

Nanostructure and optical properties of porous silicon layer

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Received date: 14 / 9 / 2014

Accepted date: 8 / 3 / 2015

ABSTRACT

In this paper nanostructures Porous silicon layers have been prepared by electrochemical etching (ECE) technique of (111) P-type silicon wafer with a solution Electrolytic HF: ethanol at a concentration of 1:2 with various anodization currents and etching time of 20 min. The morphological, structural and optical properties of nanostructure porous silicon were investigated by Atomic Force Microscopy (AFM), X-Ray Diffraction (XRD) and Photoluminescence (PL) respectively. From AFM images, we found that the PS layer has sponge like structure, and average diameter of pore and thickness of PS layer increased with increasing of the anodization currents. X-ray diffraction show that the crystal size was reduced toward nanometric scale, and then a broadening of diffraction peaks (111) was observed. The band gap of the samples was measured through the photoluminescence (PL) peak.

Keywords: porous Si–nanostructured; Anodization; electrochemical etching .

التركيب النانوي والخواص الضوئية لطبقة السيلكون المسامي

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تاريخ قبول البحث: 2015 / 3 / 8

تاريخ استلام البحث: 2014 / 9 / 14

الملخص

في هذا البحث تم تحضير التركيب النانوي لطبقات السيلكون المسامي بواسطة تقنية التتميش الكهروكيميائي لرقاقة السيلكون نوع (P) (111) ، مع محلول الكتروليتي مكون من حامض الهيدروفلوريد (HF) وكحول الايثانول بتركيز (2:1) بقيم مختلفة للتيار ويزمن تنميش (20) دقيقة . تم استقصاء طوبوغرافية التركيب والخواص الضوئية للسيلكون المسامي ذو التركيب النانوي بواسطة فحص مجهر القوة الذرية (AFM) ، حيود الاشعة السينية (XRD) والاستضاءة (PL) على التوالي، وجد من خلال صورة مجهر القوة الذرية ان طبقة السيلكون المسامي اسفنجية وان معدل قطر وسمك المسام لطبقة السيلكون المسامي يزداد مع زيادة التيار .

دلت قياسات حيود الاشعة السينية على ان حجم البلورة يقل باتجاه تدريج النانو ومن ثم اتساع قمة الحيود (111) .

حزمة الطاقة للعينات تقاس من خلال مقياس الاستضاءة .

الكلمات الدالة: السيلكون المسامي، التركيب النانوي، الطلاء، التتميش الكهروكيميائي .

1. INTRODUCTION

Porous silicon (PS) can be considered as a silicon crystal having a network of voids in it. The nanosized voids in the Si bulk result in a sponge-like structure of porous and channels surrounded with a skeleton of crystalline Si nanowires [1]. PS is obtained conventionally by anodization of silicon substrates. Crystallites of silicon formed by this means can present diameters varying from units of nanometers to tens of micrometers, depending on formation parameters (current density, electrolyte concentration, etching time, and substrate type). This characteristic, that is, the possibility of porosity control, makes PS suitable for several applications on gas sensing [2]. PS was discovered by Uhlir [3] in 1956 when performing electrochemical etching of silicon. In 1990, Canham [4] showed that certain PS materials can have large photoluminescence (PL) efficiency at room temperature in the visible: a surprising result, since the PL efficiency of bulk silicon (Si) is very low, due to its indirect energy band gap and short non-radiative lifetime. The reason of this was the partial dissolution of silicon, which causes i) the formation of small silicon nanocrystals in the PS material; ii) the reduction of the effective refractive index of P*Si* with respect to silicon, and hence an increased light extraction efficiency from PS; and iii) the spatial confinement of the excited carriers in small silicon regions where non-radiative recombination centers are mostly absent. In general, PS is a interconnected network of air holes (pores) in Si. Were fabricated PS by electrochemical etching of a crystalline silicon wafer in a hydrofluoric (HF) acid-based solution. The electrochemical process allows for precise control of the properties of PS such as thickness of the porous layer, porosity, and average pore diameter. The control of these properties of PS was shown to depend on the HF concentration in the used electrolyte, the applied current density, and the thickness of PS. The change in pore diameter, porosity, and specific surface area of PS was investigated by measuring nitrogen sorption isotherms.[5]. PS is classified according to the pore diameter, which can vary from a few nanometers to a few microns depending on the formation parameters [6]. Micropores with pore diameters and pore distances smaller than 2 nm. These are actually the pores which stimulate an efficient luminescence in Si. Such kind of pores form more or less a sponge like structure [7]. Mesopores, with geometries in the 2 to 50 nm range. Formation of such pores does not result in the emergence of efficient luminescence in Si. The mesopores have a more defined direction of growth; however the pore walls are still very rough with a lot of side branches. Macropores have geometries larger than 50 nm. Similar to mesopores, the formation of

macropores does not lead to efficient luminescence in Si. Nevertheless, these pores have the most exciting structure. They expose smooth pore walls and have well defined directions of growth. PS a versatile material with potential in a number of different application areas. Optical and optoelectronic applications are based on the tunable optical properties of the porous layer, such as the index of refraction and layer thickness (solar cells, PDs& reflectors), and on the various luminescence phenomena linked to PS (LEDs) [8,9].

