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Enhancement of the photoluminescence property of hybrid structures using single-walled carbon nanotubes/pyramidal porous silicon surface

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ABSTRACT

This work presents additional physical results about the enhancement of the photoluminescence property of hybrid structures using single walled carbon nanotubes/pyramidal porous silicon surface, in comparison with what has already been published on these structures in terms of synthesis conditions and FTIR investigations as reported recently by the same authors in Journal of Alloys and Compounds 694 (2017) 1036–1044. Herein, the effect of the single walled carbon nanotubes (SWCNTs) layer on the optical properties of pyramidal Porous Silicon (pPSi) in hybrid SWCNTs/pPSi structure synthesized by chemical and electrochemical etching of silicon wafer was studied. Using both scanning electron microscopy (SEM), SWCNTs formed a thin film on pPSi surface and they are partly embedded in its pores. An analysis of Raman spectra for the realized structures confirmed the passivation of pPSi surface by SWCNTs film. The surface bond configurations were also monitored. Moreover, SWCNTs modified Photoluminescence (PL) spectrum of pPSi by shifting PL peaks towards high energies, showed that the defect created in the materials can result in an efficient and stabilized photoluminescence response on Silicon (Si).

1. Introduction

Carbon nanotubes generally exhibit remarkable physical, chemical and optical properties [1]. They have also interesting electronic properties due to their metallic appearance and semiconductor behavior. Many experimental attempts focused on

hybrid structures widely used in electronic devices [2]. The single walled carbon nanotubes (SWCNTs) were used as an active layer for absorbing light in the molecules [3] and the light trapping in photovoltaic devices [4].

This unique property of quantum defects in SWCNTs, together with their compatibility with Si based nano device fabrication technology opens a new path to realize room temperature single photon sources operating at telecommunication wavelengths that are critically needed for applications in quantum communications.

The pyramidal Porous Silicon (pPSi) seems to be a suitable

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candidate to integrate SWCNTs into the substrate with a large specific surface area. It is prepared by chemical and electrochemical etching of a single crystal with the formation of small cavities, producing a thick wall between the pores whose size may be of several nanometers [5]. In fact, pPSi has some interesting physico-chemical properties such as: (i) its intense visible photo-luminescence, (ii) its anti-reflective properties and (iii) its band gap energy value that increases due to the quantum confined effect in silicon nanocrystals. Due to these characteristics, Si can be used in the production of optoelectronic and photonic devices [6]. Besides, the relatively high chemical and adsorption sensitivity of pPSi large internal surface is actively exploited in the touch sensing electronics and biomedical technologies [7].

First attempts to attach SWCNTs in specific surface were done in 2000 by Liu et al. [8] who implanted shortened SWCNTs to gold. Nevertheless, carbon nanotubes were not chemically immobilized to silicon until 2006 when Yu et al. [9] attached shortened SWCNTs to silicon by first hydrogenating a silicon (100) surface. In 2007, they refined chiefly the approach by hydroxylating silicon (100) surfaces and chemically implanting shortened SWCNTs using DCC coupling [10]. In the same period, Flavel et al. [11] obtained a SWCNTs immobilized to an amine terminated silane layer (APTES) on silicon.

By 2010, Cameron et al. [12] reported both the chemical attachment of functionalized SWCNTs to amino silane modified PSi and the formation of silane patterns on PSi. In 2012, the same authors used PSi functionalized with APTES to immobilize carboxylated SWCNTs [13]. Their work showed that there was an optimal concentration of APTES from which there is enough SWCNTs to produce a large amount of current, proving that SWCNTs surface coverage can significantly affect the solar cell performance.

In 2013, the same researchers found that both the chemical attachment and patterning of SWCNTs on PSi show the ability of SWCNTs to capture human neuroblastoma cells [14].

Recently, Gammoudi et al. [15] have modified the silicon topography by a pPSi structure to increase the surface in contact with the carbon nanotube. Then, they have attached chemically SWCNTs on pPSi surface and into the nano pores of pPSi structure. Their observations by means of the Atomic Force Microscopy (AFM) confirmed that the coverage of the attached SWCNTs decreased with decreasing APTES density on the surface.

