. In red, the band-to-band recombination. In green, the recombinations due to states within the bandgap. In blue, recombination associated to the formation of an exciton.

Defects can also create states within the bandgap leading to new ways for carriers recombination. The recombinations associated are represented by the green arrows in figure 3. As shown, these lead to the emission of photon with an energy lower than the bandgap. In addition, excited electron and hole can interact and form a hydrogen-like state which is called an exciton. This exciton has a state within the bandgap. The recombination associated to the exciton is represented by the blue arrow in figure 3.[3]

2.2.2 Power dependant photoluminescence

If the carrier density exceeds the number of allowed state at the bottom of the conduction band, the Fermi level will shift into the band. This leads to an increase of the emission peak. Consequently, the photoluminescence spectrum becomes broader. This effect is called Burstein-Moss effect and can be obtained by degenerate doping or, in the case of the laboratory, by applying a high-power pulse.[3]This is represented in figure 4.

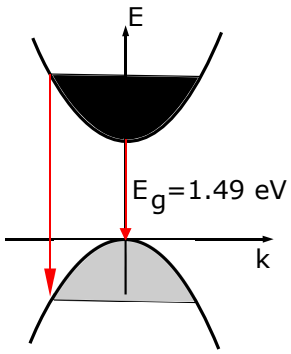

Figure 4: Photoluminescence due to the application of high-power with the red arrows which represent the recombination process.

2.3 Time Resolved Photoluminescence spectroscopy

This technique gives the spectral evolution and temporal evolution of the emission of the InP nanowire after the generation of electron-hole pairs by a short pulse of light. The emission due to photoluminescence is composed of a set of wavelengths. These wavelengths correspond to the radiative recombination of electrons and holes in the sample. Consequently, it is possible to measure the recombination lifetime associated to the recombination of electrons from the bottom of the conductive band and holes from the top of the valence band.

2.4 Recombination lifetime

As said before, the absorption of light leads to the creation of electron-hole pairs. The evolution of the concentration of electrons and holes is given by the following equation [4]:

$$\frac{dn}{dt} = \frac{dp}{dt} = G - R \tag{1}$$

with G, the generation rate and R, the recombination rate. The generation rate is defined by this equation:

$$G = Bn_o p_o \tag{2}$$

with B, the probability of radiative recombination and n_o/p_o, the equilibrium concentration of electrons/holes. The recombination rate is given by the following equation:

$$R_{rad} = Bnp = B(n_o + \Delta n)(p_o + \Delta p) = B(n_o p_o + (\Delta n)^2 + \Delta n(n_o + p_o)) \tag{3}$$

with Δn and Δp, the concentration of electrons and holes due to the excitation by external light. Consequently,

$$\frac{d\Delta n}{dt} = -B((\Delta n)^2 + \Delta n(n_o + p_o)) \tag{4}$$

Two limits can be determined:

- In the case of a low-level injection, the first term in the equation 4 can be removed. Consequently, the solution of this equation is:

  $$\Delta n(t) = \Delta n(t_o) e^{\frac{t-t_o}{\tau}} \tag{5}$$

  with $\tau = \frac{1}{B(n_o+p_o)}$. The lifetime in this case is independent of the concentration of electrons and holes generated by the external light;

- In the case of a high-level of injection, the first term of equation 4 dominated. Consequently, the solution of the equation is given by equation 5 with $\tau = \frac{1}{B\Delta n}$.

3 InP Wurzite Nanowires Sample

We have done our experiment on two InP wurzite nanowire sample grown by the vapor-liquid-solid growth (VLS) mechanism.Growth time for one sample is 20 min(left fig4) and for another one it is 2 hours(right fig5).So we can see there is difference in height of nanowire.The height of the nanowire wih shorter growth time is .812um while the nanowire with longer growth time has 1.95um height.Though both nanowires are grown from 30nm gold particle, but they have got different diameter at the end of the process due to different growth time and this cause different core to shell ratio for short and long nanowire.

