Photoluminescence investigation methods of residual defects in SiC

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Abstract

Photoluminescence (PL) is a most powerful technique that allows a fast and non-destructive investigation of wide band gap semiconductors. In SiC it has been used for about half a century to collect information on the polytype, the crystal quality, the value of the residual doping level (including the nature and the concentration of doping species) and to identify polytypic defects. In this work we present a brief description of the experimental technique and comment some of the experimental results collected on various SiC polytypes.

1. Introduction

Silicon carbide is a wide band gap semiconductor well suited for high temperature and high-voltage power device applications. It is also of interest for optical sensors and detectors working in the ultra-violet part of spectrum. The bulk material is characterized by a large number of crystalline structure (the so-called polytypes) but, whatever is the polytype under consideration, SiC has always an indirect bandgap structure. The bandgap energy (and phonon structure) depends on the polytypic form, with extreme values ranging from ~ 2.35 to 3.25 eV at LHT (liquid helium temperature) when moving from the cubic (3C-SiC) to the uniaxial structure of 4H-SiC. In some cases, other hexagonal or rhombohedral structures also manifest, like 6H-SiC or 15R or 21-SiC. For a more general review, see Ref.[1]. Whatever is the polytype, and because all possible crystal growth technologies are still far from perfection, many defects manifest in the raw material. They are usually identified using luminescence techniques, like photo luminescence and cathode luminescence.

In this way one can probe most of the basic aspects of samples, without a risk of destroying or negatively impacting them.

- First, the polytype can be assessed (type and symmetry of the SiC unit cell) and, when necessary, a polytype map can be constructed through a measure of the LTPL (Low Temperature PhotoLuminescence) signature [2].
- Second, overall ideas on the crystal quality and residual doping level can be obtained through the consideration of spectra and line broadening [3, 4].
- Third, usual point defects (like doping impurities) can be can be identified. This includes the (intentional) nitrogen and phosphorus doping species in

n-type SiC, or the N contamination in low doped SiC, or the Al or B-doping of p-type SiC, or the Al or B contamination (compensation) of low doped SiC epilayers. Dependin on the polytype and impurity under consideration they substitute on either the C or Si-sites. This gives specific features in the optical "signature" [1, 5, 6].

- Fourth, finally, in some cases more complex defects like 2d-extended in-grown stacking faults (SFs) or process-induced defects like implantation or irradiation-induced defects can be detected. This is important for nuclear and space applications in which the material can be locally damaged. Only 1d-extendedefects like micropipes or dislocation are not easy to examine because they set more as luminescence killers than optically active recombination centers [2, 7, 8].

2. Basic experimental setup

A typical example of photoluminescence set up is shown in Fig.1. A FreD (Frequency Doubled) argon-ion laser with emission wavelength at 244 nm (~ 5eV) is used for excitation. The beam is focused inside a liquid helium cryostat which operates at low pressure and allows easily sample cooling from 300K at 5K. The emitted luminescence signal is collected by a system of achromatic parabolic mirrors and analyzed by a spectrometer, fitted with a cooled CCD camera. The spectrometer is equipped with 3 different gratings with 600, 1200 and 2400 gr/mm and, finally, the data are sent to a computer for processing. In such a way, using different cryostats it is possible to study samples with surface ranging from mm^2 to 4-inch diameter.

