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**Formation of silicon nanocrystals by thermal annealing of low-pressure chemical-vapor
deposited amorphous SiN_x (x = 0.16) thin films**

Hakim Haoues^{*.1}, Hachemi Bouridah^{**1}, Mahmoud Riad Beghou¹, Farida Mansour²,
Riad Remmouche¹, Pierre Temple-Boyer^{3.4}

¹ Département d'Electronique, Université de Jijel, B.P. 98, OuledAissa, Jijel 18000, Algeria

² Département d'Electronique, Université Mentouri, Route d'Ain El-Bey, Constantine 25000,
Algeria

³ CNRS, LAAS, 7 av. du colonel Roche, F-31077 Toulouse, France

⁴ UPS, INSA, INP, ISAE, LAAS, Université de Toulouse, F-31077 Toulouse, France

* Corresponding author: e-mail h.haoues2@gmail.com, Phone: +213 661 183 167

** e-mail hbouidah@yahoo.fr

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Abstract

Silicon nanocrystals have been produced by thermal annealing of SiN_x thin film obtained by low pressure chemical vapor deposition using a mixture between disilane and ammonia. Morphological, structural, and photoluminescence properties of the thin film were investigated using X-ray diffraction, scanning electron microscopy, Raman spectroscopy and photoluminescence spectroscopy. The results revealed a high crystallinity of film with a crystalline volume fraction exceeded 70 %, and a dominance of silicon nanocrystallites having the sizes within the range 2.5-5 nm and density $\sim 1.98 \cdot 10^{12} / \text{cm}^2$. The PL peaks consist of nanocrystalline silicon and amorphous silicon. The luminescence from the silicon nanocrystals was dominant.

1. Introduction

A great deal of interest has been devoted recently to silicon nanocrystals (Si-NCs) due to the potentiality of Si-NCs in nanoelectronic applications such as channel layer of thin films transistor leading to a great enhancement in carrier mobility [1], and in optoelectronic applications because Si-NCs is expected to exhibit a quantum size effect [2– 4]. The origin of photoluminescence (PL) was described by the quantum confinement model and by the surface model. Fabrication of Si-NCs films, having a highly efficient quantum-size effect, requires both a reduction in the grain size, and an enhancement in the crystallites density.

For the proper application of photoluminescent Si-NCs in devices, the silicon crystallites must be embedded in a dielectric matrix. Many researchers have investigated the light

emission from silicon nanostructures embedded in silicon oxide films due to its easy processing, and its full compatibility with complementary metal oxide semiconductor (CMOS) technology [5,6]. However, a too large band gap of the silicon oxide handicaps the injection of the carriers that reduces the efficiency and reliability of the devices. SiN_x is a preferred dielectric matrix because of its low barrier high charge trapping capacity and high carrier mobility. Several chemical vapor deposition (CVD) techniques were used for Si-NCs production in SiN_x with various compositions [7-9]. Depending on the preparation parameters, the PL was attributed either to the quantum confinement of Si-NCs or to radiative defects [10-13]. The type of defects strongly depends on the deposition parameters such as stoichiometry and post deposition treatments. Indeed, the presence of nitrogen with high proportions favors the appearance of radiative defects.

In order to enhance the quantum confinement effect, we propose a method allowing the formation of Si-NCs in an intermediate structure between amorphous silicon and silicon nitride. In the quest to develop such a material, we anneal at high temperature amorphous SiN_{0.16} thin film obtained by low pressure chemical vapor deposition (LPCVD) using a mixture between disilane (Si₂H₆) and ammonia (NH₃). LPCVD which is a process compatible with CMOS technology offers several advantages such as the reduction of both the rate of the reaction permitting greater control over film thickness, and the thickness variations. It also improves the film's purity (low defects number) and internal structure. The simplicity of the process permits the processing of large wafer batch sizes.

The crystallization of amorphous LPCVD silicon thin film by using Si_2H_6 gaseous that allows deposits at very low temperatures (420-520 °C); i.e. lower than the silicon crystallization temperature (≈ 580 °C) with a high deposition rates, allowing to separate the deposition and the crystallization phenomena, provides a polycrystalline structure characterized by a high crystalline volume fraction (X_c) and micrometric grains sizes [14]. Si_2H_6 and NH_3 gas mixture offers the possibility to realize different types of materials between the silicon nitride and amorphous silicon, and hence it is possible to introduce low nitrogen content necessary to obtain high silicon crystallites concentration with smaller sizes. Indeed, the excess of silicon in films allows high silicon crystallites concentration after heat treatment while the nitrogen atoms increase the disorder in the silicon network during the film deposit phase [15] in one hand and suppress the crystallites growth during the thermal annealing process, in the other hand. We combine in our crystallization process a high temperature annealing (1100 °C) to activate the nucleation phenomena with a short annealing duration (1 min) in order to avoid an eventual enhancement in the silicon crystallites sizes.