Creating hybrid structures or composite materials allows minimizing the size effects and creating a large specific surface area between silicon and SWCNTs [16]. Besides, an interaction between nanoparticles in the hybrid structures can lead to the appearance of new unique properties compared to those of the individual components. In particular, the modulation of fluorescent radiation is detected in SWCNTs/pPSi structures [17]. The pPSi based photo detectors with surface coated by reducing SWCNTs have high sensitivity and quantum efficiency over a wide spectral range—from near UV to IR regions [18].

From an overview of the literature, we note that the use of pPSi surface modification with the SWCNT and the effects of SWCNTs on the luminescence of the of pPSi surface in such structures were not been extensively studied [15]. Thus, it would be quite interesting to make physical investigations for the PL properties of this hybrid structure, which could open alternative applications for pPSi as substrates in various optoelectronics and sensitivity devices.

In this work, SWCNTs was used to modify pPSi layers in order to improve its process ability. Due to the high stability of SWCNTs, special attention was focused on the effects of SWCNTs implantation on pPSi photoluminescence. Moreover, further physical investigations by means of RAMAN and SEM were carried out.

2. Experimental procedure

2.1. Materials

Single wall carbon nanotubes (SWCNTs) (Fig. 1) containing carboxylic acid functionality were purchased from Sigma Aldrich. The diameter range of SWCNTs was 4–5 nm, the length was between 0.5 and 1.5 μm , and the purity was above 90%. APTES: 3 aminopropyltriethoxysilane with purity of 99% (Aldrich) was used to attach functionalized SWCNTs with a carboxylic acid on a porous silicon pyramidal structure (Fig. 1).

2.2. Substrates preparation

P type (1 0 0) oriented silicon wafers were used in the experiment. The resistivity of the samples was between 0.01 and 0.02 $\Omega\text{ cm}$. The surface of samples was of the order of $20 \times 20\text{ mm}^2$. First, pyramidal silicon (pS) structures were formed after chemical etching in NaOH (1M) solution at 85 °C during 6 min to remove Si damage (Table 1) [15,19,20].

Second, pPSi structure was prepared by electrochemical anodization of electrolyte solution of HF (25%) and EtOH, respectively. A computer controlled current source was used to fabricate porous pyramidal structured silicon from the selected current density and time data, as shown in Table 1. After the electrochemical attacks, all the samples were rinsed with ethanol and dried in the ambient air to form an oxide layer SiOx [15,21]. After that, APTES was prepared in the mixture with ethanol (Table 1) [15,21]. The sample of pPSi structure was then immersed for 8 h in the solution of APTES. Later on, it was rinsed with ethanol to remove APTES that was not attached to the surface of porous silicon pyramidal structure [15]. Afterwards, a heat treatment to activate pPSi surface with APTES was carried out. This treatment led to the formation of APTES network, which progressively covered the inside of the pores and the entire porous surface. Finally, after being mixed with Dimethylformamide (DMF, 10 ml) and dispersed via ultra sonication for 30 min, the solution of SWCNTs (Table 1) was deposited applying spray method on pPSi 3 aminopropyltriethoxysilane (pPSi A) surface [15]. The obtained samples, named pPSi A SWCNTs (pPSi A CN), were heated for 1 h at 150 °C to dry and tail the disposal.

2.3. Technical details of the realized structures

The elaborated structures were studied in detail by both SEM and Atomic Force Microscopy (AFM) in a recent publication by the same authors [15].

SEM images reveal that the properties of pPS layer (porosity, thickness, pore diameter and microstructure) mainly depend on the operating parameters of the layer formation, including the HF concentration ratio, the presence of surface active compound additives, the duration, the temperature as well as the wafer type and its resistivity. The wafer surface was homogeneously covered (85% coverage) by pyramidal structure of silicon (pS). The sizes of the pyramids are not uniform and ranging from 2 mm to 7 mm, with an average pyramid size of 4.5 mm. The facets of the pyramids are all smooth. The obtained porosity was about 80%. The diameters of the pPS pores are identical and their sizes are around 20 nm.

AFM analysis is in accordance with the results obtained by scanning electron microscopy, that confirm the successful implantation and dispersion of each SWCNTs into the pPS A surface.

