

# POROUS SILICON DECORATED METALLIC NANOPARTICLES FOR GROWING VERTICALLY ALIGNED CARBON NANOTUBES

L. Monica Veca, Florea Craciunoiu, Mihaela Kusko, Mihai Danila, Adrian Dinescu

National Institute for Research and Development in Microtechnologies IMT - Bucharest

E-mail: monica.veca@imt.ro, florea.craciunoiu@imt.ro, mihaela.kusko@imt.ro, mihai.danila@imt.ro, adrian.dinescu@imt.ro

**Abstract**—Carbon nanotubes have been envisioned as promising functional materials in nanoelectronics and electron field emitters. All these applications require that the CNT are highly oriented. There are many studies to improve the growth process but only few research studies have investigated new methods to deposit metallic nanoparticles on the porous silicon. Thus this paper is aiming at synthesizing metallic nanoparticles on top of porous silicon.

**Keywords:** porous silicon, metallic nanoparticles.

## 1. INTRODUCTION

Owing to their high aspect ratio, high electrical conductivity (current carrying capacity of  $10^9$  (amp/cm<sup>2</sup>), nanometer-sized radius of curvature, high chemical stability, and high mechanical strength, carbon nanotubes (CNTs) are promising candidates for electron field emitters and nanoelectronics. Nonetheless, a large surface of highly aligned CNTs is the prerequisite to fulfill their potential in these applications. Therefore, the alignment of CNTs on solid substrates in a controlled manner, with good location selectivity, and ordered orientation is the main challenge of improving the performance of many nanotube-based devices such as field emitters in panel display. An ideal template material for creating arrays of vertically aligned nanostructures is the porous silicon (PS) layer which offers not only confined space for growing ordered carbon nanotubes but also higher efficiency of the growth process than the plain silicon substrate. [1,2,3] Another advantage of using porous silicon layer is the strong interaction between the metallic nanoparticles of the catalyst and the porous substrate which will prevent the catalyst particles from sintering during chemical vapor deposition (CVD) growth of carbon nanotubes, generating thus CNTs with narrow range of diameters. Beside the “typical” iron – family metal catalyst (Fe, Ni and Co) used to synthesize CNTs by CVD, metals like Al, Pt, In, Mg have also successfully catalyzed the CVD

growth of CNTs.[4] While the “typical” metallic catalysts are showing the highest catalytic activity, the other metals may offer the control over the chirality of the CNTs. Up to date, the catalysts deposition on top of the supporting substrate have been limited to the electron beam physical vapor depositions (PVD). Chemical deposition of the metallic nanoparticle onto the porous silicone is an attractive alternative to the PVD method due to the low cost of the process and to the flexibility of controlling the size of the nanoparticles, offering thus the possibility of fine-tuning the diameter of the CNT. In this context, the aim of this work is the chemical deposition of both “typical” and “atypical” metallic catalysts on porous silicon. The metallic nanoparticles thus obtained are going to serve as the seeds for the subsequent CVD growth of carbon nanotubes.

## 2. EXPERIMENTAL DETAILS

### 2.1. Materials

Chemical reagents and solvents were of analytical grade, purchased from Sigma-Aldrich and used as received without additional purification. The synthesis of the porous silicon was carried out in a single-tank AMMT wet etching system for 4 inch diameter Si wafers with programmable power supply and dedicated software for time based current profiles.

### 2.2. Methods

*Porous silicon support fabrication:* The porous silicon layer was obtained on a boron-doped p-type (100) Si wafer, with resistivity of 5-10 Ωcm. Firstly, in order to remove any organic impurities, the Si wafers were cleaned for 30 minutes in a solution of 97 wt % H<sub>2</sub>SO<sub>4</sub> and 30 wt % H<sub>2</sub>O<sub>2</sub> (1:3 v/v) at 80°C, subsequently washed with plenty of deionized water (18 ΩM) and dried with nitrogen. After removing the native silicon dioxide layer (few minutes dipping

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of the substrate in a solution of 5 wt % HF and subsequent rinsing with deionized water) the wafer was placed into the electrochemical cell (AMMT GBH - single-tank cell). The design of the electrochemical cell is such that the metallic (Al) back-side of the wafer is not in contact with the hydrofluoric acid (HF) solution of the electrolyte. The anodization process was carried out in a mixture of 50% HF and N,N dimethylformamide (DMF) with a volume ratio of 1 to 11, while the wafer was anodically polarized at constant current density of  $3\text{mA}/\text{cm}^2$  for 60 minutes. At the end of the anodization process the PS was rinsed with ethanol and isopropanol sequentially. After morphological characterization the PS support was retained for further use.