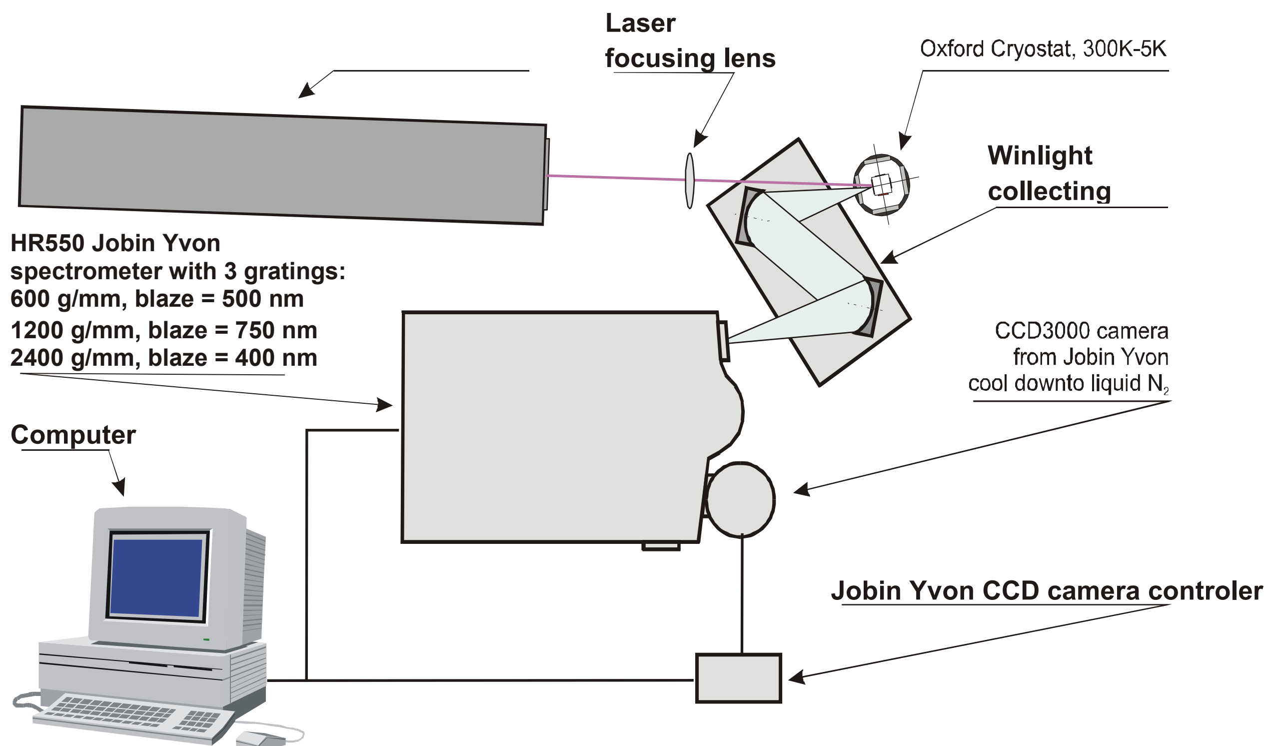

Figure 1. Standard photoluminescence setup.

3. Analysis of spectra

Generally speaking, even for non-intentionally doped SiC material, it is rather difficult to observe free exciton lines. Most of the time, impurities are present and

rule the LTPL signature. This is the case of experimental spectra displayed in Fig.2. In all four examples, the impurities are residual nitrogen impurities substituting for carbon. They come from the gas phase and, according to the polytype structure, can be localized on different hexagonal or cubic sites. At low temperature in low doped material, one neutral donor can trap one exciton forming then a four-particle complex denoted D_0X.

The different types of D_0X lines in Fig.1 come from the number of inequivalent sites available for nitrogen in a given polytype. For instance 4H-SiC has one hexagonal site and one cubic site while in 6H-SiC exist one cubic site and 2 hexagonal sites. This is why three different type of D_0X complex can be found in 6H-SiC, while there are only two in 4H-SiC [1, 3, 5, 6].

Remember now that, in both cases, we are dealing with an indirect bandgap semiconductor. The probability to find a strong ZPL (Zero-Phonon Line) depends only on the perturbation introduced in the crystal lattice by the foreign (N) atom. In a uniaxial polytype (either hexagonal or rhombohedral) it is always larger for a foreign atom substituting on a cubic site than a hexagonal one. This is why in 4H-SiC a strong (Q_0) peak appears ~ 382 nm. It corresponds with N substituting on the cubic carbon sites.

The second (P_0) line which would correspond with N substituting on the hexagonal sites has much lower intensity. It is not found in Fig.2 but, at lower energy, manifests as large phonon replicas.

