

Optical and Morphological Analysis of c-Si/PSi and c-Si/PSi/MWCNT/SiO_x Heterostructures [†]

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Abstract: In the present work, the optical and morphological properties of Porous Silicon (PSi) in the c-Si-n/PSi and c-Si-n/SiP-n/MWCNT/SiO_x structures are studied and analyzed. The PSi layer is grown on n-type c-Si (<0.005 Ω·cm <100>) by electrochemical anodization using different currents as: 10, 50 and 100 mA. The etching solution used was C₂H₆O:HF:C₃H₈O₃ in a proportion of 6:3:1 by volume, respectively. The deposition of multi wall carbon nanotubes (MWNTs) on the PSi was done by spin coating, and later the surface was passivated by thermal oxidation. The porosity and thickness were obtained by gravimetry. UV-VIS spectroscopy and photoluminescence were used to obtain the optical properties and SEM was used to analyze the morphology.

Keywords: porous silicon; MWNTs; photoluminescence; morphology; SEM

1. Introduction

In 1956 the porous silicon was discovered by Uhler, later for the decade of the 70's and 80's it is applied to chemical sensors, however until 1990 Leigh Canhan discover the luminescence at room temperature and explained it in terms of quantum confinement. There have been several studies and various applications, mainly optical sensors and biomedical applications among others [1]. In many works have been reported the properties of porous silicon with different materials. Nowadays, the carbon nanotubes (CNTs) are very studied because of the properties that the nanostructured form and the hybridization sp^2 present. In this work, we have deposited MWCNT's on PSi, which were dispersed by spin coating on different PSi single layers with different anodizing parameters. The optical and morphological properties of PSi in the c-Si-n/PSi and Al/c-Si-n/PSi/MWCNT/SiO_x/Al structures are studied and analyzed.

2. Materials and Methods

PSi was obtained by electrochemical anodization of <100> n-type c-Si wafers with low resistivity (<0.005 Ω·cm). Such process was carried out with the experimental setup shown in Figure 1. The electrolyte used in this experimental setup contained C₂H₆O: HF: C₃H₈O₃ in a proportion of 6:3:1 by volume, the applied currents were the following 10, 50 and 100 mA in an area of 1.32 cm². A white LED was used as light radiation source in order to trigger the electron photo-generation which is necessary to supply holes for the formation of pores and also to reduce other undesirable light sources. The process was realized under dark conditions. The experimental arrangement is shown in Figure 2.

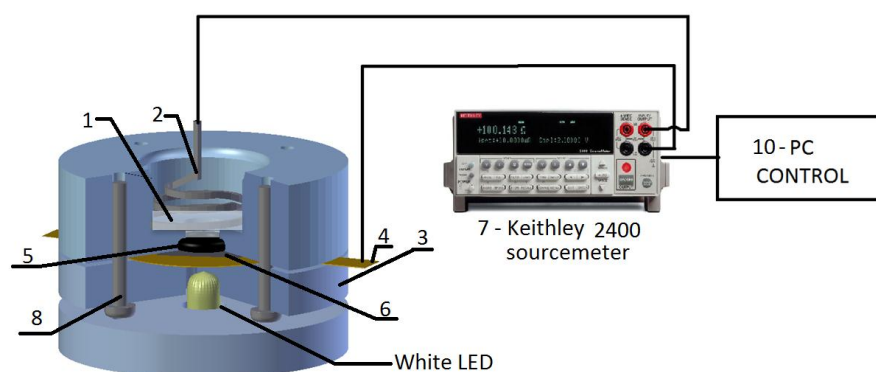


Figure 1. Diagram of the experimental setup: (a) cross-section view; (b) side view of the electrochemical etching tank (M1: 3.5 cm) 1—electrolyte, 2—stainless steel cathode, 3—electrochemical teflon etching tank, 4—aluminum anode, 5—seal, 6—Si wafer, 7—voltage meter, 8—ampere meter, 9—DC source, 10—grips, 11—rheostat [2].

To study the effects of MWCNTs dispersed in the monolayers of PSi it was necessary to deposit them on PSi. The deposition of the MWCNTs was carried out by the spin coating technique; 10 drops were placed on the sample at 3000 rpm for 15 s, rising the spinning at 5000 rpm to infiltrate them, this process was repeated 5 times since previous research confirms a greater presence of CNT that reduces the sheet resistance in the monolayer. MWCNTs with lengths ranging from 2.5 to 4.5 micrometers and outer diameters between 15 and 25 nm were used. With the thermal oxidation in a tubular furnace at $T = 300\text{ }^{\circ}\text{C}$, along with a flow of O_2 at 5 mL/min, the surface of the PSi layer is expected to be passivated. Through the oxidation process, chemical bonds are generated in such a way that MWCNTs are better anchored to the PSi layers grown. We have finally a phase composition material of SiO_x , CNTs, PSi, and c-Si forming a complex structure.