*Porous silicon decorated metallic nanoparticle synthesis:* (i) Platinum nanoparticles were chemically deposited on top of the porous silicon following a modified method reported in the literature.[5] In a typical experiment, the porous silicon was initially rinsed with acetone and ethanol, followed by 15 seconds dipping in 5 wt % HF and rinsing with water and acetone sequentially. Thereafter, the substrate was immersed in a solution of HF and hydrogen hexachloroplatinate hexahydrate ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ) with the final concentration of 2 M and 0.6 mM, respectively. The reaction was carried out at  $50^\circ\text{C}$  for 5 minutes. The substrate thus obtained was rinsed with water and ethanol followed by morphological and structural characterization. (ii) Magnetite nanoparticles were deposited on the porous silicon substrate in two steps – first the substrate was impregnated, under nitrogen protection, for one hour with solution mixture of iron (II) chloride tetrahydrate (0.08 M) and iron (III) chloride hexahydrate (0.16 M) at a pH of 2. The mixture was then stirred magnetically and the pH was adjusted to above 9 with drop wise addition of diluted NaOH. After 30 minutes at  $60^\circ\text{C}$  the substrate was removed from the reaction solution, washed several times with water and ethanol and then dried under nitrogen.

### 2.3. Characterization

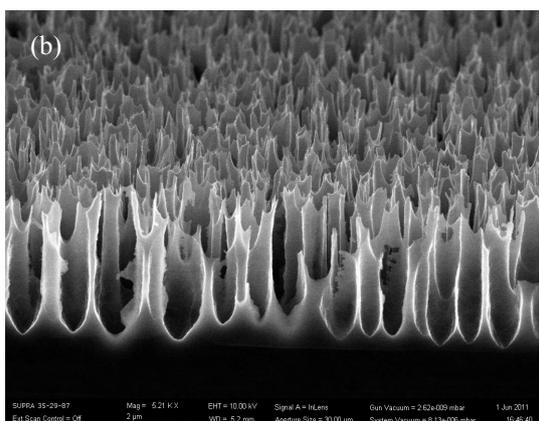
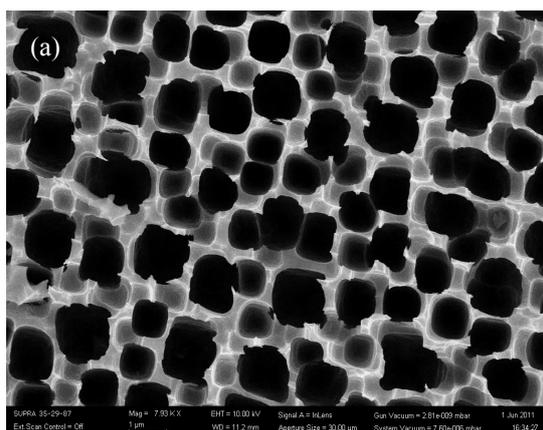
X-ray diffraction measurements were performed at room temperature on SmartLab - 9kW rotating anode diffractometer. SEM images

were recorded with Raith GmbH Scanning Electron Microscope operated at 10 kV.

## 3. RESULTS

As presented in the experimental section, the PS layer has been prepared by electrochemical etching of the silicon in HF with applied forward bias between the metal back-side of the wafer and Pt cathode placed in the electrolyte solution. Even though the mechanism of porous silicon formation is a complex one, there is a general agreement that the formation of the PS is due to the holes injected from the bulk towards the silicon/electrolyte interface. In other words, the dissolution reaction begins at defects on the silicon wafer surface, forms the pores whose walls are then eroded until they are emptied of the holes. As illustrated in the Figure 1a, in this case the dissolution of the silicon lead to uniform PS layer dominated by macropores of regular shape with the diameter of about  $1\ \mu\text{m}$ . This surface morphology is in good agreement with the previous reported results of PS obtained from p-type Si wafers having resistivity below  $1000\ \Omega\text{cm}$ . As the dissolution occurs only at the pore tips, because there is the highest hole concentration, the etching of the silicon proceeds along the  $\langle 100 \rangle$  direction, with an overall directionality which is running perpendicular to the surface. The morphology of the PS layer shown in Figure 1b is revealing very regular arrays of strait channels, with clear orientation, penetrating about  $5\ \mu\text{m}$  deep into the bulk of the silicon substrate. The pores are having smooth walls with short branches characteristics to the macropores. It has been noted that the use of DMF has not only offered higher homogeneity due to a better wettability of the surface than the aqueous solution but also has decreased the etching rate to  $80\ \text{nm}/\text{minute}$ .

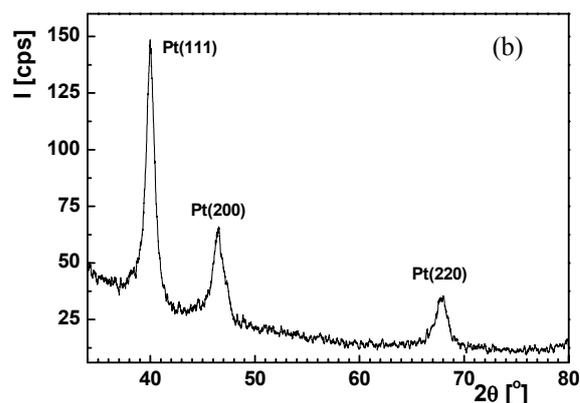
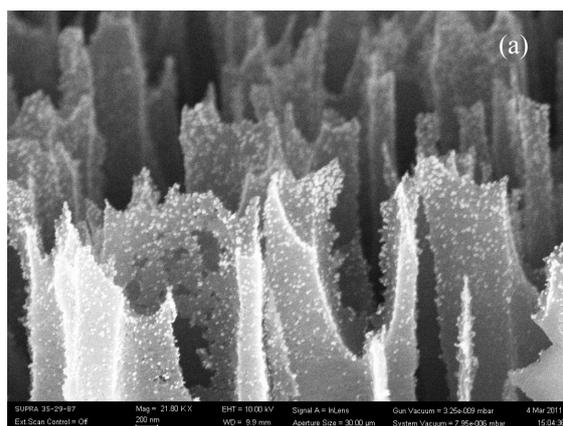
There is a general agreement that controlling the growth kinetics one can tune the shape of the crystals. As have been previously reported, the concentration of the free HF and platinum salt is the driving force of platinum crystal growth [5].