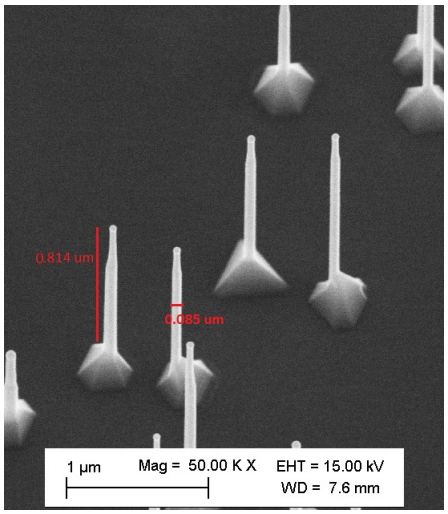

Figure 5: SEM of nanowire with height of 0.812 μm and diameter of 0.085 μm.

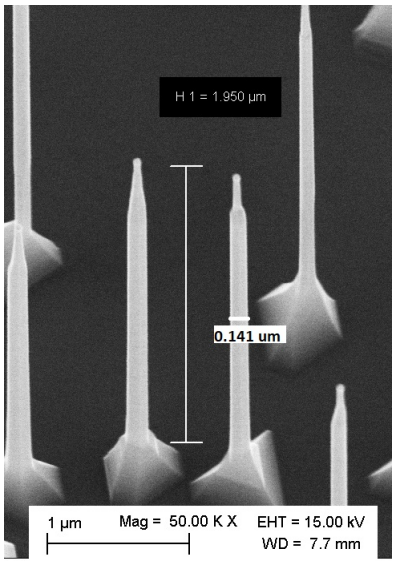

Figure 6: SEM of nanowire with height of 1.95 μm and diameter of 0.141 μm.

4 SetUp

With the advent of fast detectors and ultra-fast laser sources, time-resolved photoluminescence (TRPL) techniques have emerged as useful tools to understand carrier dynamic processes. The general concept of all TRPL techniques is exciting the sample with a pulsed- or an on/off-modulated light source, and detecting the emission from sample while the excitation source is off. For optical excitation a short pulse excitation source is necessary because the temporal response of the TRPL detection system and the temporal width of the excitation pulse determine the overall time resolution of spectrum.[5]
In our experiment we use a streak camera as detection instrument and samples are excited with pulses from a Ti:sapphire laser. This pulse-mode locking laser provides 62fs pulse with a pulse repetition rate of 81.8MHz and 6.5W average power. It is pumped by a Nd:YAG laser. The limit to the repetition rate is set by resonant frequency of streak camera and the recombination time of the excited electrons is also shorter than excitation pulse rate.