2. AIM OF THE STUDY

Preparation and study of nanostructure porous silicon PS layer with different characterizations, by using electrochemical etching (ECE).

3.EXPERIMENTAL

The PS samples used in these experiments were formed on the polished surfaces of (111) oriented p- type wafers of (500 μm) thickness with resistivity ($\rho=0.01\text{-}0.02 \Omega\cdot\text{cm}$). Before etching process, the silicon wafers were rinsed with ethanol and action to remove dirt followed by dilute (20%) hydrofluoric (HF) acid to remove the native oxide layer and dried by nitrogen. We deposited aluminum film on the back side of silicon wafers in order to creating an ohmic contact. This has been achieved by using thermal evaporation process in vacuum chamber (10^{-4} torr). After etching process, the samples were rinsed with ethanol and pentane and dried by nitrogen The ethanoic solution (15%) was obtained by 1 volume of HF (48%) and 2 volume of $\text{C}_2\text{H}_5\text{OH}$ (99%). **Figure (1)** shows a schematic diagram of the ECE set-up the etching cell made from Teflon because the Teflon not interaction with HF acid, rubber O-ring is used before the upper part of cell. The latter has a central circular of 1cm^2 to allow touching the silicon wafer. And the two electrodes are used to apply current across the cell .

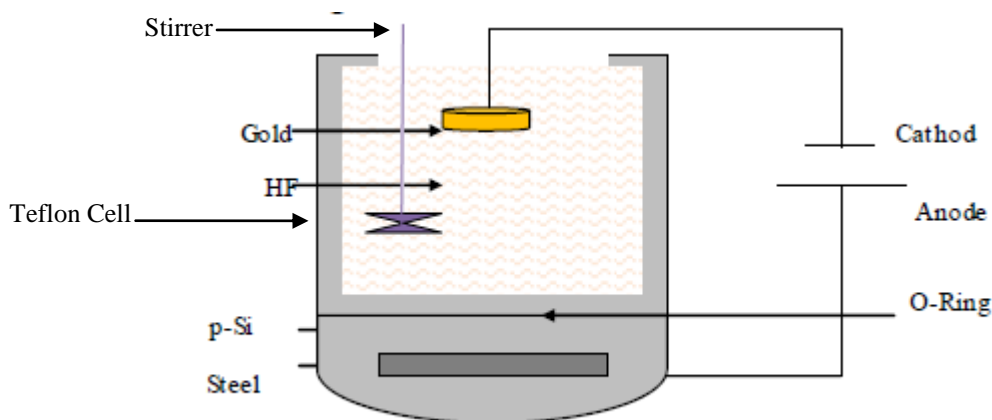
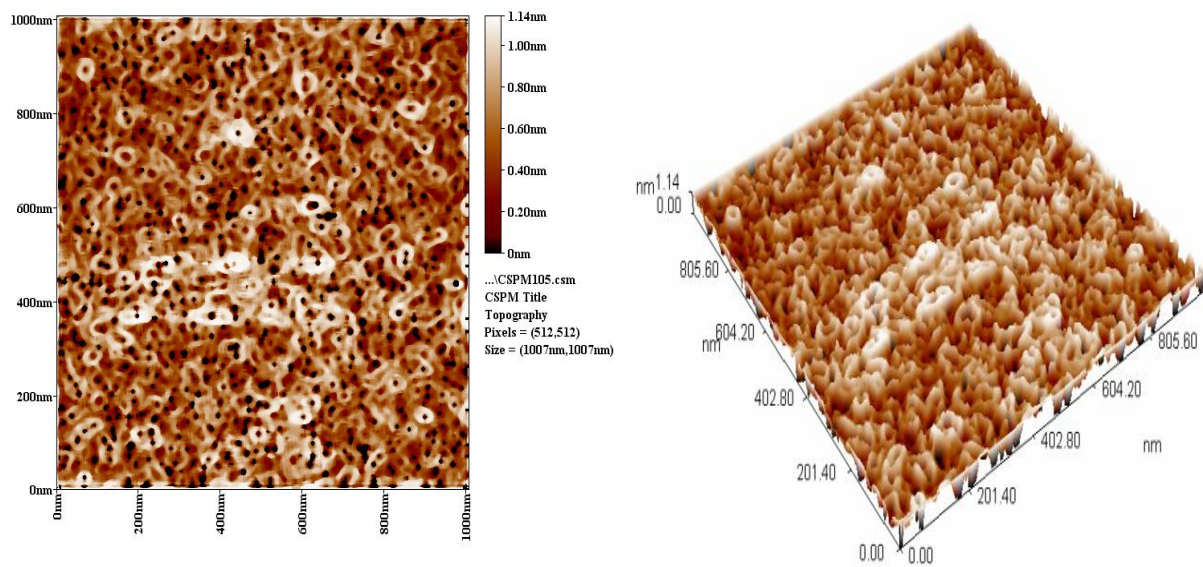


