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The influence of anodization time with the electrochemical cell design on the fabrication process of porous silicon nanostructures

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Abstract
The influence of anodization time with the electrochemical cell design on the fabrication process of porous silicon (PS) nanostructures based on two electrochemical anodization cells (designed single tank cell and double tank cell) with two anodization times (10 and 30 minutes) was studied. Atomic force Microscopy (AFM) characterization had revealed three types of pores, mesopores, mesopore fill of mesopores, and macropore fill of mesopores were obtained from designed single tank cell with (10 and 30 minutes) of anodization time, whilst for double tank cell has not revealed precise information about the size and type of pores. Pores formation have been further approved by current-voltage (I-V) measurement and photoluminescence emission by ultraviolet-lamp (254-366) nm for both electrochemical cells.

Keywords: Electrochemical cells design, porous silicon nanostructure, atomic force microscopy (AFM), Ultraviolet emission (UV).

تأثير زمن الانوده مع تصميم الخلية الكهروكيميائية على عملية تخليق بنى نانوية مسامية من السيلكون

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الخلاصة
تمت دراسة تأثير زمن الانوده مع تصميم الخلية الكهروكيميائية على عملية تخليق بنى نانوية مسامية من السيلكون إعتمادا على المقارنة بين تصميم خليتين كهروكيميائيتين (خلية ذات خزان منفرد و خلية ثنائية الخزان) وعلى زمني انوده (10 و 30دقيقة). كشف مجهر القوة الذرية (AFM) ثلاثة انواع من المسام ميزو و ميزو ملئ ميزو وماكرو ملئ ميزو، تم الحصول عليها من الخلية ذات الخزان المنفرد مع زمني انوده (10 و 30 دقيقه)، في حين لم يمكن الحصول من الخلية ثنائية الخزان على نتائج دقيقه حول نوع و حجم المسام. تم أيضا اثبات تشكيل المسام من خلال قياس الفولطية–تيار و التألق ضوئي وباستخدام مصباح اشعة فوق بنفسجية (254–366) نانوميتر لكلا الخليتين الكهروكيميائيتين.

1. Introduction

Porous silicon (PS) is prepared by electrochemical anodization of silicon wafers in electrolyte solution which consists of hydrofluoric acid (HF) and ethanol by providing the silicon wafers with the required current for a specific period of time [1]. The electrochemical anodization is performed in the electrochemical etching cell [2]. Mainly there are two types of anodization cells single tank cell and

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double tank cell [3]. Anodization parameters which are crucial in determine pore morphology and pore size are current density, electrolyte composition, silicon wafer type and doping concentration [4]. According to IUPAC “Recommendations for the characterization of porous solids” porous structures are typically classified based on pores size: Micoropores have diameters less than 2nm, Mesopores have diameters between 2-50nm, Macropores have width more than 50 nm [5]. The influence of andoization time on the fabrication process of porous silicon (PS) nanostructures with respect to the electrochemical cell design has been studied. This study included two anodization times 10 and 30 minutes with two electrochemical cells design (designed single tank cell and double tank cell). The Atomic force Microscopy (AFM) was utilized to study the morphological features of the porous silicon layers depending on manually analyzing the profile section analysis, Keithley semiconductor characterization system model 4200-scs was used to measure current-voltage characteristics, the photoluminescence emission of PS was tested by ultraviolet - lamp at (254-366) nm wavelength.

2. Experimental part

Two electrochemical etching cells (designed single tank cell and double tank cell) with etching surface areas of 6.15 cm^2 and 0.785 cm^2 was utilized to prepare porous silicon samples from P-type, Si(100), boron doped resistivity of (1-10Ωcm) substrates. Prior to the anodization process and before setting up in the etching system the silicon wafers cleaned thoroughly by using absolute ethanol and deionized water for 3 minutes. The native oxide SiO_2 was removed by an ethanolic solution containing 1% HF [6]. The anodization electrolytes of this study were a mixture of an ethanolic 48wt% hydrofluoric acid HF with 99.8wt% ethanol (C_2H_5OH) at ratio (1:1) in volume which is used by many authors [6, 7] for the anodization times of (10, 30) minutes. With the constant current density of 30mA/cm^2 [6] which provided by current source Keithley 200-60-2 **(**Programmable DC power supply. 60 V, 2.5 A, 1 channel, USB, GPIB). After the anodizaton, porous silicon samples rinsed with methanol many times and dried with pentane. Atomic Force Microscopy (AFM XE-100 Park Systems) was used to investigate the pore formation and the morphology of porous silicon, Keithley semiconductor characterization system model 4200-scs was used to measure current-voltage characteristics, the ultraviolet photo-luminescence emission of porous silicon was tested by a UV-lamp at (254-366) nm wavelength.