In 6H-SiC and 15R-SiC, the situation is exactly similar. The strong peaks at 414-415 nm in 6H-SiC correspond with the (two) distinct possibilities that exist for N to substitute on a cubic site. The corresponding ZPL have been termed R_0 and S_0. In 15R-SiC there are four possibilities for a N atom to substitute on a C site. The four ZPLs manifest as P_0, Q_0,
R_0 and S_0 in Fig.2 and, again, the strong peaks correspond with the (two) distinct possibilities that exist for N to substitute on a cubic site. For a general description, see again Refs.[1, 3, 5, 6].

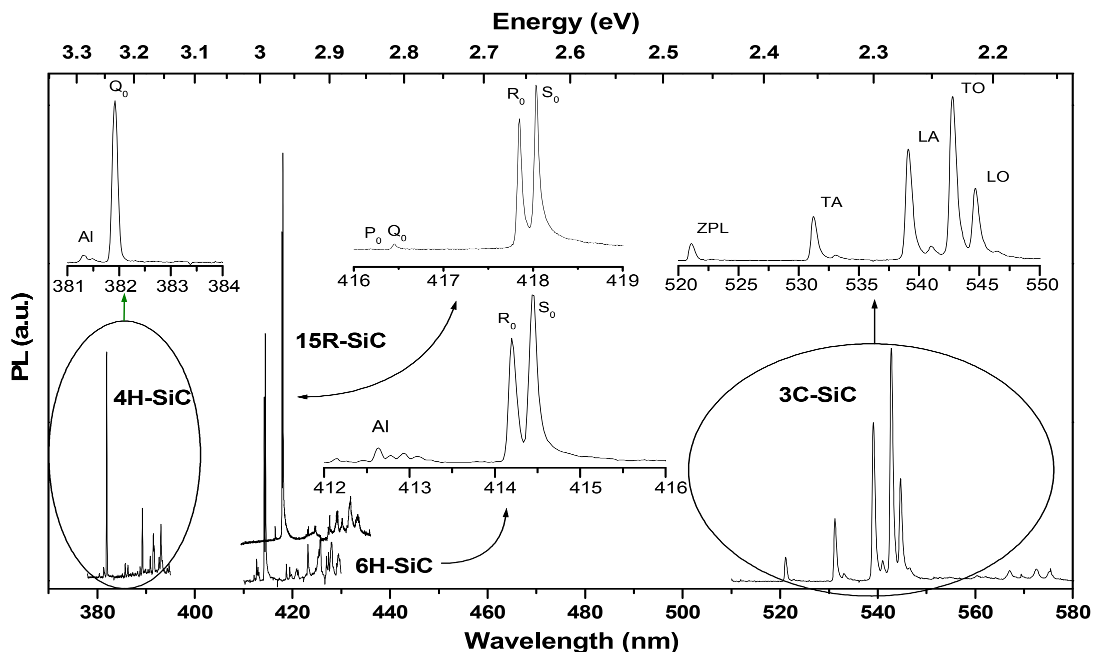

Figure 2. Different PL signature of SiC polytypes.

Of course, since all SiC polytypes have an indirect bandgap structure, one ZPL line is always associated with several phonon replicas but the intensity of replicas is not always the same. The basic rule is that a strong ZPL always corresponds with weak replicas and vice-versa.

In the simple case of 3C-SiC, for instance, there is only one cubic site and one ZPL. It appears near 520 nm, is weak but is associated with strong momentum-conserving phonon lines. There are four of them, associated with TA, LA, TO and LO phonon branches at the X-point of the Brillouin zone. They manifest from ~ 530 to 545 nm and are much more instance than the ZPL. Notice also that, at lower energy, two-phonon overtones manifest. In 4H or 6H-SiC the situation is basically similar, but complicated by a larger number of phonon modes. For a general description conserning 4H-SiC, see

Ref.[6].

