Morphology of the porous silicon obtained by electrochemical anodization method

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Abstract. In this report, the dependence of porous silicon with the synthesis parameters and their correlation with the optical and morphological properties is studied. The P-type silicon-crystalline samples and orientation <1 0 0> were prepared by electrochemical anodization and were characterized using SEM in order to know the evolution of the pore morphology. It was observed that the porosity and thickness of the samples increased with the increase of the concentration in the solution and a high pore density (70%) with a pore size between 40nm and 1.5μm.

1. Introduction
Porous silicon (PS) was initially observed by Uhlir in the 1950s when developing an electrochemical polishing mechanism with hydrofluoric acid (HF) on crystalline silicon wafers to be used in microelectronic circuits [1]. Recently, a wide variety of porous and amorphous materials (including Ti, Al₂, Si, and silica) are investigated for their use on different applications, ranging from optoelectronics to medicine [2-8]. PS, due to its biostability and zero toxicity, is a potentially important material to be considered in many applications including biomedical ones [9,10]. The physical properties of the PS, e.g., electrical resistance, homogeneity in pore formation, thickness, morphology and structural properties, depend on the synthesis parameters during the electrochemical anodization. Thanks to these studies the porous structure is considered as a host matrix for growing hydroxyapatite (HA), thus improving its adhesion and integration with implants and regeneration at the bone level [11-15].

One of the most important properties of HA as a biomaterial for bone regeneration is the dependence with the high pore density of the PS and the possibility of interconnection between them. In this work, PS samples were prepared using as substrate crystalline silicon wafers type-p with <1 0 0> orientation and resistivities varying between 0Ωcm and 100Ωcm. The samples were prepared by varying the synthesis parameters such as proportion in the mixing solution, current density, anodizing time, etc.

2. Experimental procedure
Figure 1 shows a schematic diagram of the system used to manufacture PS by the electrochemical anodization method.

HF and Ethanol were obtained from the pharmaceutical company MERCK KGaA, with a purity of 40% and 99.9%, respectively. The substrates used were P-type crystalline silicon wafers (doped with Boron), which had a diameter of approximately 100mm, crystallographic orientation <1 0 0> and a resistivity between (0 – 100)Ω.cm. The concentrations in the [HF: C2H5OH] solutions were (1:2),
and the currents were varied between 5mA and 150mA, respectively. The reaction times were from 5min to 30min.

Figure 1. Teflon-based o-ring cell used to carry out electrochemical anodization in the synthesis of PS samples.

The SEM measurements and EDX were performed using a JEOL model JSM 6490-LV microscope. On the other hand, the measures of reflectance were realized with a VARIAN UV-Vis-NIR spectrometer model Cary 5000.

3. Results and discussion

SEM images are presented in the Figure 2 along with the reflectance measurements of PS samples with concentrations (1:2) varying the current density.

It can be seen in the Figure 2 that an increase in the attacking time during the PS synthesis process, influences significantly the formation of grains and non-homogeneous regions on the material surface triggering the loss of the developing silicon porous layer, for 5min, see Figure 2(a), a current of 5mA incentives the formation of pores with average diameters of 15nm. The pore density at the surface of the PS was established around 70%, taking into account the current density described by the equation (1).

\[ J_{PS} = \frac{A_{cell} \times N_{cell}}{A_{pore}} \]  

where \( J_{PS} \) is the current in the pore, \( A_{pore} \) is the transversal area of the pore, \( A_{cell} \) is a cross-section of a cell of the porous grid and \( N_{cell} \) is the number of attacked cells on the silicon surface.

The reflectance measurements obtained for both samples (see Figure 2), are around 25%, with the contribution of reflections corresponding to the near IR being even higher; however, it is possible to observe that the sample made with a time of 30min (see Figure 2(b)) presents a greater number of reflections in the ultraviolet region associated to a high absorption and roughness on the surface of the material. Accord to what is observed in Figure 2.

The percentage of reflectance is strictly linked to the pore morphology, for the applications required HA growth of the order of a few hundred nanometers and up to microns has been reported [2,16-22], ergo in case of need of growth of HA the PS porous layers are required to correspond to this order, to promote mechanisms of nucleation of HA within the pore [23].

To study the effect of current density on pore formation, samples of PS were made by maintaining a current of 100mA and varying the reaction time.
Figure 2. SEM micrograph and reflectance measurements of sample m080711-a obtained with concentration of the mixture (1:2) and current density 5mA: (a) electrochemical etching time 5min, (b) 30min.

A significant increase in the pore diameter of the samples with increasing current at 100mA for 10min and 20min can be observed in Figure 3. By increasing the reaction time from 10min to 20min, keeping both the solution and the current constant, it is observed that the average pore size increases to the order of microns; however it can be seen that the pore density is not completely homogeneous throughout the region. When the applied current was increased to 150mA, it was possible to observe a pore diameters with various sizes, with a tendency to form pores of diameters up to the order of 4 microns, see Figure 4.

Figure 3. SEM micrograph of samples of PS attacked (a) during 10min, with 100mA anodizing current and; (b) 20min with a current of 150mA.
The sizes obtained could be an interesting feature depending on the application required. However, this result contributes to studies of bone tissue growth using the PS as host substrate [12,24]. The Figure 4(a) shows the SEM micrograph corresponding to the PS sample obtained with a current of 150mA. Similarly, the Figure 4(b) shows the EDX analysis of the sample in question, showing silicon as a 100% constituent material in the PS formation.

