Porous silicon prepared by photo electrochemical etching assisted by laser

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Abstract

Porous silicon (PS) layers are prepared by anodization for different etching current densities. The samples are then characterized the nanocrystalline porous silicon layer by X-Ray Diffraction (XRD), Atomic Force Microscopy (AFM), Fourier Transform Infrared (FTIR). PS layers were formed on n-type Si wafer. Anodized electrically with a 20, 30, 40, 50 and 60 mA/cm^2 current density for fixed 10 min etching times. XRD confirms the formation of porous silicon, the crystal size is reduced toward nanometric scale of the face centered cubic structure, and peak becomes a broader with increasing the current density. The AFM investigation shows the sponge like structure of PS at the lower current density porous begin to form on the crystalline silicon, when the current density increases, pores with maximum diameter are formed as observed all over the surface. FTIR spectroscopy shows a high density of silicon bonds, it is very sensitive to the surrounding ambient air, and it is possible to oxidation spontaneously.

Key words

Porous silicon, nanostructure materials, AFM, XRD, FTIR, Crystalline silicon.

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تحضير السليكون المسامي بالتنميش الكهروكيمياوي بمساعدة الليزر

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الخلاصة

في هذا البحث تم تحضير طبقات السيليكون المسامي التركيب بطريقة التنميش بالليزر لكثافات تيار مختلفة، شخصت خصائص العينات المحضرة بواسطة فحص حيود الأشعة السينية، مجهر القوة الذرية، تحويل فورير للأشعة تحت الحمراء حيث ان طبقات السيليكون المسامي تتكون على السطح حيث يتم تأينها بتيارات مختلفة 20, (30, 40, 50, 60 mA/cm^2) لزمن تنميش 10 min. من خلال فحص حيود الاشعة السينية يؤكد تكوين السيليكون المسامي وان الحجم البلوري يقل باتجاه الاحجام النانوية، ولوحظ ان القمة تزداد في العرض بزيادة تيار التنميش. من خلال مجهر القوة الذرية تبين ان عند التيارات الواطئة تبدأ طبقات السيليكون المسامي بالتكون وعند زيادة تيار التنميش سنحصل على اعرض قطر مسامي على السطح. من خلال تحويل فورير للأشعة تحت الحمراء تبين وجود أواصر كثيفة خاصة بالسيليكون حيث ان هذه الاواصر تكون قابلة للتأثر بالبيئة والهواء المحيط ويمكن ان تتأكسد باستمرار.

Introduction

Crystalline silicon (C-Si) is one of the important material of the last century that has been the corner stone of the semiconductor industry and has spear headed extraordinary technological advancement. Bulk C-Si, however, has an indirect band gap that make it unsuitable for integrating light with electronics (optoelectronics). Thus, C-Si has only very poor luminescence in the near infrared (1100nm) region [1] consequently; there have been great efforts in last decade to produce controlled light

emission from silicon in the near infrared and visible regions [2].

Silicon substrate is a single crystal with high quality. It has very low volume density of impurities and a controlled amount of dopants; it can be fabricated to create silicon with structure in the range of nano size (1-100 nm) by using electrochemical etching (ECE) technique .The resulted silicon is called PS because its surface has a web of disordered pores. The properties of porous silicon are different from bulk silicon [3, 4]

PS considered as a silicon crystal have large network of voids in its crystal. The Nanosized voids in the Si bulk resulting in a sponge-like structure of porous, and channels surrounded with a skeleton of crystalline Si nanowires [5].Therefore, to combine PS layer into electronic circuits or to develop PS based devices, the electrical properties of this material must be studied thoroughly[6].

Photo electrochemical etching (PECE) technique deal with semiconductors is used to fabricate unique structures in electronic and photonic devices, like integral lenses on light-emitting diodes, gratings in laser devices [7].

Experimental work

PS samples are prepared from n-type silicon wafer of resistivity 0.015 ohm.cm and <111> orientation. Electrochemical etching system used to fabricate with the assistance Diode laser of wavelength 650 nm and power of 30 mW was used to illuminate the Si surface. Laser power was obtained after calibration by using (Genetic-EO SOLO2) power meter. A composition of HF (48%) and ethanol in a ration 1:2 is used for electrolyte and the anodization was carried out with constant time 10 minutes. The samples of 1 x 1 cm^2 dimensions were cut from the wafer and rinsed with ethanol to remove dirt. In order to remove the native oxide layer on the samples, after cleaning the samples they were immersed in HF acid in a Teflon beaker. The cell is made out of Teflon that is resistive against attack from the Hydrofluoric acid electrolyte. The silicon wafer serves as the anode and it is sandwiched between the top and the bottom parts of the Teflon. The cathode is a circular gold that is submerged in the Hydrofluoric acid electrolyte, the cathode is held in place by the top part of the Teflon cell and an aluminum ring see Fig. 1.