2. Experimental

The deposit of amorphous SiN_x ($x = \text{N/Si}$) thin film (thickness around 200 nm) was carried out in a conventional hot-wall, horizontal, LPCVD furnace by using Si_2H_6 and NH_3 gaseous mixture, on 10 cm, (111), oxidized (about 120 nm of oxide) silicon wafers. The deposition pressure P and the temperature deposition T were respectively fixed to 200 mTorr and 465°C. Ellipsometry and energy dispersive X-ray spectrometry confirmed the

composition of the film to be $\text{SiN}_{0.16}$. The film thickness was measured by ellipsometry and checked by profilometry. Thermal annealing process was performed at 1100 °C during 1 min into a conventional furnace under nitrogen (N_2) ambient.

The X-ray diffraction (XRD) study of film was performed on a D8 Advance Bruker AXS diffractometer with $\text{CuK}\alpha$ radiation equipped with a curved graphite monochromator. According to both the thicknesses of SiN_x thin film (200 nm) and underlying oxide layer (120 nm) the incidence ray was oriented with an angle of 0.3° , so that the Bragg condition can not be satisfied for the substrate. The data were collected in the $2\theta^\circ$ range of $25\text{--}80^\circ$ with a step size of 0.03° and a count time of 2 s per step. Scanning electron microscopy (SEM) analysis of the sample was done using Philips model XL 30. The grain size distribution (GSD) and the crystalline volume fraction X_c were determined via image-processing techniques. Raman spectroscopy analysis has been carried out using a LabRAM Jobin -Yvon spectrometer. The excitation wave-length was the 488 nm line of an Argon laser in the backscattering configuration. The laser spot on the sample was kept at a power density low enough to avoid temperature effects (about 6 mW over the sample). The PL was measured using a laser excitation source wavelength of 355 nm. The laser beam has a power density of 3.27 mW and a spot diameter of few mm and a resolution of 6.8 nm.

3. Results and discussion

Figure 1 shows the XRD spectrum of the $\text{SiN}_{0.16}$ film. The film deposited in the amorphous state crystallizes in the (111) crystalline direction. Based on Scherer formula, the

average crystallite size of nanocrystalline silicon is calculated from the full width at half-maximum (FWHM) of the (111) diffraction peak as 7 nm. Noticing, that XRD spectrum represents the deconvolution of the diffraction of all silicon crystallites with different sizes. Thus, this size value represents an average size of all silicon crystallites.

Figure 1

To have a direct view of the silicon crystallites, SEM measurements were performed. Figures 2 and 3 depict, respectively, the SEM image and GSD of SiN_{0.16} film annealed at 1100 °C during 1 min.

Figure 2

Figure 3

The SEM image shows clearly the crystallization of film characterized by the existence of nanocrystalline silicon (bright regions) in contrast to the amorphous matrix (dark regions in SEM image). As shown in the inset, each cluster consists of subgrains and amorphous phase between the grains.

The grain size distribution and the crystalline fraction are determined by image analysis using the wavelet edge detection method [16]. The equivalent diameter g of a grain is obtained using the following expression [17]:

$$g = 2\sqrt{\frac{A}{\pi}} \quad (1)$$

Where A is the surface of a grain.

The wavelet edge detection method can be used for drawing the contours of grains before determining their size distribution. Thus, the grain size distribution is determined in two steps. The first one concerns the extraction of the grains' outline. The second concerns the calculation of the grains' size in order to determine their distribution according to:

- determining the number of pixels in the image scale;
- determining the number of pixels in each grain;
- calculation of the grains number in the image;
- calculation of the grains diameters using the expression (1) and thus the maximum size and average grain size.

The GSD is then normalized by dividing the corresponding value for each size by the total number of grains.

The crystalline fraction X_c is calculated using the following expression [18]:

$$X_c = \left(\frac{S_{crystallites}}{S_{crystallites} + S_{amorphous}} \right)^{3/2} \quad (2)$$

Where $S_{amorphous}$ and $S_{crystallites}$, represent the total amorphous area, respectively.