**Fig. 1.** SEM images of porous silicon (a) top view and (b) cross-section after anodization at 3mA/cm<sup>2</sup> in the electrolyte of 50% HF and DMF solution with a volume ratio of 1 to 11.

Thus we have found that Pt nanoparticles can be deposited on PS from solution containing 0.6 mM H<sub>2</sub>PtCl<sub>6</sub> after 5 minutes at 50°C. As shown in the SEM image (Figure 2a) the nanoparticles were uniformly distributed on the PS and their diameter was in average 10-11 nm. The presence of the platinum nanoparticles was confirmed by the X-ray diffraction measurements. The diffractogram of the PS substrate decorated with platinum is presented in Figure 2b, together with the diffraction peaks from the (111), (200), and (220) planes. The crystallite size of the nanoparticle was calculated to be around 6-7 nm from the Williamson-Hall method, value which is in a good agreement with the microscopic results.

Similar to the platinum nanocrystals, the size, shape and composition of the iron oxide nanoparticles depends on the type of the salts used in the synthesis, the ratio of the Fe<sup>2+</sup> and Fe<sup>3+</sup>, the pH and ionic strength of the reaction media.



**Fig. 2.** (a) SEM image and (b) XRD diffractogram of the platinum nanoparticles decorated porous silicon.

For the synthesis of magnetite we have used the classical co-precipitation reaction of Fe<sup>2+</sup> and Fe<sup>3+</sup> salt solutions by addition of a base. [6] A slight modification of the well-known method consists of an initial impregnation of the PS substrate into the acidic solution of Fe<sup>2+</sup> /Fe<sup>3+</sup> of 1:2 molar ratio. After one hour at room temperature the reaction was completed by precipitation of the Fe<sub>3</sub>O<sub>4</sub> into the PS in the presence of base by raising the pH above 9. In order to avoid the oxidation of the magnetite the reaction was carried out under nitrogen protection.

The SEM image presented in Figure 3a is showing the presence of the nanoparticles with average diameter of 5-6 nm. The X-ray diffractogram in Figure 3b is showing the presence of the magnetite and the broadening of the (331) diffraction peak is a good indication of their small diameter. The size of the magnetite nanoparticles was estimated at 8 nm using once again Williamson-Hall method.

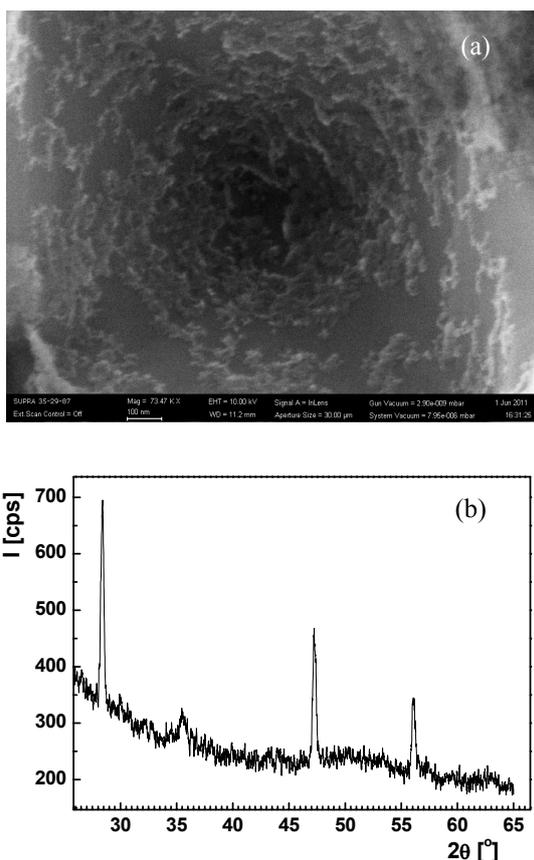


Fig. 3. (a) SEM image and (b) XRD diffractogram of the magnetite nanoparticles decorated porous silicon.

#### 4. CONCLUSIONS

In conclusion we were able to synthesize metallic nanoparticles of 6-7 nm on the PS. These nanoscale catalysts, densely formed onto porous silicon layer, assisted by the van-der Waals interaction between the nanotubes should definitely favor the growth of the carbon nanotubes perpendicular to the substrate.

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