4. Conclusions
PS The porous silicon samples were prepared by the electrochemical anodization by varying the concentration of the mixture, the current and the time of attack during the reaction. It was found that for the concentration (1:2) the reaction time significantly influences the formation of grains and non-homogeneous regions on the surface of the material triggering the loss of the developing silicon porous layer. A high pore density was obtained that varied between 50% and 70%. The pore size varied between 40nm and 1.5μm when the current is increased. The changes in the morphology make PS an interesting material for optoelectronic applications and the growth of hydroxyapatite its use as a bone substitute.

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References
[1] Uhlir A 1956 Electrolytic shaping of germanium and silicon Bell System Technical Journal 35 333–347
[2] Rhaïti H, Laghzizil A, Saïaibi A, El Asri S, Lahlil K and Gacoin T 2012 Surface properties of porous hydroxyapatite derived from natural phosphate Mater. Chem. Phys. 136(2) 1022–106
[3] Zhou H and Lee J 2011 Nanoscale hydroxyapatite particles for bone tissue engineering Acta Biomater. 7(7) 2769-2781
[4] Nieto A, Hou H, Sailor M, Freeman W and Cheng L 2013 Ocular silicon distribution and clearance following intravitreal injection of porous silicon microparticles Exp. Eye Res. 116 161-168
[5] Wang C, Feng L, Li W, Zheng J, Tian W and Li X 2012 Shape-stabilized phase change materials based on polyethylene glycol/porous carbon composite: the influence of the pore structure of the carbon materials Sol. Energ. Mat. Sol. C 105 21-26
[6] He G, Liu P and Tan Q 2012 Porous titanium materials with entangled wire structure for load-bearing biomedical applications J. Mech. Behav. Biomed. 5(1) 16-31
[7] Vlahinić I, Jennings H, Andrade J and Thomas J 2011 A novel and general form of effective stress in a partially saturated porous material: The influence of microstructure Mech. Mater. 43(1) 25-35
[8] Jianyong W, Huiping T, Yuan G, Baojun Y, Xinting K and Pei W. 2012 Shear behavior on money alloy porous sheet materials Procedia Engineering 27 742-746
[9] Lawrence B, Alagumanikuman N, Prithivikumaran N, Jeyakumaran N, Ramadas V and Natarajan B 2013 Effect of surface modification on the porous silicon infiltrated with biomolecules Appl. Surf. Sci. 264 767-771
[10] Yokoi K, Godin B, Oborn C, Alexander J, Liu X, Fidler I and Ferrari M 2013 Porous silicon nanocarriers for dual targeting tumor associated endothelial cells and macrophages in stroma of orthotopic human pancreatic cancers Cancer Lett. 334(2) 319-327
[11] Dian J, Macek A, Nižňanský D, Němec I, Vrkoslav V, Chvojka T and Jelínek I 2004 SEM and HRTEM study of porous silicon—relationship between fabrication, morphology and optical properties Appl. Surf. Sci. 238(1) 169-174
[12] Tripathi G and Basu B 2012 A porous hydroxyapatite scaffold for bone tissue engineering: Physico-mechanical and biological evaluations Ceram. Int. 38(1) 341-349
[13] Demetrescu I, Pirvu C and Mitran V 2010 Effect of nano-topographical features of Ti/TiO 2 electrode surface on cell response and electrochemical stability in artificial saliva Bioelectrochemistry 79(1) 122-129
[14] Zhang E and Zou C 2009 Porous titanium and silicon-substituted hydroxyapatite biomodification prepared by a biomimetic process: characterization and in vivo evaluation Acta Biomater. 5(5) 1732-1741
[15] Singh G, Singh H and Sidhu B 2013 Corrosion behavior of plasma sprayed hydroxyapatite and hydroxyapatite-silicon oxide coatings on AISI 304 for biomedical application Appl. Surf. Sci. 284 811-818
[16] Meza D, Figueroa I, Flores-Morales C and Piñá-Barba M 2011 Nano hydroxyapatite crystals obtained by colloidal solution Rev. Mex. Fis. 57(6) 471-474
[17] Sequeda L, Díaz J, Gutiérrez S, Perdomo S and Gómez O 2012 Obtención de hidroxiapatita sintética por tres métodos diferentes y su caracterización para ser utilizada como sustituto óseo Revista Colombiana de Ciencias Químico Farmacéuticas 41(1) 50
[18] Feng W, Mu-Sen L, Yu-Peng L and Yong-Xin Q 2005 A simple sol-gel technique for preparing hydroxyapatite nanopowders Mater. Lett. 59(8) 916-919
[19] Liu D, Troczynski T and Tseng W 2001 Water-based sol-gel synthesis of hydroxyapatite: process development Biomaterials 22(13) 1721-1730
[20] Melde B and Stein A 2002 Periodic macroporous hydroxyapatite-containing calcium phosphates Chem. Mater. 14(8) 3326-31
[21] Nayak A 2010 Hydroxyapatite synthesis methodologies: an overview International Journal of ChemTech Research 2(2) 903-907
[22] Aminian A, Solati-Hashjin M, Samadikuchak saarei A, Bakhshi F, Gorjipour F, Farzadi A and Schmücker M 2011 Synthesis of silicon-substituted hydroxyapatite by a hydrothermal method with two different phosphorous sources Ceram. Int. 37(4) 1219-1229
[23] Gross K, Muller D, Lucas H and Haynes D 2012 Osteoclast resorption of thermal spray hydroxyapatite coatings is influenced by surface topography Acta biomaterialia 8(5) 1948-1956
[24] Pimenta L, Pesántez C and Oliveira L 2008 Silicon matrix calcium phosphate as a bone substitute: early clinical and radiological results in a prospective study with 12-month follow-up SARS Journal 2(2) 62-68