We calculate an average silicon crystallites size of 6.3 nm in good agreement with the size provided by XRD and a crystalline volume fraction $X_c = 80 \%$. This large value of X_c

implies the presence of a high density of silicon crystallites. Indeed, through the analysis of GSD, it may be noted that 71 % of nanocrystallites have sizes within the range 2.5-8 nm, among this proportion, 90 % of the crystallites have sizes within the range 2.5-5 nm and density $\sim 1.98 \cdot 10^{12} / \text{cm}^2$. The lowest value of the crystallites proportion (0.26 %) is attributed to crystallites having sizes within the range 30 - 40 nm.

Raman spectroscopy is a sensitive tool for studying Si-NCs material because it gives direct structural evidence quantitatively related to the nanocrystalline and amorphous component in the material. The formation of Si-NCs in the $\text{SiN}_{0.16}$ film after 1100°C annealing is also confirmed by Raman spectrum as shown in figure 4. The Gaussian deconvolution of the spectrum shows the presence of two peaks, a peak around 480 cm^{-1} which indicates the presence of amorphous silicon [19, 20] and another at 514 cm^{-1} originating from nanocrystalline phase in the film [19]. Note that the peak characteristic of Si-NCs is more intense than that of amorphous silicon showing a formation of a significant portion of nanocrystalline silicon in the annealed thin film. Quantitative estimation of X_c can be performed via the two Gaussian components by using the following formula [21]:

$$X_c = I_c / (I_c + \eta * I_a) \quad (3)$$

Where I_c is the Gaussian integration intensity related to crystalline composition, I_a is the integration intensity related to amorphous composition in Raman spectrum and $\eta = 0.88$ represents the fitted factor. The X_c extracted from Raman spectra is equal to 73 %. The slight difference of this value, comparing it with the data provided by SEM analysis (a difference of 7 %) can be attributed to the specificity of measurement and calculation of each method.

Figure 4

Figure 5

The PL spectrum of SiN_{0.16} film as a function of photon wavelength is plotted in figure 5. This spectrum shows an emission band between 500 nm and 740 nm corresponding to luminescence energies of 2.5 eV and 1.68 eV respectively, with a maximum at 578 nm (2.13 eV). Gaussian deconvolution of the PL spectrum clearly identifies three peaks of different wavelength, namely, a peak at 617 nm (2 eV) related to the quantum dots in the amorphous silicon [22], a peak characterized by the highest intensity at a wavelength of 578 nm (2.13 eV) and a peak at 673 nm (1.84 eV). The latter two peaks are associated with Si-NCs [23, 24].

By using the expression proposed by Kim et al [25], it is possible to access to the size of silicon nanocrystallites knowing their luminescence energies by the following formula:

$$E_c = 1.13 + 13.9/d^2 \quad (4)$$

Where d is a diameter of nanocrystals.

We calculate a nanocrystallites size of 3.72 nm corresponding to the PL energy $E_c = 2.13$ eV and a nanocrystallites size of 4.42 nm corresponding to $E_c = 1.84$ eV. Both sizes are in the range of crystallites having the largest proportion as it has been provided by the SEM data. The light emission originating from quantum confinement effect, can be attributed

to the high density of Si-NCs having the lowest sizes in one hand, and to high crystalline volume fraction level obtained after high thermal annealing, in the other hand [26].

Several of works have been published on photoluminescence from nanostructured silicon, which includes crystalline or amorphous silicon quantum dots embedded in amorphous silicon matrix or SiN_x dielectric matrix synthesized by various chemical and physical vapor deposition routes [10-13, 26, 27]. The investigations have mainly concerned the formation of Si-NCs by using silane (SiH₄) as precursor gas. In such structures, the crystallinity in terms of volume crystalline fraction and crystallites size, and the PL origin are a compromise between a large process parameters number, which makes difficult a rigorous comparison between the different methods. The originality of this work is that the proposed method (LPCVD deposit process, Si₂H₆ precursor gas, high thermal annealing), allowed us the production of a high density of luminescent Si-NCs in SiN_x matrix.

4. Conclusion

Silicon nanocrystallites formation in annealed amorphous LPCVD SiN_{0.16} thin film has been investigated. The results revealed the production of nanocrystals film characterized by a large crystalline volume fraction in which the highest silicon crystallites proportion is attributed to the crystallites having the lowest sizes. PL spectrum has been separated into three Gaussian peaks. Two peaks were attributed to silicon nanocrystals and one peak to amorphous silicon. The luminescence from silicon nanocrystals was dominant. The high crystallinity of the obtained silicon nanocrystals film offers to the material large applications in nanoelectronic and optoelectronic fields.