2.4. Characterisation techniques

The morphology of the samples was characterized using HITACHI S 4800 scanning electron microscopy (SEM). Raman spectra

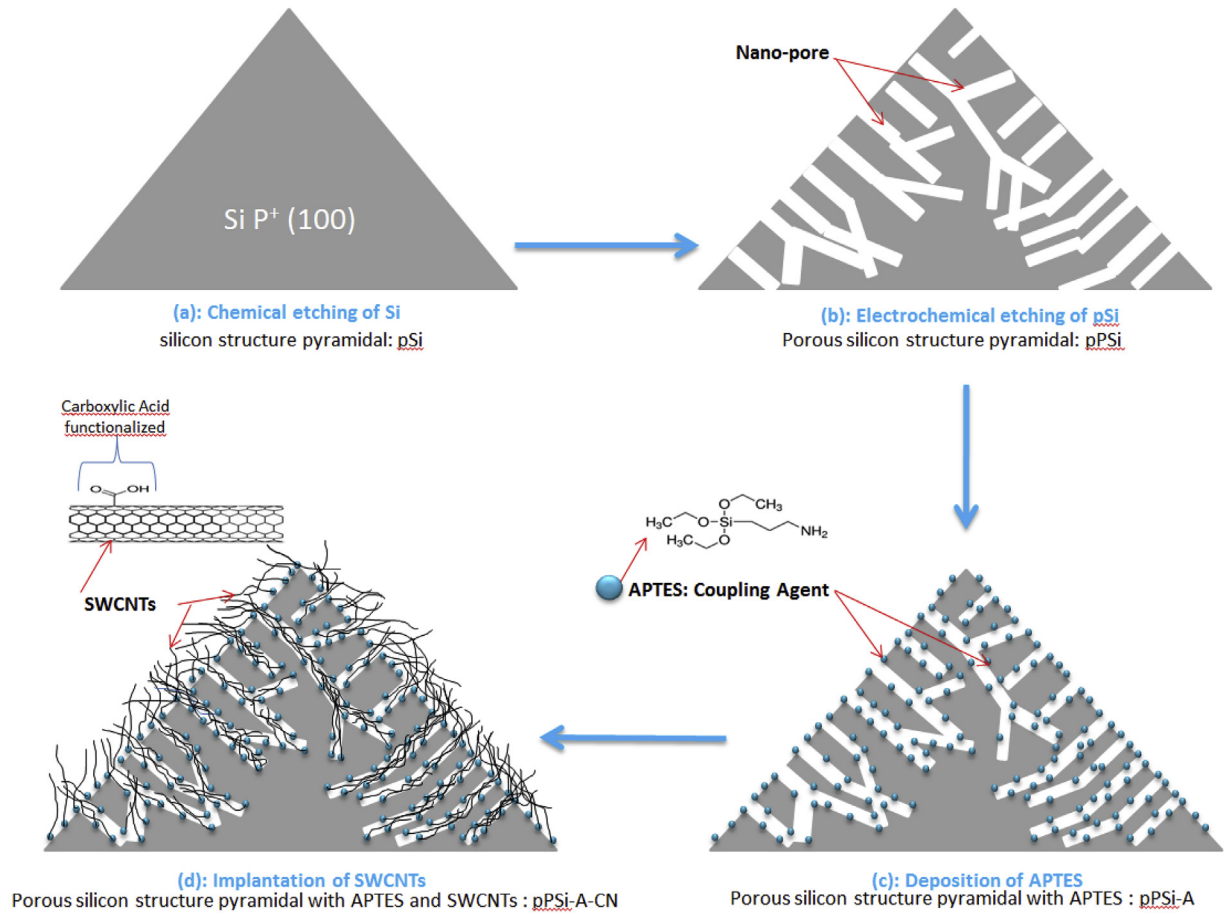


Fig. 1. Schematic procedure of: (a) Formation of pyramids on silicon surface; (b) Porosification of pyramids on silicon surface; (c) Deposition of APTES in the surface of silicon porous structured pyramidal; (d) Deposition of carbon nanotubes on silicon porous structured pyramidal surface with APTES.