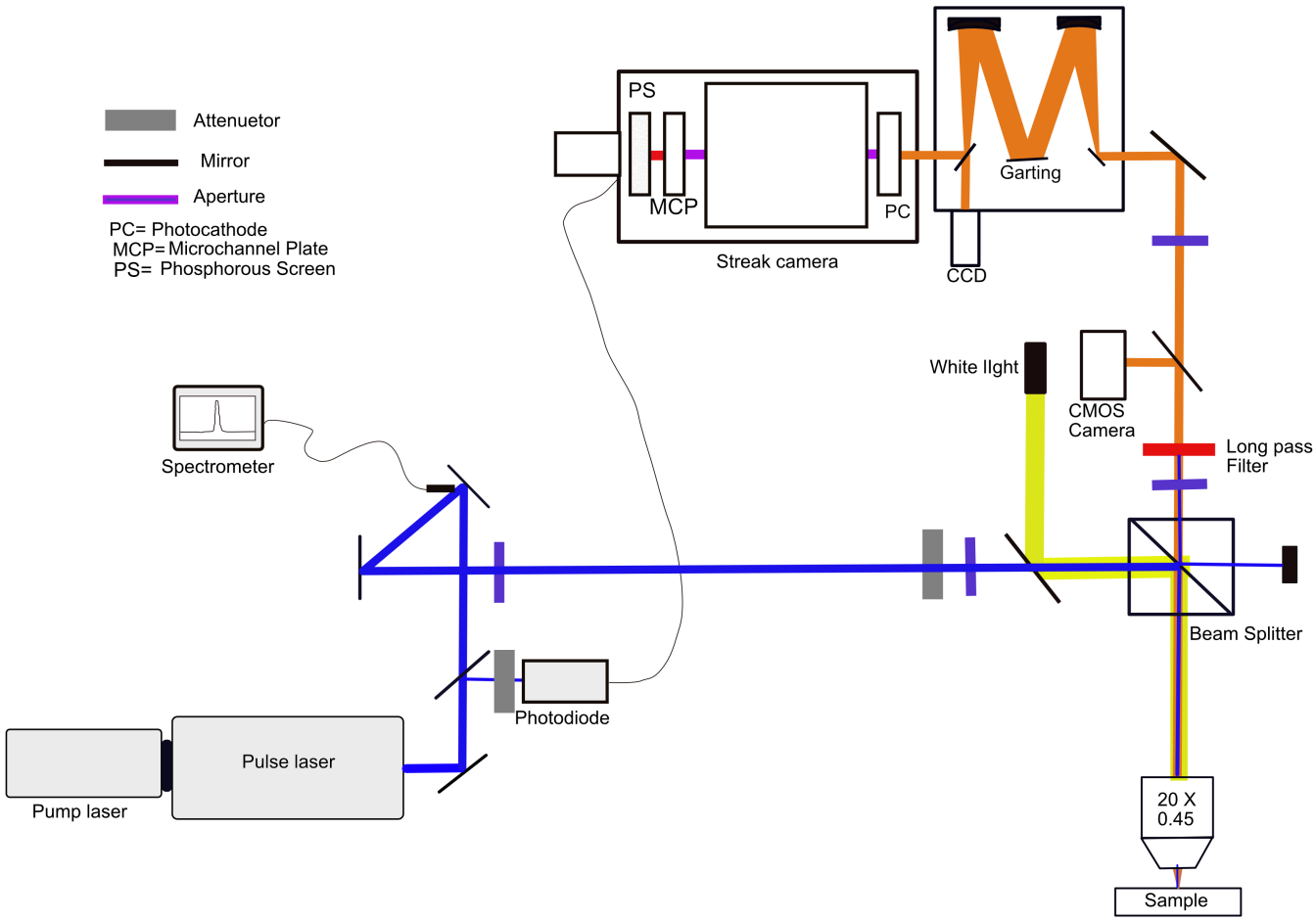

Figure 7: Experimental setup for time-resolved photoluminscence

A typical TRPL setup is schematically shown in Figure 6.One part of attenuated and focused pulse laser excites the nanowire (NW) sample loaded into a He flow optical cryostat and other part of the beam goes to a photo diode in order to send a trigger to the streak camera for generating synchronous sinusoidal electric field.After excitation we use high pass filter to cut laser line from the luminescence of sample. That luminescence is collected and focused onto a spectrometer that spreads different wavelengths spatially using grating for obtaining PL imaging through CCD Ccamera.After confirming the PL peaks associated with luminescence,the optical path of luminescence is directed towards streak camera for PL dynamics as a function of wavelength.We use white light to detect the position of nanowire on the Si-substrate through CMOS camera.

4.1 Streak Camera

The general purpose of a streak camera is to convert the temporal dependence of an optical signal into a spatial profile that is recorded with an optical camera. And that is done by following processes

- Conversion of photons to photoelectrons
  Monocromator grating diffracts emitted photons from sample and the horizontally dispersed light impinge on a photocathode (PC) that produces electrons through the photoelectric effect and the electrons are accelerated while keeping their energy proportional to the intensity of incident light
- Deflection of the photoelectrons by a transverse electric field
  Synchronized sinusoidal voltage from electrode create a high-speed sweep that displaces electrons in vertical direction, such that typically, the early time electrons give the signal at the top of the image, whereas the later electrons give rise to the signal lower on the screen.
- Detection of the transverse position of impact of the photoelectrons on a phosphor screen

Electrons passes through a microchannel plate (MCP) .Then deflected and amplified photoelectrons distribution hit a phosphor screen that converts electrons to light which is recorded most often by a digital charge-coupled device (CCD) camera.