Figure (1): Schematic diagram of anodization cell.

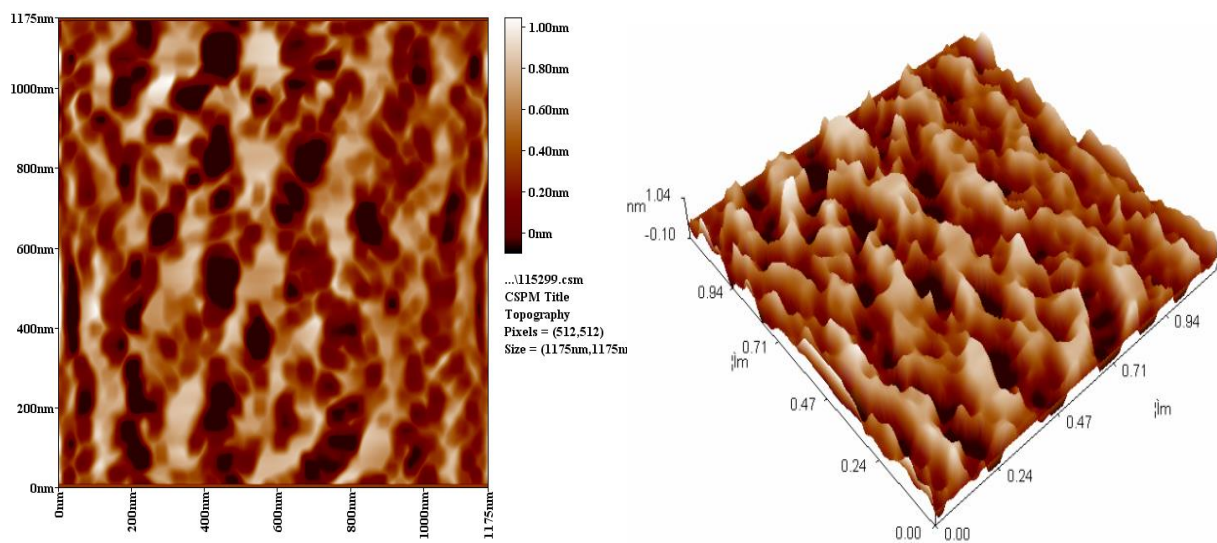
The lower one is stainless still foil below silicon wafer and the upper one is gold mesh connected with the HF solution. And after etching process, the sample were rinsed with ethanol and pentane and dried by nitrogen. The morphology characteristics of porous silicon nanostructure could be studied by AFM. Atomic Force Microscopy (AFM) gave a direct surface image of porous silicon layer. A CSPM-AA3000, AFM instrument was used and achieved in department of Chemical Science-University of Baghdad. Structural properties of PS have been investigated by X-ray diffraction techniques. A SHIMADZU (XRD-6000, 220/50Hz, JAPAN) of 1.54\AA from Cu-K α was used. This measurement was achieved in the ministry of sciences and technology. Photoluminescence spectroscopy was performed by using (CW 325nm, 400mW He-Cd laser), having an excitation wavelength of 405 nm. The luminescence emitted is analyzed by (CCD-equipped spectrometer) (Acton 300).