Table 1
Preparation parameters of the porous pyramidal silicon structures and concentration of APTES and SWCNTs.

Samples	Chemical etching (min)	Electrochemical etching		Concentration of APTES (%)	Concentration of SWCNTs (M)
		Current (mA)	Time (S)		
pS	6				
pPSi	6	60	35		
pPSi-A	6	60	35	5	
pPSi-A-CN	6	60	35	5	1

were collected by means of a Raman spectrometer (HORIBA Jobin YvonLabram, HR 800) employing the Argon laser excitation line of 514.5 nm. All spectra were obtained in normal and side view backscattering geometries using a microprobe device that allowed the incident light to be focused on the sample as a spot with a diameter of about 2 μm . The photoluminescence (PL) measurements of the prepared structure were performed at room temperature. In PL measurements, the samples were excited with wavelength of 380 nm.

3. Results and discussion

3.1. SEM observations

Fig. 2 shows the SEM images of the entire structure pPSi A CN. Fig. 2a displays especially the micrograph of pyramidal structure with SWCNTs. The whole wafer surface is covered by pyramidal

structure of silicon as shown by Fig. 2a. Furthermore, the sizes of the pyramids are not uniform. The silicon wafers are electrochemically etched to form porous silicon [15]. It is generally assumed that pores initiation occurs at surface active sites defects or irregularities [12,15]. More precisely, the image inset with 100 nm as scale (Fig. 2a) shows the carbon nanotubes which are implanted in the facets of the pyramidal silicon.

3.2. Raman study

Raman scattering is a very sensitive technique applied to the microstructure of nano sized materials and to obtain additional information about the properties of all our prepared structures. Fig. 3 depicts the Raman spectra of the realized structure between 100 cm^{-1} and 3000 cm^{-1} . We observe a peak at 520 cm^{-1} corresponding to the silicon in Fig. 3a and b [22]. Another peak appears at $\sim 500 \text{ cm}^{-1}$ from pPSi spectra. It is assigned to porous silicon

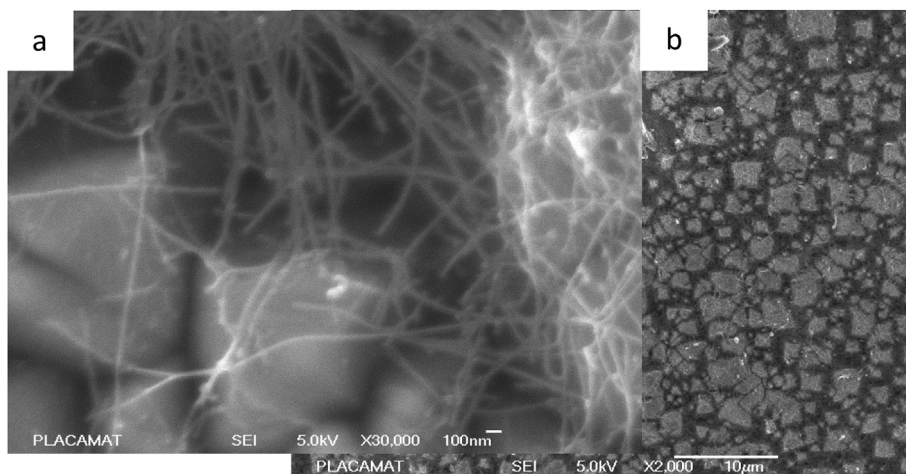


Fig. 2. SEM Images of: (a) pyramidal silicon structure (pSi), (b) Porous pyramidal silicon structure (pPSi), (c) Porous pyramidal silicon structure with APTES and SWCNTs with a low-scale view and a large-scale view (pPSi-A-CN).