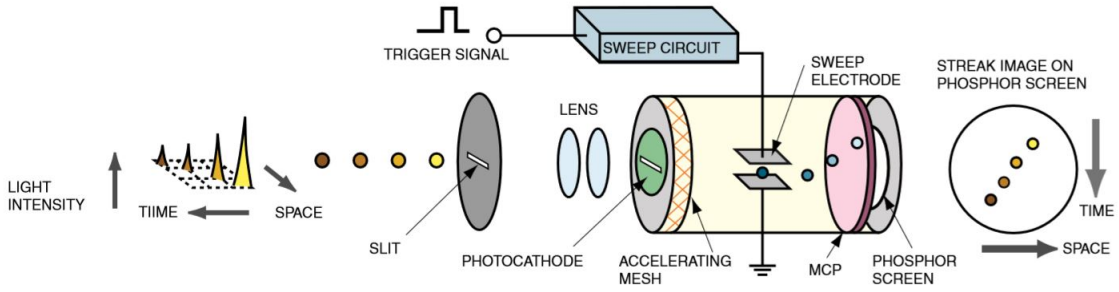

Figure 8: Streak Camera

5 Results and discussions

5.1 Short NW

Figure 9 and 10 represent the results obtain during the TRPL experiement for a low excitation power and a high excitation power respectively.

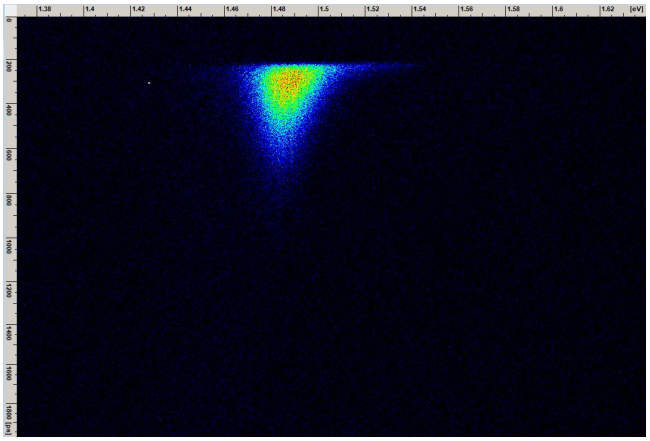

Figure 9: Results of TRPL for short nanowire at low power of 0.005 μW with x-axis, the energy of the detected light [eV] and y-axis, the time [ps].

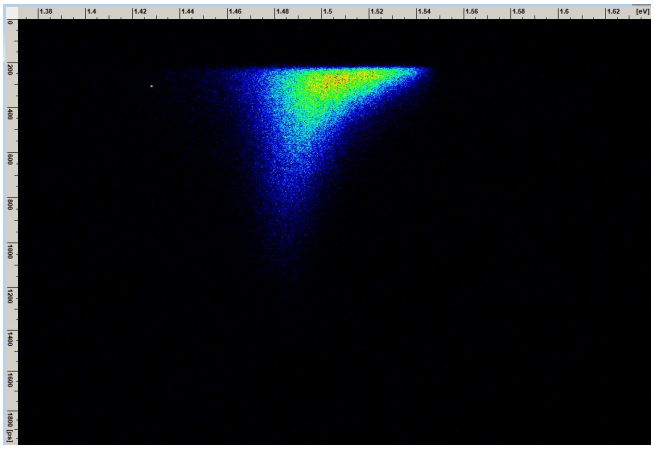

Figure 10: Results of TRPL for short nanowire at high power of 4.2μW with x-axis, the energy of the detected light [eV] and y-axis, the time [ps].

Figure 11 represents the intensity in function of the time for, in blue, a low excitation power and in red, a high excitation power for the emitted energy of 1.49eV which corresponds to the band gap of InP.