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Figure Captions

Figure 1: XRD spectrum of SiN_{0.16} film annealed at 1100 °C for 1 min.

Figure 2: SEM image of SiN_{0.16} after heat treatment at 1100 °C for 1 min.

Figure 3: Histogram of grain size distribution of SiN_{0.16} film annealed at 1100 °C for 1 min.

Figure 4: Deconvoluted Raman spectrum of SiN_{0.16} film annealed at 1100 °C for 1 min.

Figure 5: PL spectrum of SiN_{0.16} film annealed at 1100 °C for 1 min with deconvoluting Gaussian peaks.

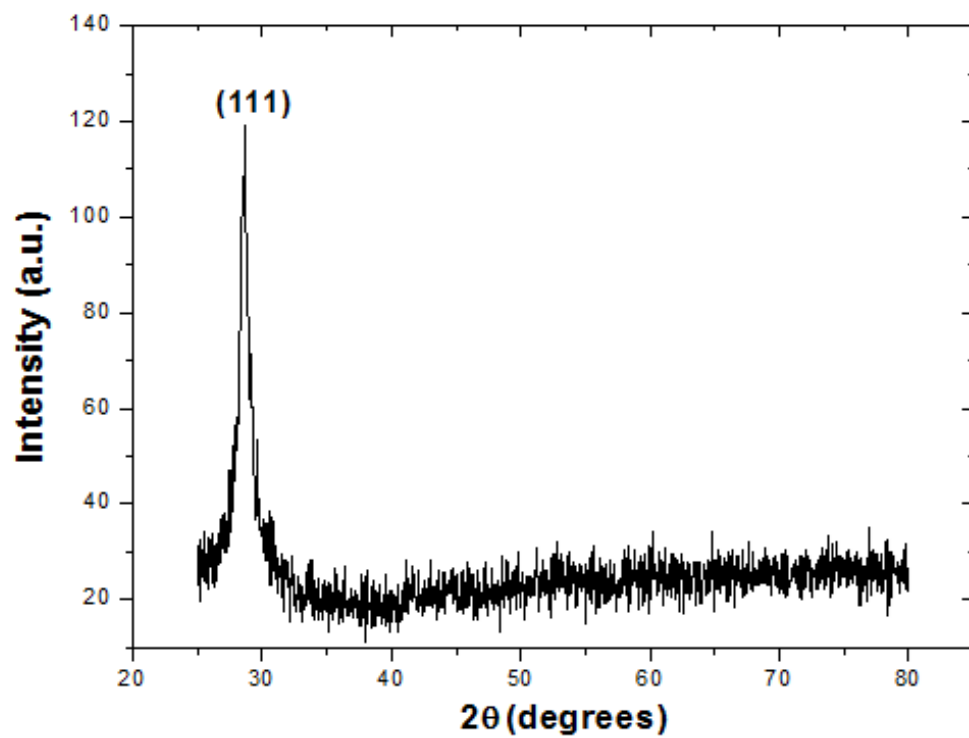


Figure 1

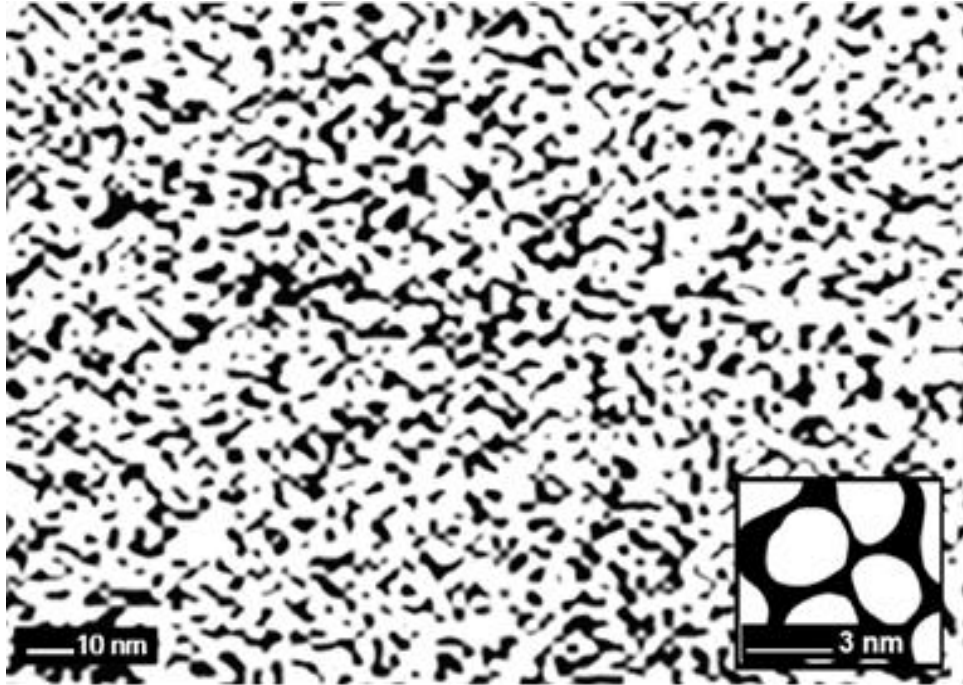


Figure 2

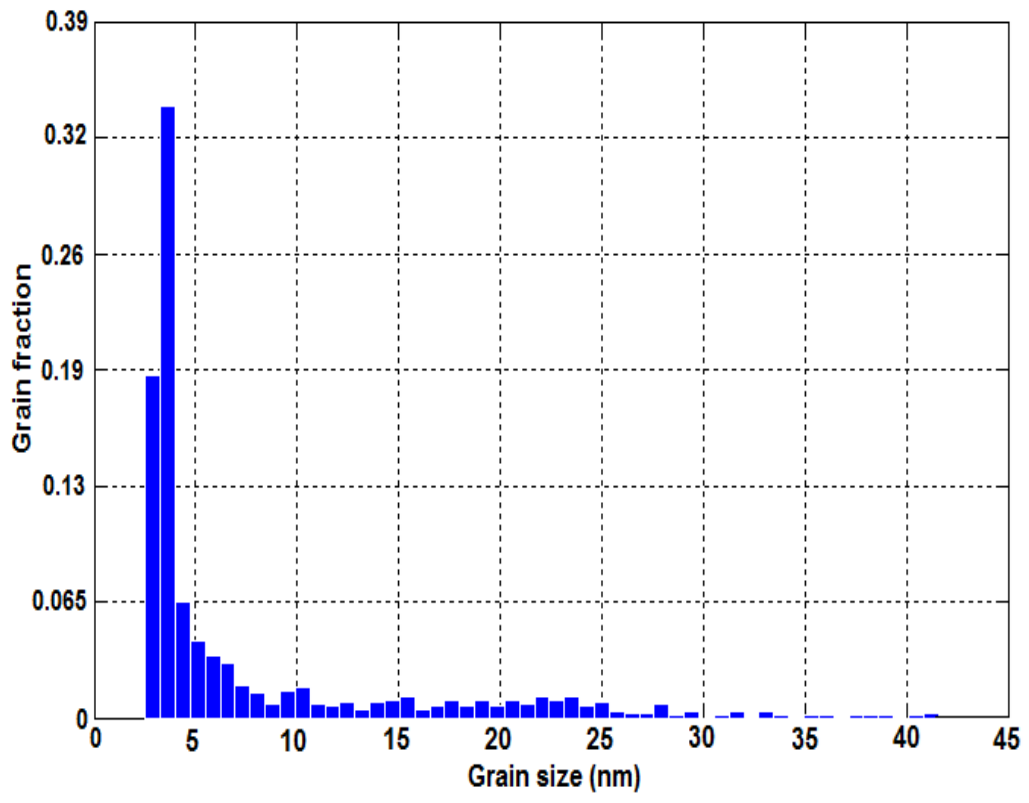


Figure 3

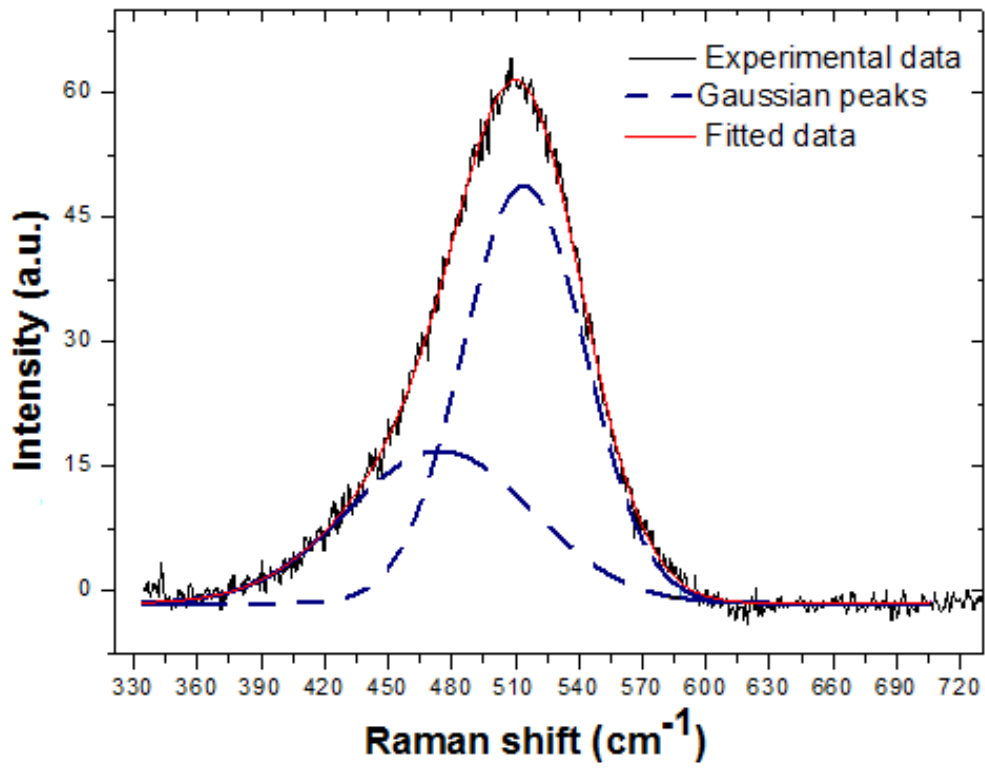


Figure 4

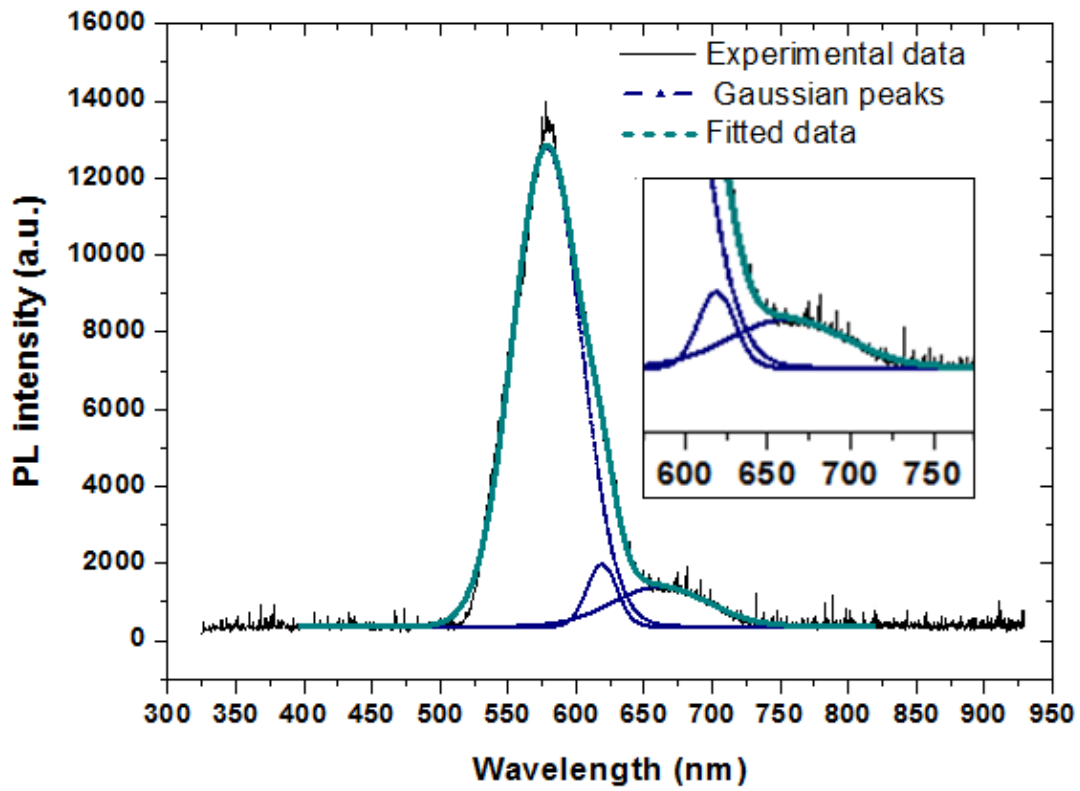


Figure 5