In this experiment, five n-type samples were prepared each with constant anodization time 10 min, at different current densities 20, 30, 40, 50 and 60 mA/cm^2 respectively. The Laser source was adjusted in such a way so that the beam area is the size of the exposed surface (0.5 cm^2) of n-silicon so that the Photo induced etching is uniform. For this, we used a convex lens of high radius of curvature (not measured). At the end of the PECE process, the samples were rinsed with ethanol and stored in a glass.

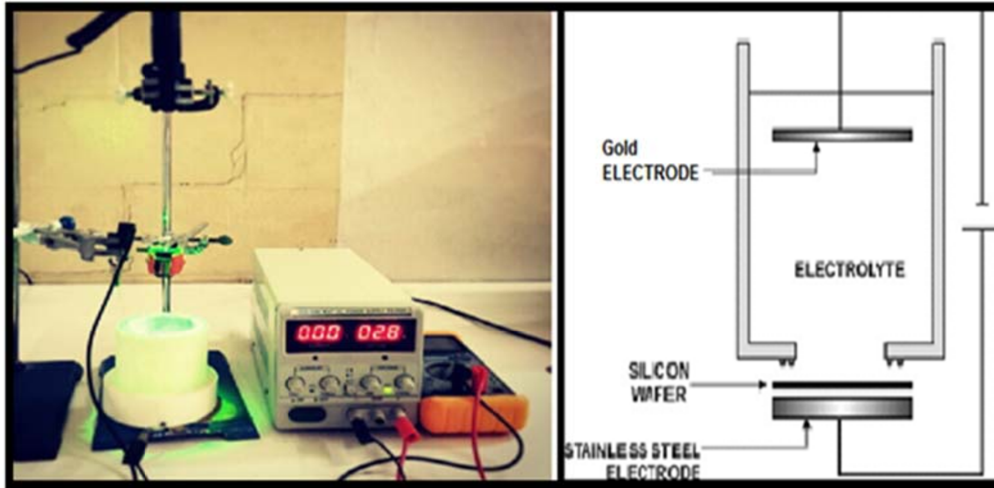

Fig. 1: Schematic diagram of (A) image of the set-up PS anodization (PECE) and (B) anodization cell.

Results and discussion

The surface morphology properties studies

The surface morphology properties prepared by PECE technique of (111) n-type silicon wafer was investigated using AFM. The surface morphology of PS samples that prepared with different current density (20, 30, 40, 50 and 60 mA/cm^2) at etching time 10 min and HF construction (16%) as shown in Fig. 2. The images in this Figure show that PS has sponge like structure.

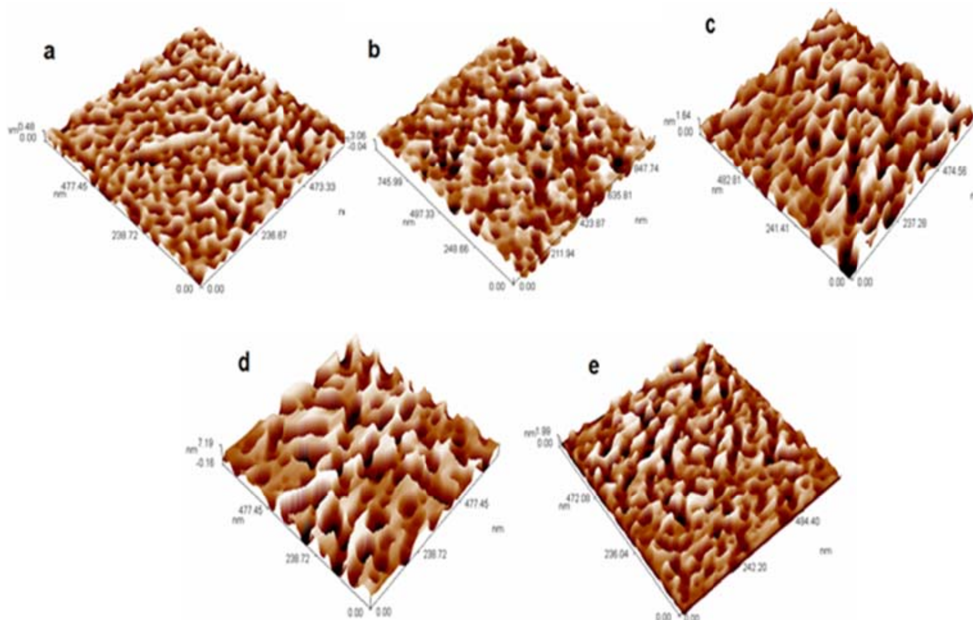

Fig.2: 3D AFM images for PS with current density of (a) 20, (b) 30, (c) 40, (d) 50, and (e) 60 mA/cm^2 at 10 min and 16% HF concentration

From Fig. 2, at the lower current density of 20 and 30 mA/cm^2 porous begin to form on the C-Si, which indicate etching process has already started. When the current density increase to 50 pores with maximum diameter are formed as observed all over the surface region of the etched silicon layer.