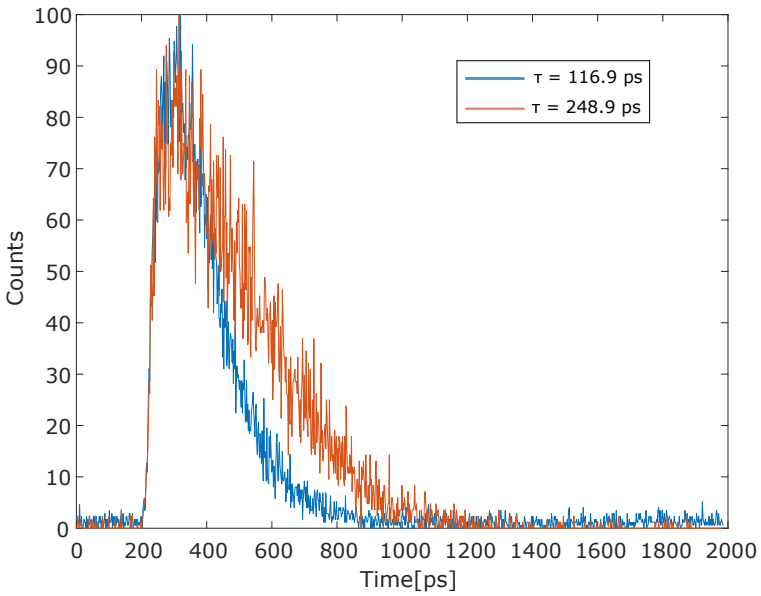

Figure 11: Intensity in function of time: in red, for a high power of 4.2 μW and in blue, a low power of 0.005 μW for short nanowire at 1.49eV.

As shown in figure 11, the radiative recombination lifetime increases by increasing the power which is the opposite of the theory.
Figure 12 represents the evolution of the intensity in function of the energy for different powers obtained by PL spectroscopy with a continuous laser. Figure 13 represents the intensity in function of the energy detected and the time obtained by TRPL spectroscopy.
There is a correlation between the evolution of the intensity over time in the case of TRPL spectroscopy and over

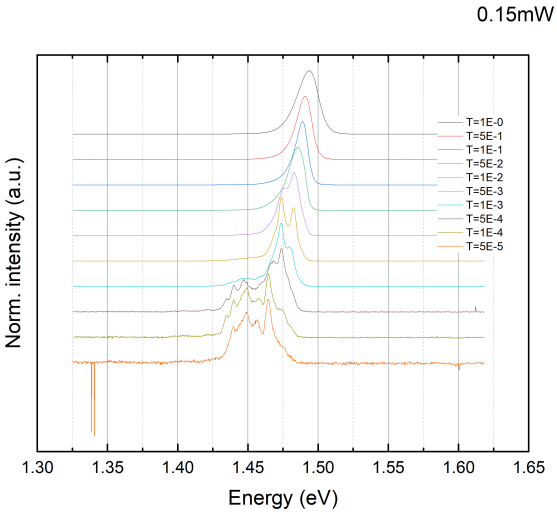

Figure 12: Intensity in function of detected energy [eV] for different powers obtained by PL spectroscopy.

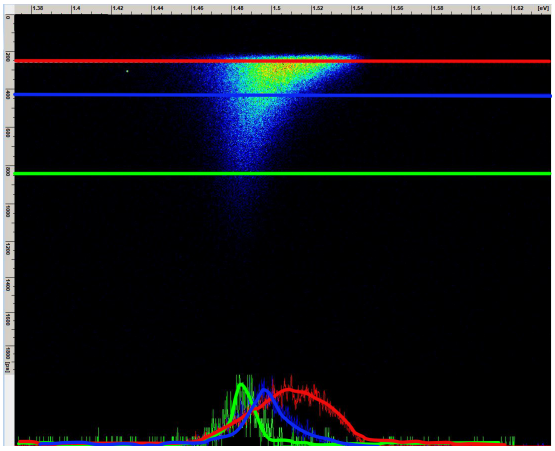

Figure 13: Intensity in function of detected energy [eV] for time obtained by TRPL spectroscopy

decreasing laser power in the case of PL spectroscopy. Indeed, in both cases, we observe that the peak moves towards lower energy.