Other specific polytypic signatures can be identified using LTPL, which depend on the amount and nature of the existing impurities in a given sample. Typical examples are shown in Fig.[3]. They have been collected on similarly compensated materials with 4H, 6H and 3C polytype structures. In all three cases strong DAP (Donor-Acceptor Pair) transitions manifest, which come from the simultaneous presence of donor and acceptor impurities with close nearest neighbor distance. They induce broad recombination peaks which, in the case of N-donors and Al-acceptors, appear at 420 nm, 490 nm and 630 nm in 4H, 6H and 3C polytypes, respectively.

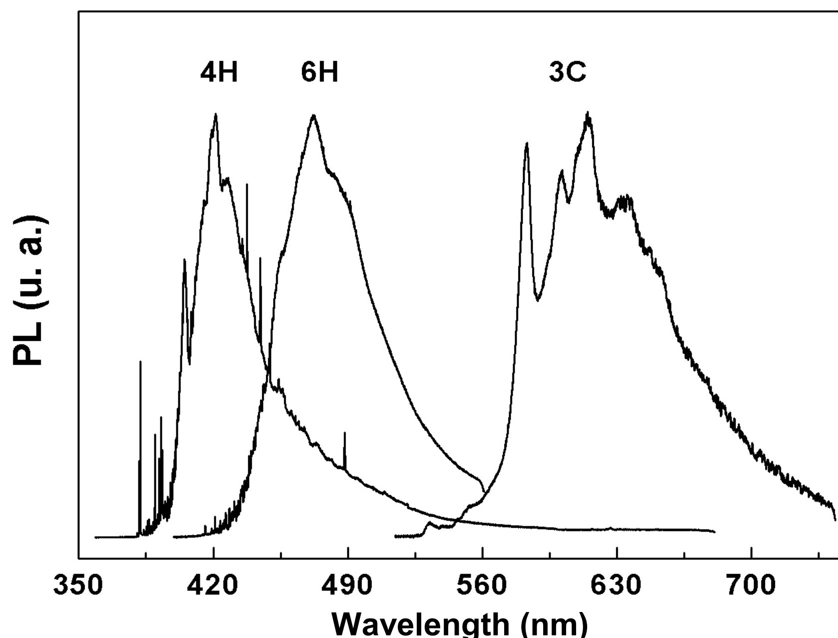

Figure 3. PL signature of donor-acceptor pairs in SiC for 4H, 6H and 3C polytypes.

4. Recombination process of carriers in SiC

The physics of recombination processes depends on the residual doping level. In very low doped (intrinsic) SiC materials, only intrinsic lines should exist. They result from elementary Coulomb interaction in the cloud of 2N excited particles forming N excitonic complexes. Every complex behaves like a simple H atom and, upon radiative recombination, results in a ZPL just below the bandgap energy plus associated phonon replicas. This FE line process is prominent in high quality material and mainly documented in 4H-SiC [3, 4, 9]

In the following we call FEs (Free Excitons) the corresponding electron-hole pairs. The density of Fes can be computed from Eq.1, while the corresponding luminescence intensity in a given radiative recombination spectrum can be obtained for Eq.2 :

$$\frac{dn_{FE}}{dt} = g_{FE} - \left(\frac{1}{\tau^{r}_{FE}} + \frac{1}{\tau^{nr}_{FE}} \right) n_{FE}$$

$$I_{FE} = \frac{n_{FE}}{\tau^{r}_{FE}}$$

In these equations n_{FE} is the density of free excitons, g_{FE} is the generation rate of free electron-hole pairs, τ^{r}_{FE} and τ^{nr}_{FE} are, respectively, the radiative and non radiative lifetimes of free excitons while I_{FE} is the LTPL intensity of the free exciton recombination
line under consideration.