3. RESULTS AND DISCUSSION

3.1 Atomic Force Microscopy

Figure-1-(a)-(d) shows three dimensional Atomic force Microscopy images with scale (500 nm x500nm), operated under contact mode of porous silicon layers, prepared by utilizing two electrochemical etching cells with the anodization times of (10, 30) minutes and constant current density of 30mA/cm^2. Pore size (diameter and depth) and morphology of porous silicon samples were analyzed by employing Section Analysis of Atomic Force Microscopy image [8, 9]. By manually analyzing each image profile of Figure 1-(a)-(d) we could have obtained different sizes of pores on PS layer for designed single tank cell but it did not reveal precise information about the size and type of pores that formed on the porous silicon layers for double tank cell.

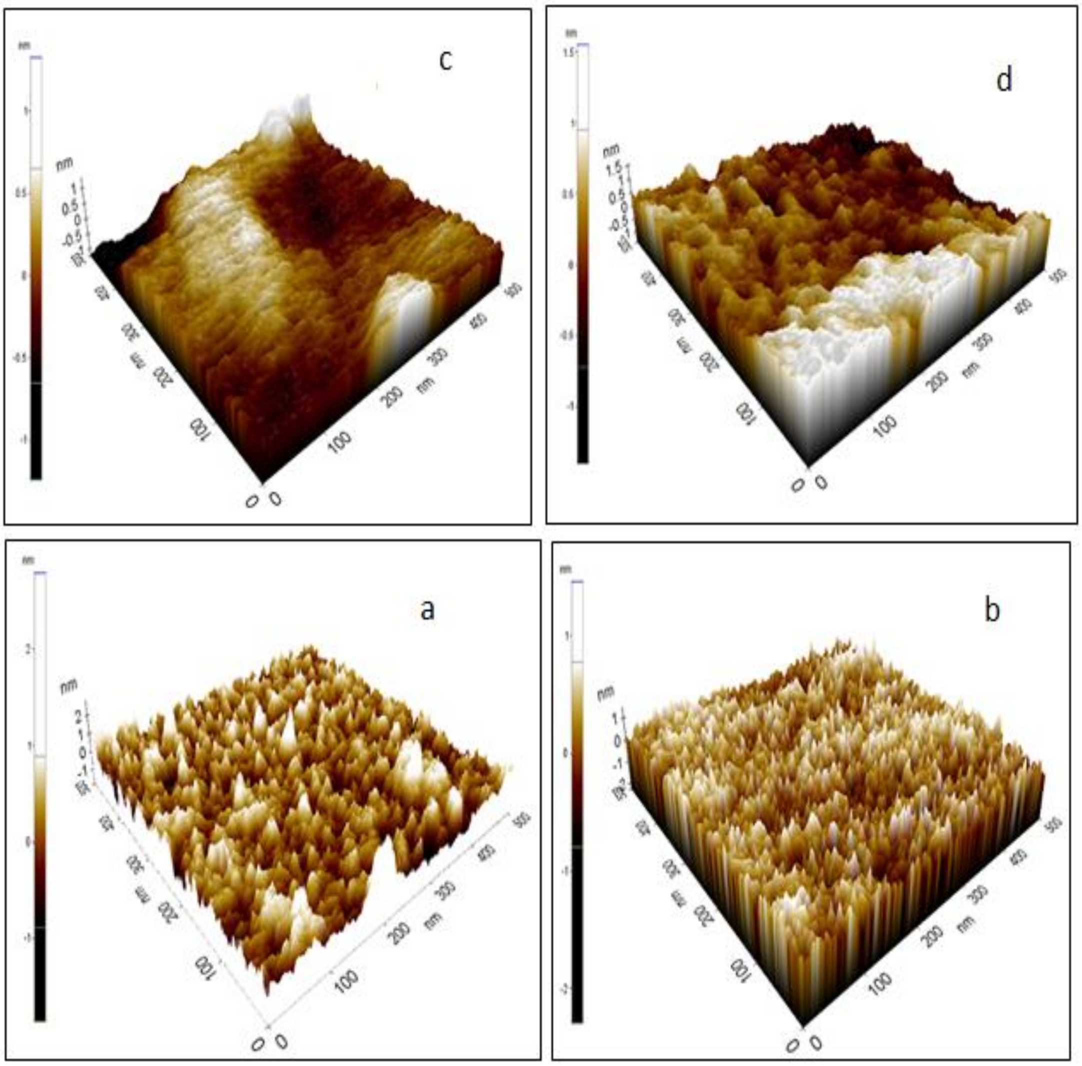


Figure 1-3-D AFM image of PS layer in single tank cell and double tank cell, with etching solvent HF: EtOH at ratio (1:1) in volume with different etching time used: (a) 10 min single tank cell, (b) 30min single tank cell (c) 10 min double tank cell, (d) 30 min double tank cell.