5.2 Long NW

Figure 14 and 15 represent the results obtain during the TRPL experiement for a low excitation power and a high excitation power respectively.

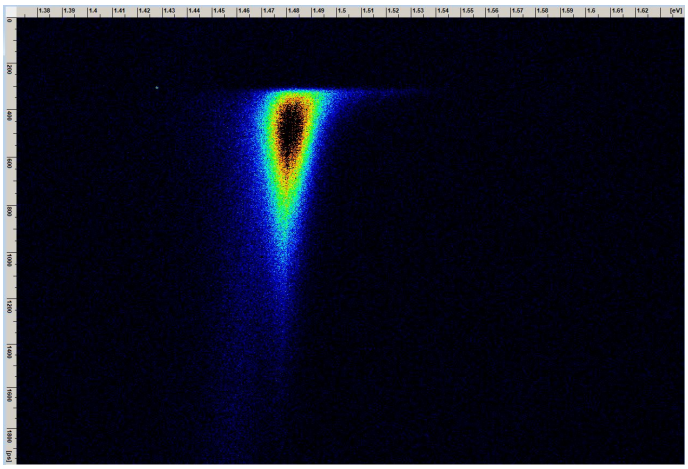

Figure 14: Results of TRPL for long nanowire at low power of 0.005 μW with x-axis, the energy of the detected light [eV] and y-axis, the time [ps].

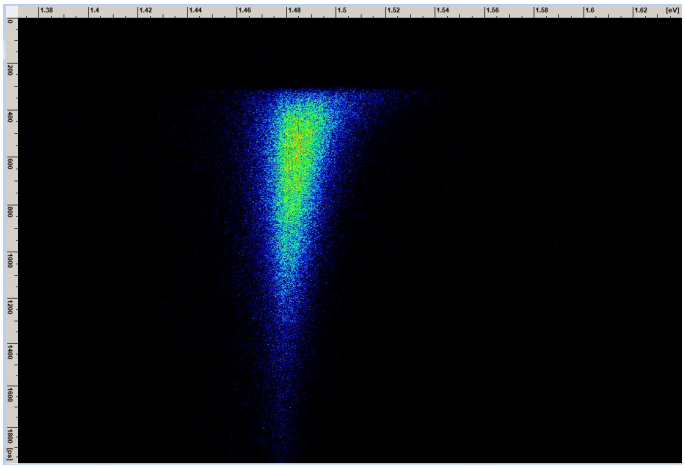

Figure 15: Results of TRPL for long nanowire at high power of 4.2 μW with x-axis, the energy of the detected light [eV] and y-axis, the time [ps].

Figure 16 represents the intensity in function of the time for, in blue, a low excitation power and in red, a high excitation power for the emitted energy of 1.49eV which corresponds to the band gap of InP.