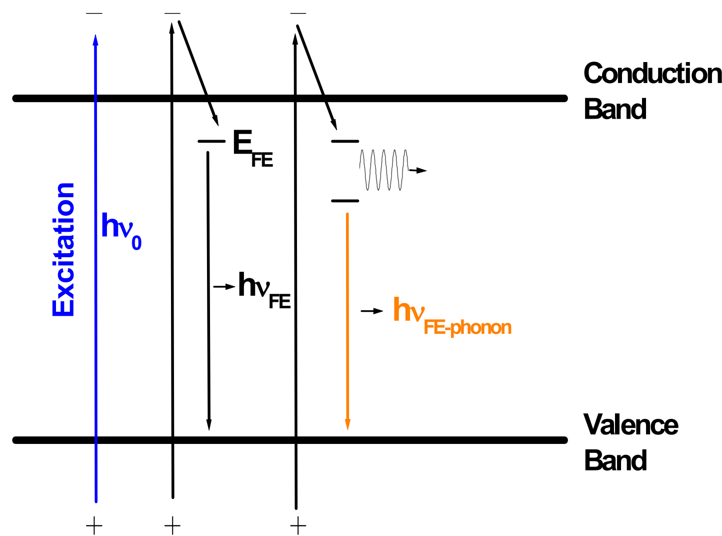

Figure 4. Recombination process of free excitons in intrinsic material.

As already mentioned, this process is only documented in very high quality 4H-SiC. In Fig.5, for instance, three lines appear which have been denoted $I_{76.4}$, I_{104} and I_{107}. They correspond to FE recombination lines in which no ZPL is found but only phonon replicas with 76.4, 10^4 and 10^7 meV phonon energy.

When the material is low-doped but still n-type, the intrinsic lines become weaker and weaker while the N-bound exciton lines manifest more and more. This is because when a shallow neutral donor level appears below the conduction band (i.e. below the FE level) a FE can always lower energy by trapping around the neutral donor atom. It forms in this way a four particles complex, with one bound donor nucleus, two electrons and a hole called D_0X complex. As already said, both P_0 and Q_0 lines are ZPL associated with such D_0X complexes in 4H-SiC. Notice the low intensity of the P_0 line and the high intensity of phonon replicas, to be compared with the high intensity of the Q_0 line and the low intensity of corresponding phonon replicas. As just explained in Section 3, this comes only from the difference in lattice perturbation associated with a donor nucleus sitting at a hexagonal (P_0) or a cubic (Q_0) site.

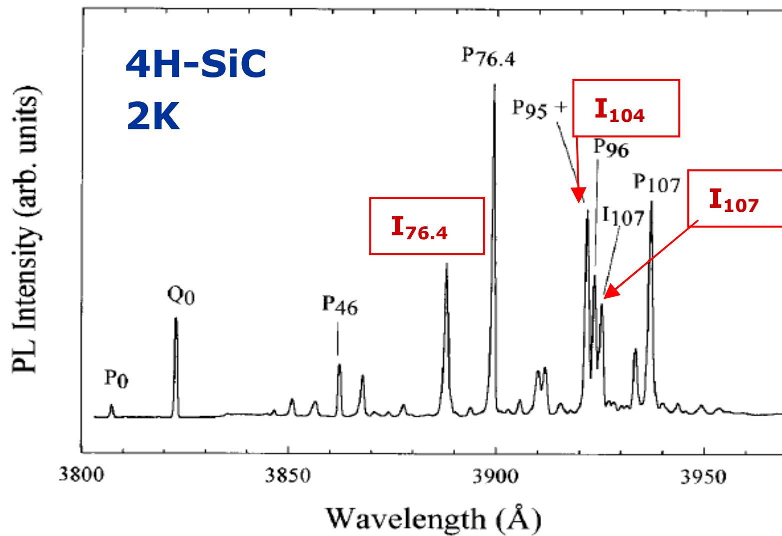

Figure 5. PL signature of 4H-SiC where intrinsic lines (I) are evident.

If the material is low doped but compensated with acceptor impurities, an acceptor level is localized above the valence band (Fig.6). An exciton is trapped on this level and form a complex of acceptor bound excitons called A_0X [4]. For instance, Al acceptor lines are observed in 4H-SiC doped with [Al]=2.5 $10^{16}cm^{-3}$.