Table 1-The type of pores obtained for designed single tank cell based on diameter and depth of pores.

Cell type	Time(min.)	Type of pores	Diameter(nm)	Depth (nm)
Single tank cell	10	meso pores	06-40	0.20- 0.54
		meso pores fill of meso pores	27-49	0.53-1.00
	30	meso pores	06-20	0.20-1.10
		meso pore fill of meso pores	25	0.40
		macro pore fill of meso pores	61	1.10
Double tank cell	10	Non		
	30	Non		

A very important requirement to be controlled during the etching process is local current density, for single tank cell is provided by uniform back side contact with low resistance, in contrast to double tank cell which does not allow considerable amount of current flow due to the electrolytic back side contact which has the tendency to work in the reverse in direction. From this property and depending on our results we can deduce that the longer the anodization time for double tank cell is more effective in the fabrication process of porous silicon nanostructures. The performance of double tank cell for 60 min. of anodization time [9] could prove the above fact due to the formation of three types of pores mesopores, mesopores fill with mesopores, macro pores fill of mesopores which have a close similarity to the type of pores obtained with the single tank cell for 10 and 30 minutes with a slight difference in diameters and depths of pores in a scale of few nanometers.

3.1 Ultraviolet Photoluminescence Emission of PS Layer

The ultraviolet (UV) photoluminescence (PL) emission from porous silicon was tested by UV lamp (254-366) nm. The influence of anodization time could be seen reflected in the Table-2 and Table-3 which show (UV) photoluminescence (PL) emission from porous silicon samples fabricated with two electrochemical cells with (10,30) minutes of anodization time. In the nano-crystallites of porous silicon when photo excited with blue or UV light, confined electron-hole pairs are generated. Upon recombination of electron-hole pairs a visible red-orange, or green photoluminescence (PL) is observed this is related to the fact that the band gap of bulk silicon which is 1.1eV equivalent to spectrum near infrared-region is smaller than the energy gap of the nano-crystallites of porous silicon by the confinement energy [7].

Table 2-The images of PS samples prepared by using designed single tank cell, under white light and UV (254-366) nm., with etching times of (10,30) minutes.

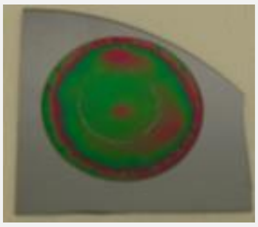
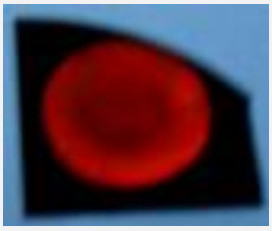
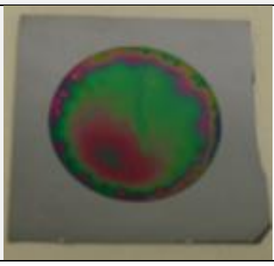
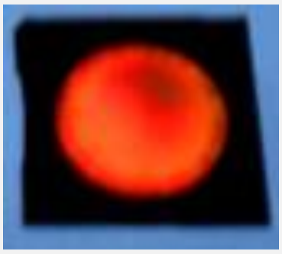
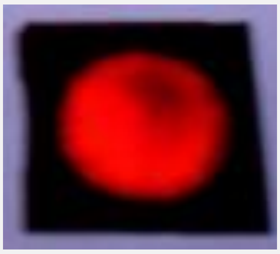
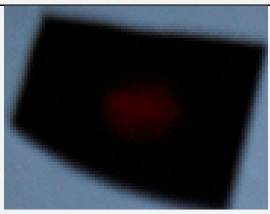
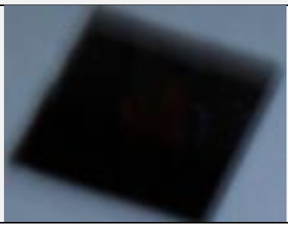
Time (min.)	White light	UV-254nm	UV-366nm
10			
30			

Table 3-The images of PS samples prepared by using double tank cell, under white light and UV (254-366) nm, with etching times of (10,30) minutes.

Time (min.)	White light	UV-254nm	UV-366nm
10			none
30			none

3.2 Current – Voltage characteristics

The electrical property of the fabricated porous silicon samples was detected by I-V measurements; Figure-2-(a)-(d) represents the I-V characteristic of porous silicon samples with two anodization time and with two electrochemical cells. The behavior of porous silicon samples show pore formation in both anodization time (10,30) minutes, porous silicon formation occurs at the exponential regions of the current-voltage (I-V) characteristic which does not show at a voltage higher than the current peak [10]. The I-V curves of our samples show a great similarity to the Schottky diode behavior, specifically for double tank cell for 10 min. and single tank cell for 30 min. zero bias Schottky curves can be clearly noticed which are generally made of p-type silicon [11].