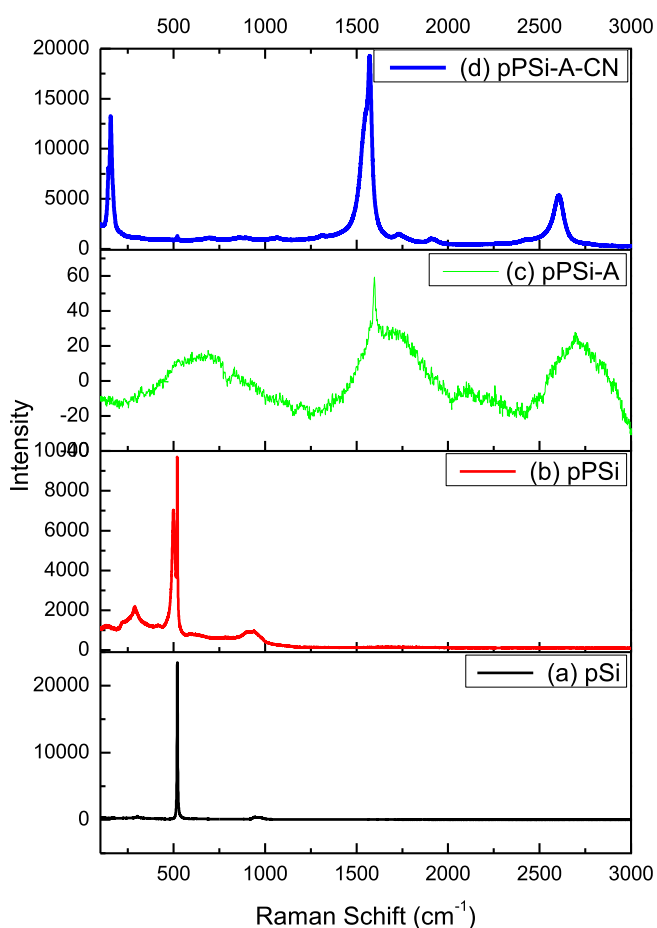


Fig. 3. Raman spectral image of (a) Pyramidal silicon structure pPSi, (b) Pyramidal porous silicon structure (pPSi); (c) Pyramidal porous silicon structure with APTES (pPSi-A), (d) pyramidal porous silicon structure with APTES and SWCNTs (pPSi-A-CN).

(Fig. 3b) [22]. The appearance of peak located at 500 cm^{-1} (Fig. 3b) is due to the optical phonon scattering at the center of the Brillouin zone of Si [22].

Raman peak intensity is proportional to Si density and photon penetration length in the material [23]. When the porosity

increases, these two factors enhance the peak intensity. In fact, if light beams collide with a PS surface, a portion of it scatters from the silicon crystallites and the rest of photons enters in the material and will be scattered by the inner silicon atoms.

Fig. 3b illustrates Raman spectra of functionalized surface with APTES molecules. The bands observed in the spectrum are attributed to amine group NH_2 (1630 cm^{-1}) [22], CH stretch modes of CH_2 groups of APTES molecules (2700 cm^{-1}) [24] and NH_2 bending mode (1600 cm^{-1}) [25]. Indeed, the main characteristic peaks of the silicon modified with APTES are attributable respectively to ν (Si O Si), δ (Si OH) and δ (Si O Si). They are assigned as follows: 1064 cm^{-1} , 963 cm^{-1} and 798 cm^{-1} . Moreover, the peak assigned to ν (Si-O-Si) presents a shift called "bathochromic effect" between 1064 and 1047 cm^{-1} (shift of 18 cm^{-1} for $\text{SiO}_2\text{-NH}_2$). This shift is classically attributed to the structural change of silica after modification. In addition, Raman spectra confirm the presence of bands around 2875 cm^{-1} for $\text{SiO}_2\text{-NH}_2$ characteristics for CH_2 group. For $\text{SiO}_2\text{-NH}_2$ modified silica, a peak appears at 2930 cm^{-1} . This peak indicates that the amine is covalently bound to the surface of the silica particles [26,27].

Fig. 3c depicts Raman spectra of the pPSiA CN sample. The peaks observed in the spectrum are attributed to the radial breathing mode (RBM, 146 cm^{-1}), the carbon chain vibration modes (868 cm^{-1}) [28], the stretching vibration of C C (1063 cm^{-1}), the disorder induced mode (D band, 1337 cm^{-1}), the graphitic (E_{2g}) mode (G band) split into the G band (1570 cm^{-1}) and the G+ band (1586 cm^{-1}), the M band (1725 cm^{-1}) as well as to the 2D band (2664 cm^{-1}) [29]. The presence of RBM band in pPSiA CN Raman spectrum confirms the presence of SWCNTs on the surface. The position of the RBM (ω_{RBM}) gives information on the diameter of the SWCNTs using the expression: $\omega_{\text{RBM}} = 223.5/dt + 25.5$ where dt is the radius of the studied SWCNT. The radius of SWCNTs on pPSi surfaces was calculated at about 1.9 nm , which is in good agreement with the diameter quoted by the supplier.