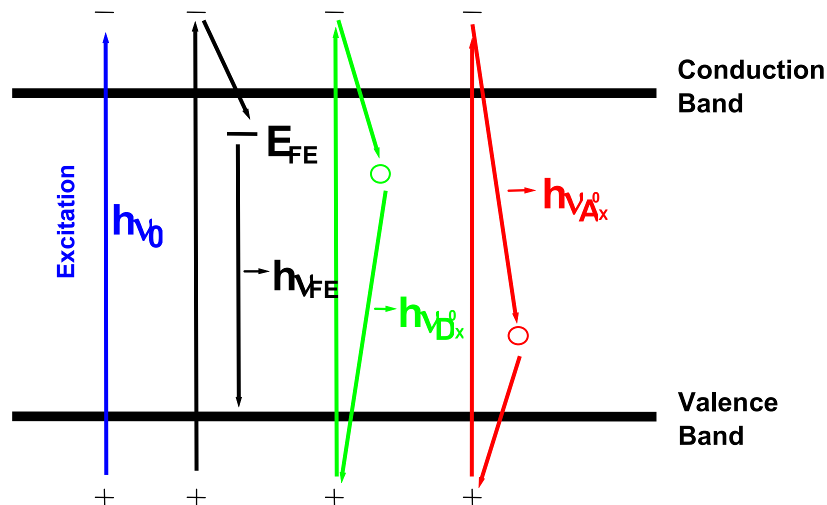

Figure 6. Recombination process of excitons in low compensated material.

Such Al-bound exciton lines can be found in the recombination spectra of 4H and 6H-SiC in Fig.2. They are weak but, normalizing the intensity of the A_0X lines to the intensity of the D_0X complex, it has been found possible to investigate quantitatively the residual compensation in n-type SiC materials [4, 10].

Finally, when both the doping level and the compensation level increase, a travelling FE can find simultaneously one neighbouring donor and one neighbouring acceptor atom. The ionized donor binds the electron while, simultaneously, the ionized acceptor binds the hole. In this way, new donor-acceptor pair transitions appear. For nitrogen and aluminium species in 3C, 4H

and 6H-SiC, they have been already shown in Fig.3 with schematics of the transitions displayed in Fig.7.

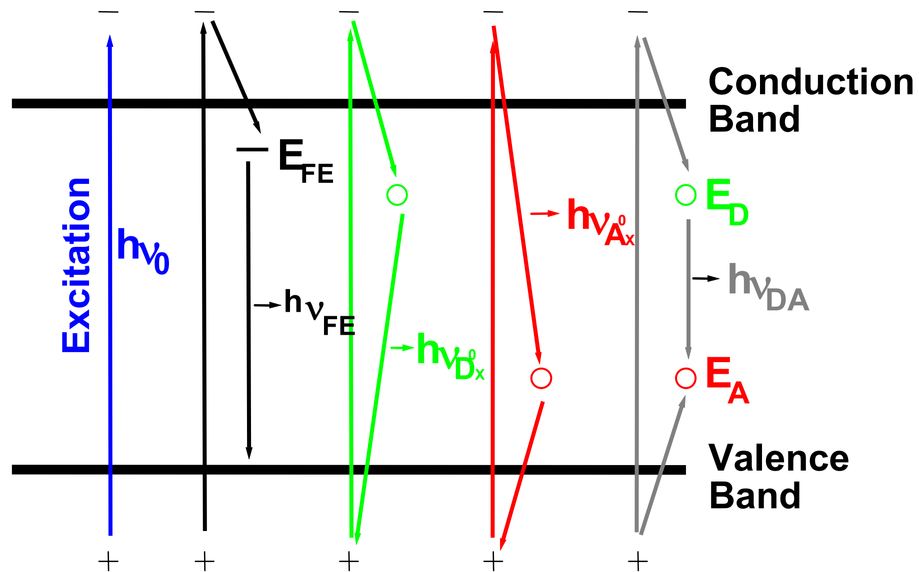

Figure 7. Recombination process of excitons in strong compensated material.