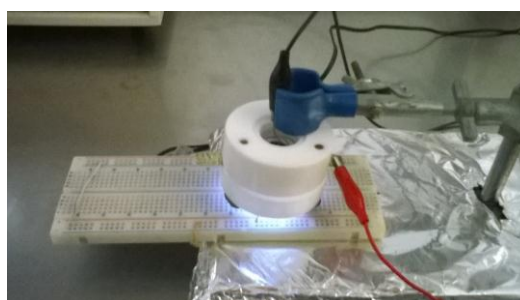


Figure 2. Photography of the experimental setup with a light white source used in this work.

3. Results and Discussion

The porosity and thickness of PSi monolayers were determined by gravimetric analysis. The porosity is given by $\%P = \frac{m_1 - m_2}{m_1 - m_3}$ where m_1 is the wafer weight before the electrochemical etching, m_2 just after the one and m_3 is finally when the porous layer has been removed from substrate, and with the equation $d = \frac{m_1 - m_3}{S \cdot \rho}$ we obtain the PSi monolayer thickness, where $s = 1.23\text{ cm}^2$ is the anodized surface and $\rho = 2328\frac{\text{mg}}{\text{cm}^3}$ is the silicon density [3].

The porosity and thickness values are plot in Figure 3. At a fixed current the porosity increases as the anodizing time increases, while keeping the anodizing time fixed and varying the anodizing current it is observed that the greater current, the greater the porosity except for anodizing times in the range 50–300 s for 10 mA and 50 mA currents where porosity overlap with constant values. The thickness in Figure 3b shows a similar general behavior although for 100 mA, thickness decreases abruptly at 300 s.

SEM micrographs in Figure 4 confirm the deposition of the MWCNTs on thermally oxidized PSi surfaces, also mesopores of different diameters are observed, which depend on the applied current with values of 10 mA, 50 mA, and 100 mA. These SEM micrographs confirm the fact that the higher currents are applied in the etching process the larger pore sizes are obtained.

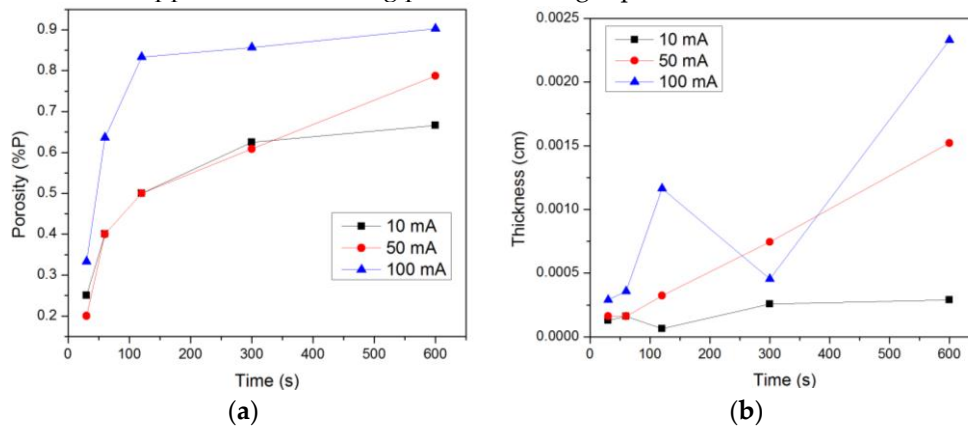


Figure 3. Plots of (a) Porosity percentage of PSi layers vs. anodizing time at different anodizing currents and (b) thickness vs. anodizing time.

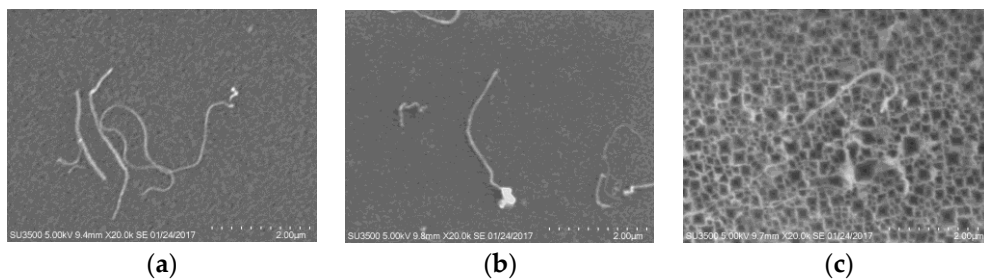


Figure 4. SEM surface morphology micrographs of PSi with MWCNTs dispersed by spin coating. PSi layers were etched at currents: (a) 10 mA, (b) 50 mA and (c) 100 mA, all for 600 s time etching.

Reflectance spectra of c-Si-n/PSi-n/MWCNT/SiO_x structures in Figure 5a present the typical Fabry-Perot oscillations due to the different PSi layer thicknesses, standing out the decreasing amplitude as consequence of the increased porosity [4–6]. According to Figure 5b, the presence of the MWCNTs affects mainly the spectrum associated with the lowest anodizing time (0.5 min), in the region from 400 to 750 nm, the oscillations are attenuated. The reasons contributing to this drop may be originated from the coated PSi surface by the MWCNTs dispersed which generates light trapping and it hinders light be reflected.