We notice the disappearance of the primary amine peaks NH_2 and the appearance of a new peak at 1638 cm^{-1} which are attributed to the N H bending of secondary amides [30].

This result is consistent with that obtained using FTIR [15] which shows the presence of silane molecules belonging to APTES attached at the surface of porous silica.

3.3. Photoluminescence study

3.3.1. Photoluminescence of the realized structure

The photoluminescence (PL) is one of the significant and powerful studies which allows obtaining more important and precise information on the energy states of impurities and defects. This information is useful in understanding the structural defects in the studied materials. We present, in Fig. 4, the PL spectra of all samples at $T = 300$ K. It can be seen that pSi has no luminescence effect. After electro etching process, a luminescent band appears at 1.9 eV which corresponds to the band gap energy distribution of porous pyramidal silicon [31]. It is found that, after deposition of APTES on pPSi surface, PL spectra essentially governed by two bands are located at 2 eV and at 2.7 eV. The band of 2 eV is attributed to porous silicon band gap energy. We notice an intensity increase and a considerable blue shift in energy position relative to pPSi sample. Besides, another band situated at 2.7 eV is attributed to the Si-O-Si bond formed after the functionalization of pPS with APTES.

For pPSi A-CN sample, SWCNTs addition in the structure shows an increase in PL intensity and a blue shift of porous silicon band. We observe also an additional band treated as two transitions located at 2.629 and 2.765 eV.

During the depot preparation step of APTES on the surface of pPSi, the molecules of APTES were attached to the porous pyramidal silicon surface as well as to the inside of the nano pores (Figs. 1c and 3). The reaction between APTES molecules and the porous silicon surface with a controlled oxide layer liberated ethanol with the chemical formula $\text{CH}_3\text{CH}_2\text{OH}$ (Fig. 5) and promoted Si-O-Si bond responsible for the increase of the PL signal and the shift to high energies, which can be explained by the quantum confinement in the nano pores of pyramidal porous silicon.

In the same way, Fig. 6 shows the PL spectra of the deposit of APTES on inert Si. Two bands are observed. The first (at 1.9 eV wide) was due to the natural oxidation of Si; whereas the second band (at 2.7 eV) resulted from the reaction between the APTES on the low layer of neutral oxide [32].

After the deposit step of SWCNTs, we noticed a visible improvement in the PL intensity. As a result, the coating of SWCNT led firstly to the increase of defect of pPSi A structure [31] which favored the quantum confinement [33]. Second, the escape of photons from pPSi A was facilitated by texturing the thin film surface, because the surface scattering phenomenon occurred strongly on the textured surfaces [34]. SWCNT film on pPSi surface

may lead to such surface scattering phenomenon. On the other hand, the PL band can be associated with the peroxy linkage ((POL, O₃Si-O-Si-O₃)) because of the fine structure. We assumed that molecular vibrations influence the PL response [35]. If this light emission originated from POL, the vibration of O-O bond would be the most likely source of the fine structure. The defect created in the materials seemed to be involved in the generation of the light emission, which was mainly due to a possible high oxygen content in the sample [36,37]. Therefore, the origin of the PL intensity resulted from the creations of defects in silicon oxide at the SWCNTs/pPSi A interface.

In addition, PL shifts towards high energy region and short wavelength may be ascribed to the recombination of electrons trapped at the states due to Si double bond leading to the quantum confinement effect [38]. In this context, Kanemitsu et al. [39] carried out PL measurements of the surface oxidized of Si nano crystals. Their results suggested that PL from oxide related interface states can improve PL response. Mahmoudi et al. [40] observed blue shift of the PL response where CH_x modified PS was placed in air without encapsulation which may be understood in terms of the reduction in the size of porous pyramidal silicon resulting in an increase in the silicon energy band gap.