5. Identification of SFs using LTPL

Numerous stacking faults have been found in 4H and 6H-SiC polytypes. They had a different thickness and, in some cases, coexisted with a larger size inclusion but, in most of the cases, manifested as an optically active defect. Basically, this is because they behave like a thin QW (Quantum Well) made of a thin lamella of foreign polytype with limited extension in the basal plane.

This is best shown in Fig.8. In this 4H-SiC sample, both a 3C macroscopic inclusion and various (thin) SFs lamellae can be observed within the same limited area [11]. The large, similar, PL responses which appear in between the 4H-matrix signal (at ~ 3.2 eV) and the 3C-SiC inclusion lines (at ~ 2.3 eV) are the specific SFs signatures and all series of broad features is indicative of a specific SF lamella.

The reason why they all have the same signature, without a ZPL and with only four phonon-assisted recombination lines, is because (similar to bulk material) the radiative recombination process calls for a momentum conserving phonon between the trapped electron in the well and the outer hole in the matrix. Since the phonons come from the TA, LA, TO and LO phonon branches of 3C-SiC, there are four modes no ZPL is seen. This is best seen in Fig.9 and shows that these SFs act like "natural" (perfect) QWs, without any interface roughness. This is true in, both, a 4H or a 6H-SiC matrix.

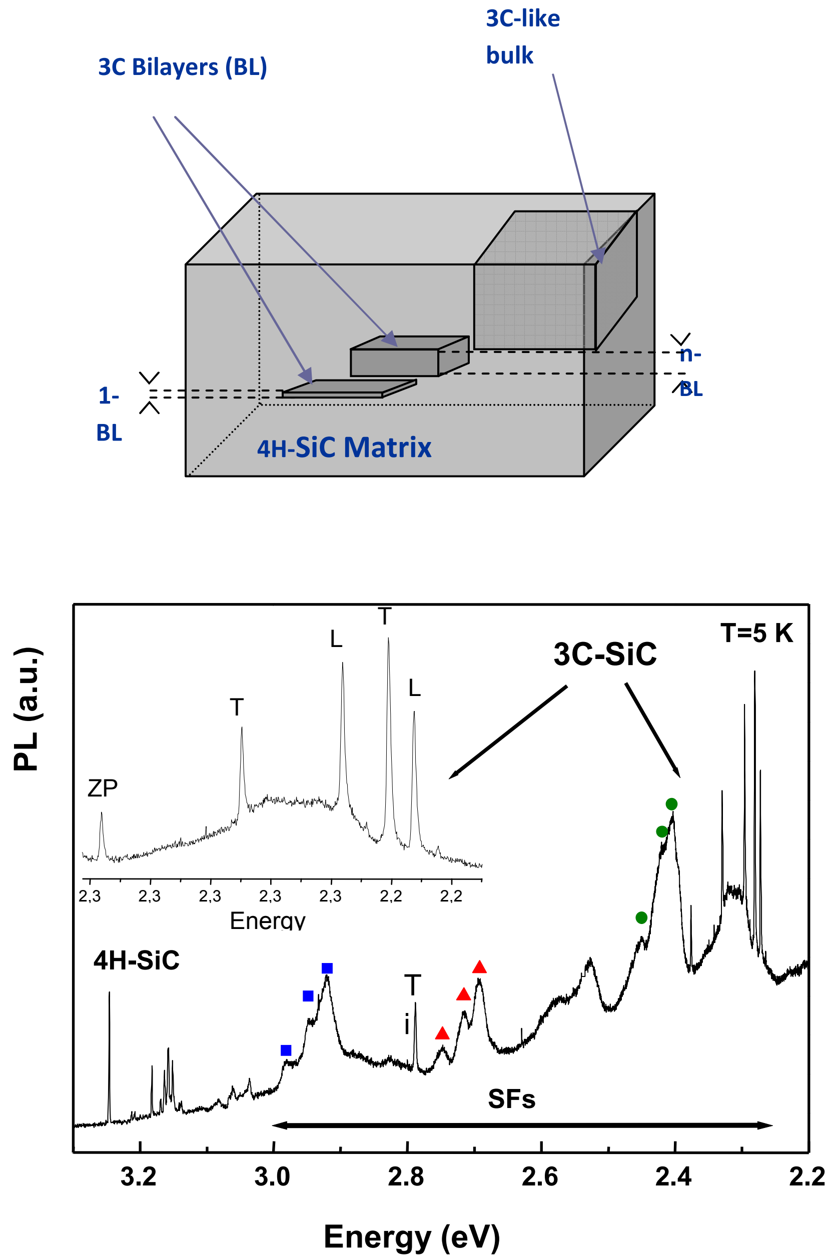

Figure 8. a) Graphical representation of 3C-SiC SFs in 4H-SiC. b) PL signature of 3C-SiC SFs in 4H-SiC matrix.