4. RESULTS AND DISCUSSION

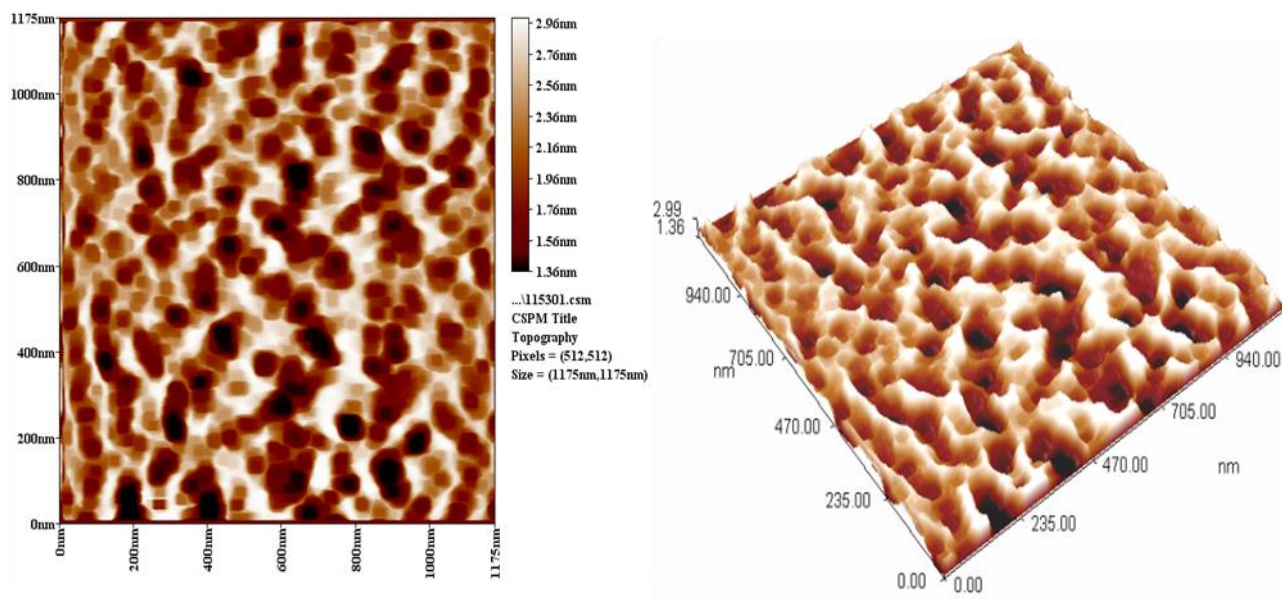
The surface morphology of the oxidized PS layers was investigated using Atomic force microscope (AFM) analysis focus entirely on the nanoscale characterization of PS films. We have studied the surface morphology of the PS layers prepared by anodized etching observations from the AFM graphs could be distinguished. A sponge-like structure is produced, see **Figure (2)**.



(a)



(b)



(c)

Figure (2): Show 2D and 3D AFM images for PS with (a) 20, (b) 30, (c) 40 mA/cm².

The surface morphology reveals that the existence of pore sponge like with different average sizes. Figure 2a, illustrates the AFM image of the structure obtained with 20 mA/cm² etching current density. The pore sizes produced are with an average diameter of (19.35nm). Increasing etching current density to 30 and 40 mA/cm², Figure 2 b and c, causes an increase in the pore size to new values of average diameter from (21.42 to 27.61 nm) respectively. The morphology characteristics of PS samples are presented in **Table (1)** .

Also we can observed that the roughens and root mean square increase with increasing of current density constant etching time 20 min.

Table (1): The calculated morphology characteristics of PS samples from AFM analysis.

Current density (mA/cm ²)	Etching time (min)	Roughness ave. (nm)	RMS (nm)	Diameter ave. (nm)
20	20	0.261	0.267	19.35
30		0.229	0.268	21.42
40		0.408	0.471	27.61

XRD studies showed the distinct variations between the fresh silicon surface and the PS surfaces formed at different anodizing current densities. XRD spectra of fresh silicon showed a very sharp peak at $2\theta = 28.49^\circ$ showing the single crystalline nature of the wafer. This peak becomes very broad with varying full-width at half maximum (FWHM) for different anodization current densities as shown in Figure (3) .