Therefore, we can say that the SWCNTs work as an amplifier of PL intensity.

According to Gammoudi et al. [15], SWCNTs cannot be attached directly to the surface of pSi, or pPSi without the use of APTES as a coupling agent. The authors explored in details the PL measurements and confirmed the important role of carbon nanotubes in enhancing PL in the realized structure.

3.3.2. The origin of photoluminescence signal enhancement

After the activation of the pPSi A layer with SWCNTs, we note a PL signal enhancement of the structures. For the band at 2 eV the signal increased 1.6 times which states that the substrate is not affected directly with the SWCNTs (The Si-O-Si was not modified by SWCNTs). For the band at 2.7 eV the enhancement is about 36 times which confirms that the SWCNTs have indeed activated the pPSi A surface and the quantum confinement have occurred.

The improvement in the PL intensity is essentially due to the presence of the SP³ quantum states which favors an increase in the luminescence of the SWCNTs after their dispersion and implanting in the pyramidal porous silicon surface functionalized by APTES. Recent studies have shown that such introduction of quantum states is also possible in semiconducting single wall carbon nanotubes (SWCNTs) through low level covalent attachment of various chemical functional groups such as APTES and ether/epoxide [41,42] and a variety of monovalent and divalent alkyl and aryl functionalities [43]. All of these lead to creation of sp³ defects that strongly localize the band edge excitons into quantum states located 100–300 meV [44].

Most defects of SWCNTs are typically known for quenching photoluminescence. However, the quantum states of the sp³ defects, which we will refer to as quantum defects or defect states, can enhance SWCNT emission efficiency significantly [45].

In fact, the sp³ quantum states originate from the redistribution of the oxygen defects after the functionalization of pPSi by APTES. Each distribution can be directly associated to the quantum states of the three oxygenated functional groups. This contrast in the spectral behavior provides indications that the attachment of the aryl groups can create a greater number of energetically distinct quantum states [46].

4. Conclusion

To conclude, we have successfully synthesized a hybrid

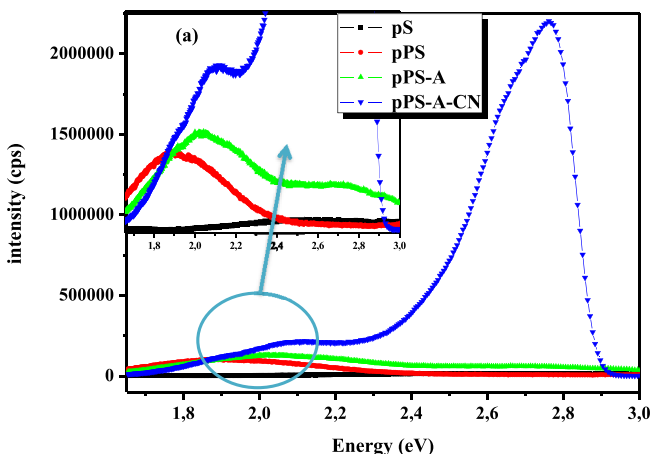


Fig. 4. Photoluminescence spectra of pS, pPSi, pPSi-A and pPSi-A-CN, excited with 380 nm.