Optical SF signatures of 3C and 8H have been observed by many authors [6], [7]. The same signature always appears without ZPL line and only the four phonons modes TA, LA, TO and LO (Fig.9). The variation of optical gap E_{gx} gives information on thickness of SFs. However, some SFs have been found at 210 meV below 3C gap at 2.177 eV. This is due to the Stark effect [8] which exists in quantum wells in SiC. A 3C-SF and 8H-SF is modelized by a II- type quantum well inside 4H-SiC in which an internal field originates from the 4H barriers. Consequently, two transitions are possible. So a SF double signature exists (Fig.10).

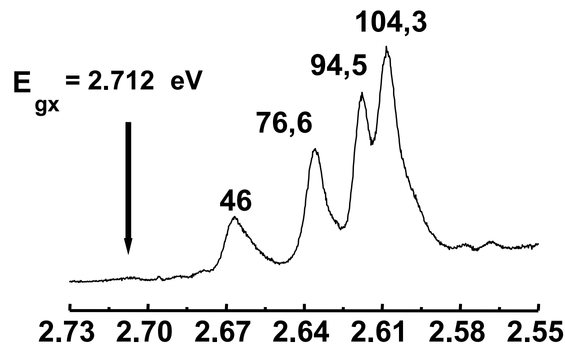

Fig.9. PL signature of 3C-SiC SF.

Accordingly, a model of 3C and 8H SF QWs has been worked out using a type-II QW model inside a 4H-SiC matrix and an internal field which originates from the 4H barriers. Since two transitions should be possible, all SFs should have a double optical signature [15]. This is schematically drawn in Fig.10.

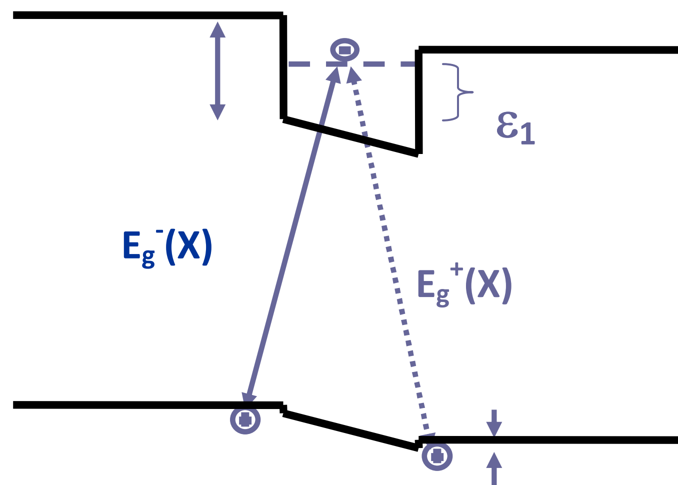

Figure 10. Schema of type II quantum well of 3C-SiC in 4H-SiC matrix. Two transitions appear (Eg^- and Eg^+) due to electric field.

6. Conclusions

Using LTPL, we have shown that it is possible to identify the polytype structure of SiC samples, to investigate the residual doping level associated with N (or AL or P) impurities and, also, to see if there are some SFs (or not) by examining the PL signature of the material.

The process is rapid and non destructive, which allows further study with other characterisation techniques. In order to investigate smaller areas of the material, complementary methods are requested like cathode-luminescence (CL) or microphotoluminescence
(μ-PL).

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