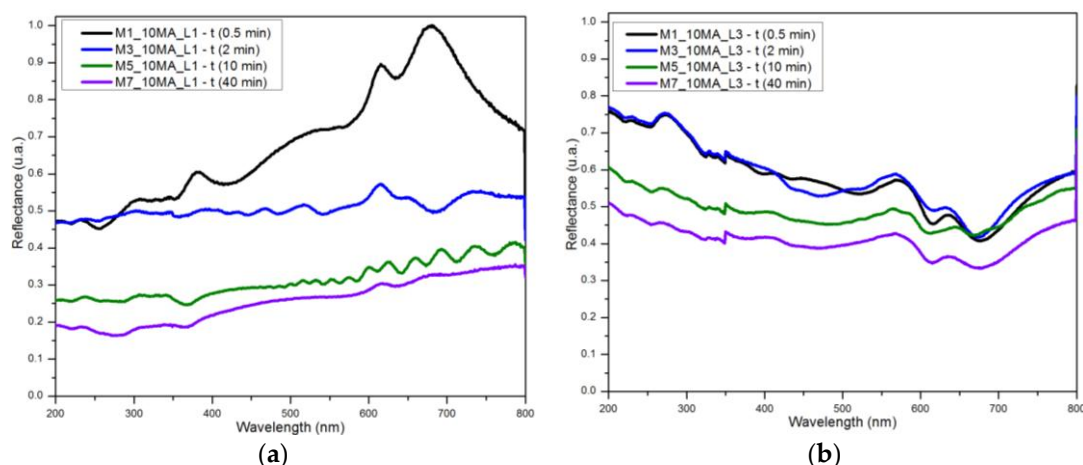


Figure 5. Reflectance spectra of PSi layers etched with 10 mA for different anodizing times (a) without MWCNTs and (b) with MWCNTs.

Spectra of photoluminescence shown in Figure 6a, were obtained from the PSi samples without MWCNTs. These ones were obtained with anodization times between 0.5 min and 40 min. They show bands in the UV and red region whose amplitudes are inverted for bigger anodization times. Figure 6b shows Photoluminescence spectra with present MWCNTs and thermal oxidation realized after MWCNTs deposition. There is a clear tendency to form two main bands in the UV and red regions according as the anodizing time is increased. Predominantly the influence of Si-O, SiHx and Si-OH bonds determine the luminescence spectra shape and to a less extent the influence of the creation of a hydrogen-carbon surface between the carbon atoms on the MWCNTs and the hydrogen-Si on PSi layer [1,6].

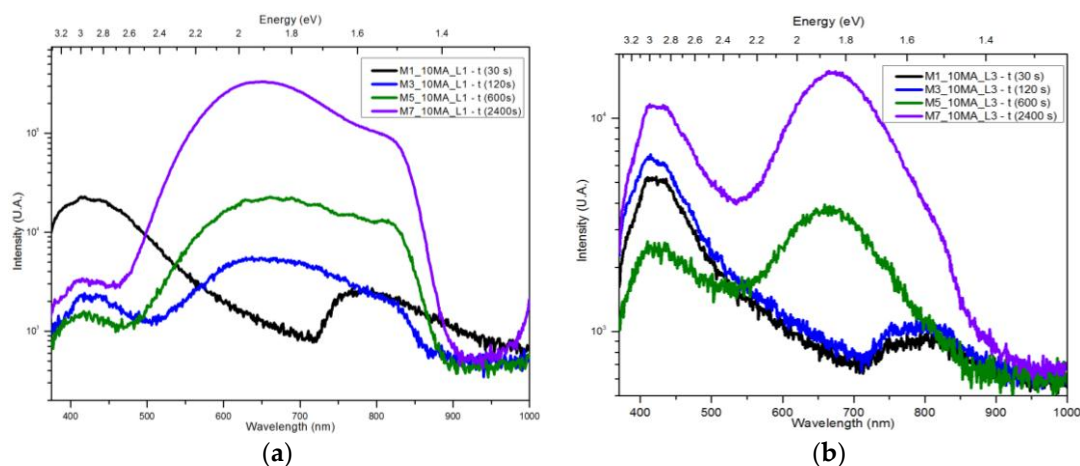


Figure 6. (a) Photoluminescence spectra of porous silicon layers synthesized with 10 mA current for different anodizing times (a) without MWCNT's and (b) with MWCNT's.

4. Conclusions

PSi samples without and with MWCNT were obtained and prepared. The results showed that when the anodization time and electrical current are increased, the samples porosity also increased. SEM micrographs showed that for large currents the diameter pore size increased on the PSi monolayer, also the MWCNTs have been dispersed horizontally on PSi surface by using spin coating technique.

Photoluminescence spectra obtained exhibit the apparition of two main bands in the UV and red regions such fact indicates that our structures studied may be focused to be applied in sensors and solar cells.

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Author Contributions: N.V.H. and J.A.L.L. conceived and designed the experiments; N.V.H. and E.G.B. performed the experiments; N.V.H., J.A.L.L., M.A.D.J. analyzed the data; N.V.H., J.D.A.H.d.I.L., E.G.B. and J.A.L.L. wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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