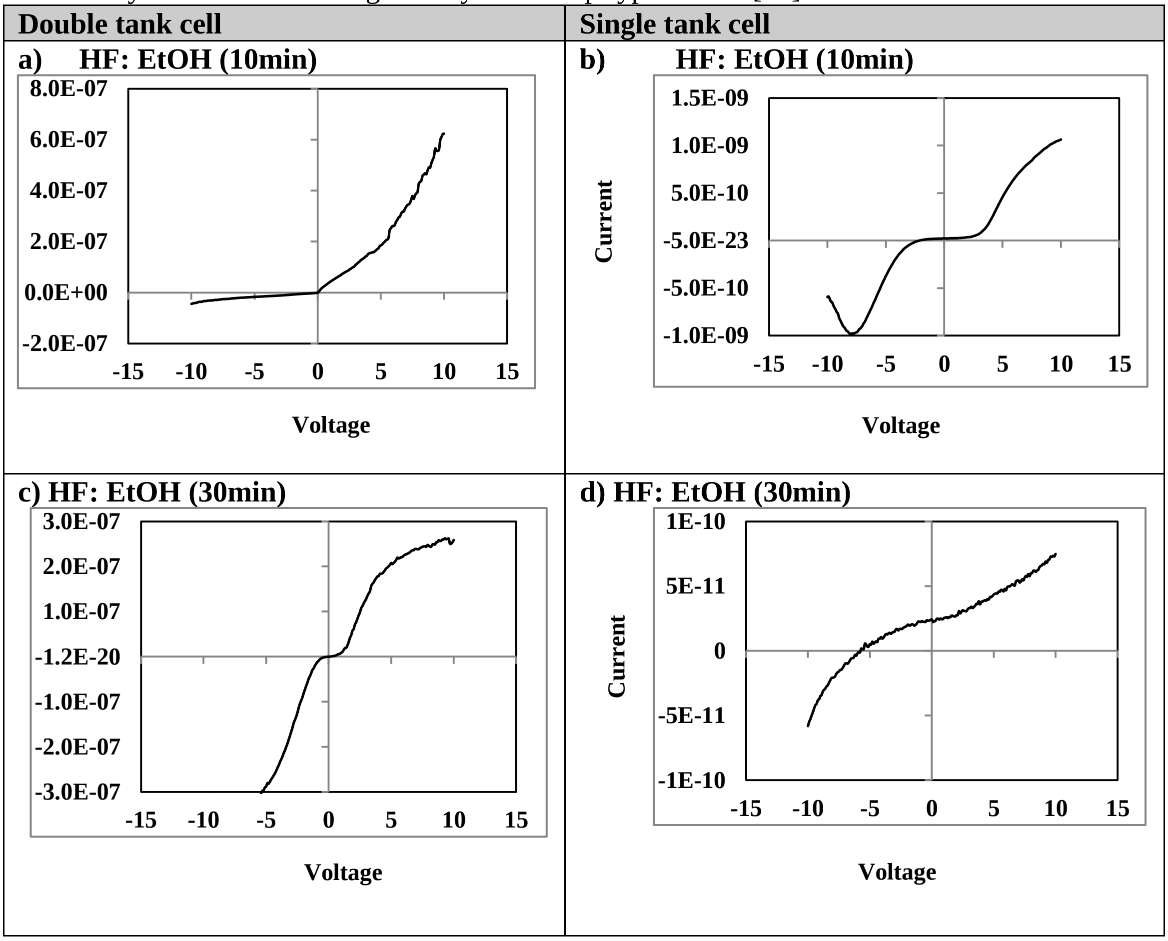


Figure 2-I-V measurement performed on prepared PS samples by using double tank cell (a)-(b), and designed single tank cell (c)-(d), with different etched times and constant current density 30 mA/cm^2.

3. Conclusion

The influence of the anodization time on the fabrication process of porous silicon nanostructures has been studied based on two anodization times (10 and 30) min. with two electrochemical cells (designed single tank cell and double tank cell). Section analysis of Atomic Force Microscopy image has revealed for designed single tank cell three types of pores, mesopores, mesopore fill of mesopores, and macropore fill of mesopores, but it did not reveal precise information about the size and type of pores that formed on the porous silicon layers for double tank cell. The I-V Characteristic shows pore formation with two anodization times with both electrochemical cells and a great similarity to the Schottky diode behavior has been realized with 10min. for double tank cell and 30 min. for single tank cell. Designed single tank cell is favorable over double tank cell with the anodization times of 10 and 30 minutes due to the structural difference between the two cells which lie on the local current density which for single tank cell provided by uniform back side contact while for double tank cell by an electrolytic back side contact. This leads us to conclude that longer andoization times are more effective in fabrication process of porous silicon nanostructures than with double tank cell.

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