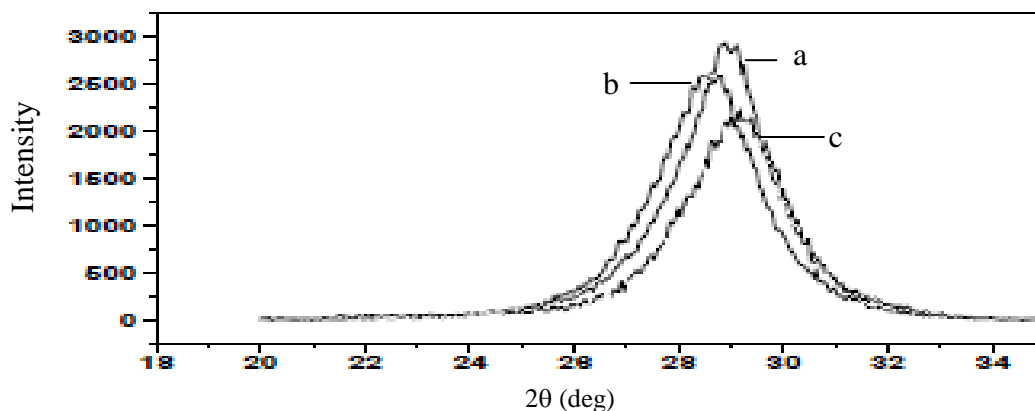


Figure (3): Shows X-ray diffraction of porous silicon prepared at different current density (a) 20, (b) 30, (c) 40 mA/cm² at etching time 20 min.

The crystallites size obtained for PS samples is shown in Table (2) , when estimated by the Scherrer equation, a significant crystallites size decrease trend can be clearly noted on increasing current density.

Table (2): Crystallites size obtained by means of Scherrer equation of PS layer which prepared under different current densities.

Etching time (min)	Current density (mA/cm ²)	FWHM (deg.)	Crystallites size (nm)
20	20	1.8632	6.21
	30	1.9312	5.93
	40	2.1708	5.51

The PL emission peaks were obtained from three samples using photoluminescence spectroscopy. The room temperature PL measurements of various samples at different anodization current densities are shown in Figure (4) . For the samples that anodized in 20, 30, and 40 mA/cm², the PL peaks, related to the S-band emission, observed at wavelength 738, 730 and 720 nm, respectively. The porosity is increased by increasing the etching time. So, clearly the silicon structure size on the surface decreases by increasing the anodization current densities. It causes the peaks to shift towards the lower wavelength or higher energy as the anodization current densities is growing up. Increasing root mean square, roughens and energy band gap with increase of current density.

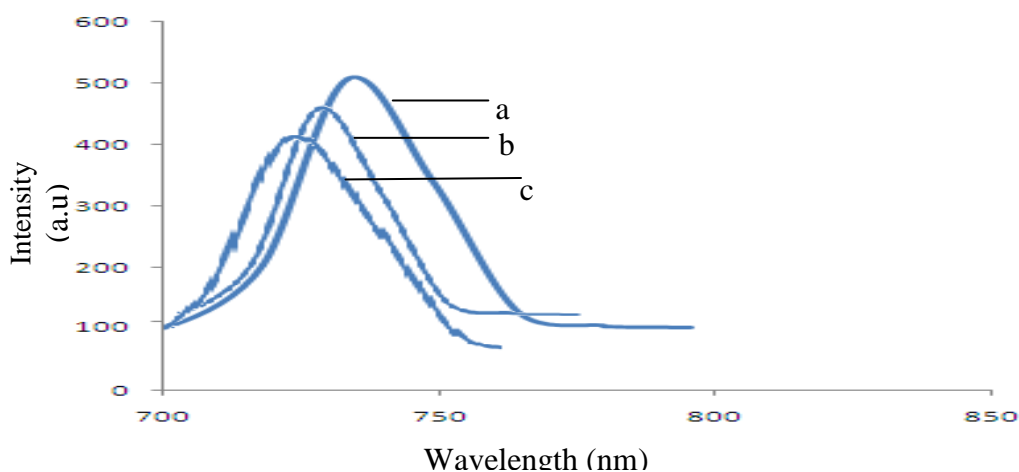


Figure (4): PL peaks for PS at different anodization currents (a) 20, (b) 30, (c) 40 mA/cm² at etching time 20 min.

5. CONCLUSION

The average pore diameter appears in good agreement with what expected for a mesoporous layer, and the structure of PS layer has a sponge-like. XRD spectra of porous silicon showing very broad with varying full-width at half maximum (FWHM) for different anodization current due to reduce the crystallite size. it was found that the band gap value increases by anodization current densities. The energy band gap of the porous silicon is 1.72 eV and it is higher than the energy band gap of bulk silicon which is 1.12eV. So, it is proved that the porous silicon is better to be used for photovoltaic devices more than bulk silicon.

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Baha T. Chiad, completed his Ph.D. at the physics department in laser spectroscopy from Baghdad University – Baghdad-Iraq in 1993. His research interests lie in the field of organic semiconductor and molecular spectroscopy. He is currently a chief of the molecular spectroscopy and laser Research Group at the Physics department of Baghdad University.