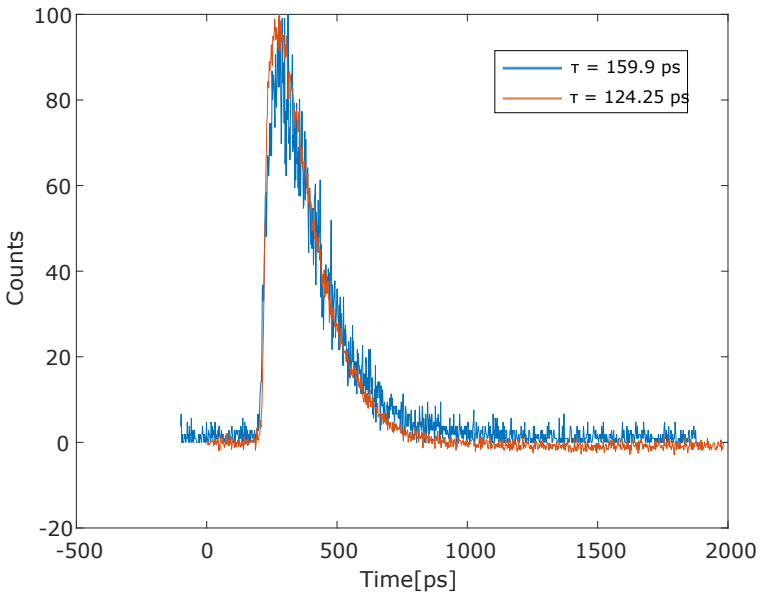

Figure 16: Intensity in function of time: in red, high excitation power of 4.2 μW and in blue, low excitation power of 0.005 μW for long nanowire at 1.49eV.

As shown in figure 16, the radiative lifetime recombination decreases by increasing the laser power which is what was described in the theory part.
Figure 12 represents the evolution of the intensity in function of the energy for different powers obtained by PL spectroscopy with a continuous laser. Figure 13 represents the intensity in function of the energy detected and the time obtained by TRPL spectroscopy.
There is a correlation between the evolution of the intensity over time in the case of TRPL spectroscopy and over decreasing laser power in the case of PL spectroscopy. Indeed, in both cases, we observe that the peak moves

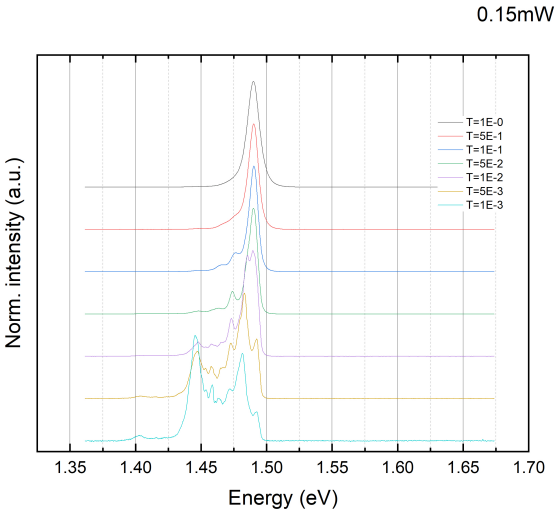

Figure 17: Intensity in function of detected energy [eV] for different powers obtained by PL spectroscopy.

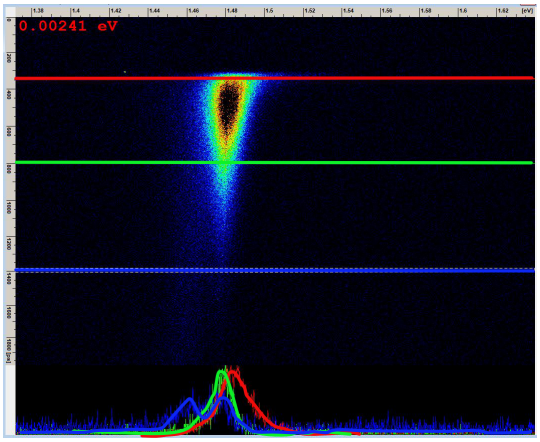

Figure 18: Intensity in function of detected energy [eV] for time obtained by TRPL spectroscopy

towards lower energy. In addition, we can see in both figures that for low power or long time, a peak at 1.45eV becomes predominant.

6 Conclusion

Major difference from short and long nanowire is coming from the peak around 1.45 eV as this peak is absent in short nanowire while it creates longer lifetime compare wurzite InP lifetime in case of TRPL date of long nanowire.We suspect it can come from some impurity related to the shell of long nanowire as longer nanowire has larger shell to core ratio compare to short nanowire and it can create a impact of the peak of 1.45 eV.As we cant see any sizeable redshift with decreasing laser power in steady state photluminscenece that rules out the origin of peak as type-II transistions due to stacking fault.May be in case of long nanowire,phosphorous vacancy creates acceptor level and that 1.45 peak is comming due to free electron to neyral-acceptor.[2]

References

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