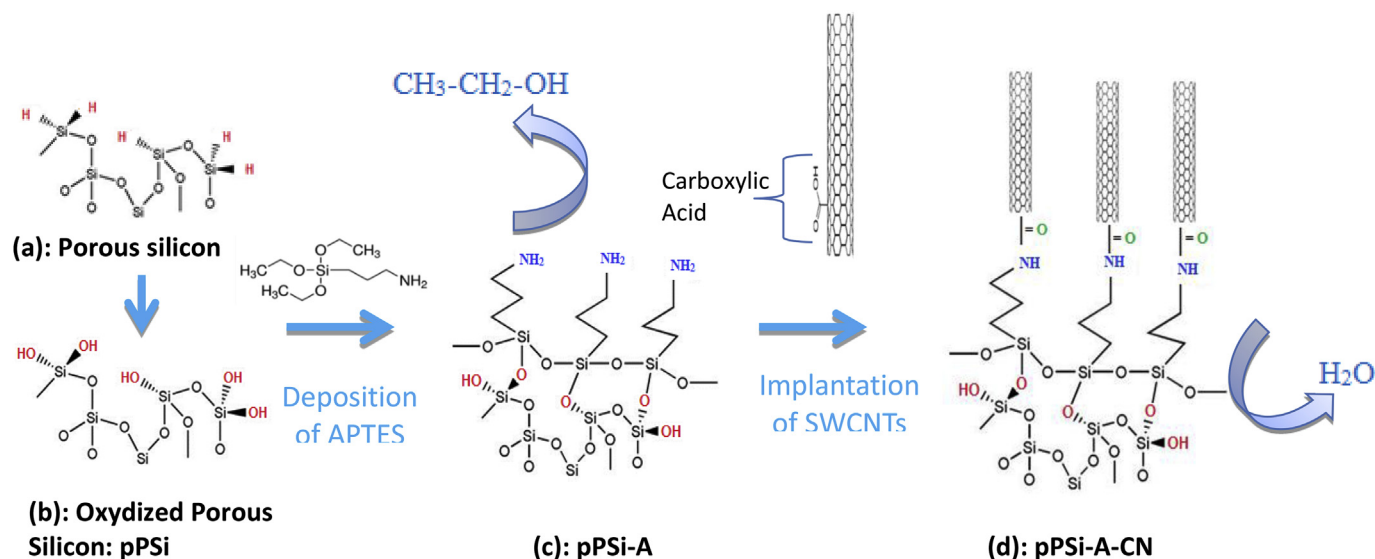


Fig. 5. Schematic representation of (a) pyramidal Porous Silicon (b) oxidized Porous Silicon (c) oxidized Si after amine immobilization (d) oxidized Si after amine immobilization and carboxylic acid attachment.

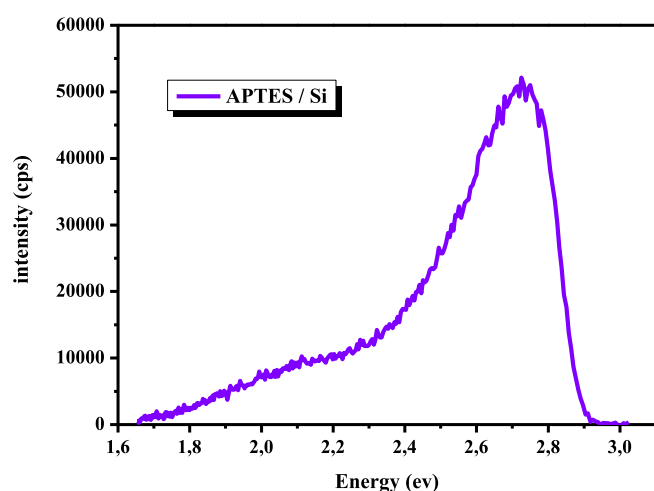


Fig. 6. Photoluminescence spectra of APTES/Si, excited with 380 nm.

structures using single walled carbon nanotube implanted on pyramidal porous silicon surface by means of coupling agent: APTES. All of these individual layers were studied applying the following techniques: SEM, Raman and photoluminescence. It is worth noting that pPSi A CN structures displayed photoluminescent properties in the visible region at room temperature with a noticeably PL response, which may be assigned to the presence of defects from oxygen vacancy. This study seems so interesting and paves the way for further physical investigations to use the method of activation of Si surface with SWCNTs in photovoltaic devices.

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Nomenclature

SWCNTs	Single Walled Carbon Nanotubes
APTES	3 aminopropyltriethoxysilane
pSi	pyramidal Silicon
PSi	Porous Silicon
pPSi	pyramidal Porous Silicon
pPSi A	pyramidal Porous Silicon with APTES layer
pPSi A CN	pyramidal Porous Silicon with APTES and SWCNTs layers
SEM	Scanning Electron Microscopy
FTIR	Fourier transform infrared spectroscopy
UV-Vis	UV-visible spectroscopy
PL	Photoluminescence
DMF	Dimethylformamide
POL	Peroxy linkage

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