The pore size distribution is relativity uniform and columnar walls are very thin and appear have to have uniform thickness that is indication of sponge like structure of the PS layer, when the current density reached to 60 mA/cm^2 some pore walls are broken exposing the next lower surface.

Moreover, when the etching current density increased from 20 to 30 mA/cm^2 the average pore diameter was decreased from 40.2 to 36.01 nm, this attributed to etching ratio high in layer more of layer other in same sample caused an increasing in porosity and pore ration, so the pores have begun again to grow and increase in an average roughness as shown in Table1. These results are in agreement with Thaira [8].

Table 1: The calculated morphology characteristics of PS samples prepared with different etching current density.

Etching Time (min)	Current density (mA/cm^2)	Avg. Pore (nm)	Avg. Roughness (nm)
10	20	40.2	0.111
	30	36.01	0.777
	40	47.53	0.396
	50	54.83	1.89
	60	31.70	0.472

Structural characteristics

Fig.3 shows typical diffraction pattern of a bulk Si and PS sample fabricated etching current density (20, 30, 40, 50 and 60 mA/cm^2) respectively, at etching time 10 min. A distinct different between bulk Si and PS can observed.

XRD pattern of bulk Si showed a very sharp peak indicating the single crystalline nature of the Si wafer. This peak becomes a broadening with increasing the current density see Table 2 and confirms the formation of pores on the silicon surface with remains PS structure crystalline even after the pore formation, these result in agreement with Jayachandran [9]. The crystallites size can be estimated from diffraction pattern by applying the Scherrer equation.

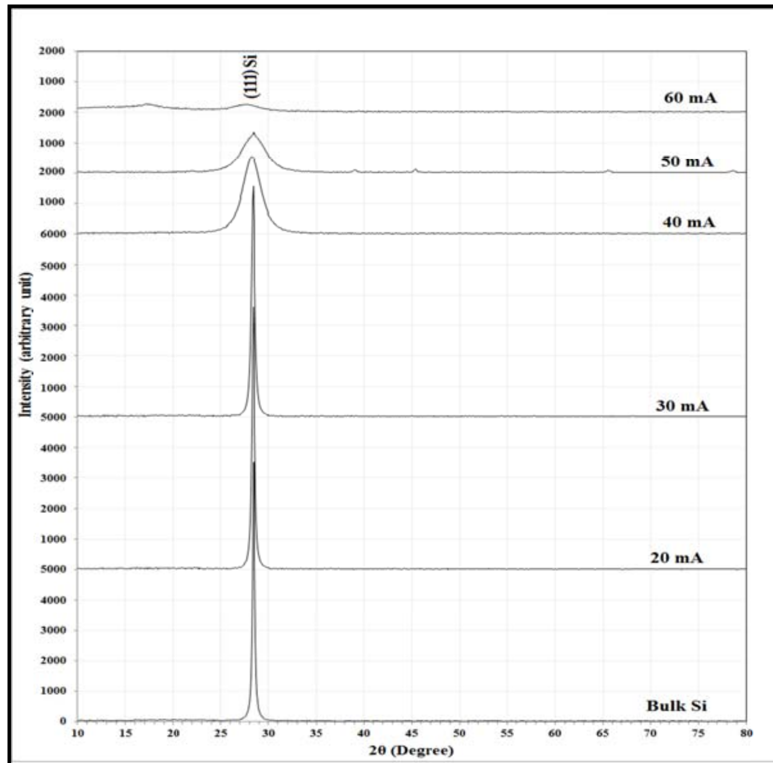

Fig. 3: X-ray diffraction of PS prepared by PECE for etching time 10 min and different current densities a) bulk Si, b) 20, c) 30 d) 40 e) 50 and f) 60 mA/cm^2.

Table 2: The crystallites size and line broadening vs. current density.

Current density (mA/cm^2)	2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	G.S (nm)	hkl	d_{hkl} Std.(Å)	Phase
Bulk	28.4400	0.2610	3.1358	31.4	(111)	3.1454	Cubic-Si
20	28.4000	0.3210	3.1401	25.5	(111)	3.1454	Cubic-Si
30	28.3800	0.3940	3.1423	20.8	(111)	3.1454	Cubic-Si
40	28.2667	2.2375	3.1546	3.7	(111)	3.1454	Cubic-Si
50	28.4350	2.9028	3.1364	2.8	(111)	3.1454	Cubic-Si
60	27.6644	3.0248	3.2219	2.7	(111)	3.1454	Cubic-Si

Chemical composition properties of PS

FTIR spectroscopy represents the most convenient technique for characterization of chemical species on PS surfaces. The FTIR signals from PS are typically stronger compared with the vibrational spectrum of a flat silicon surface due to much larger specific area of PS [10]. Such a large surface area includes a high density of dangling bonds of silicon for original impurities such as hydrogen, which is residual from the electrolyte.

In addition, it is very sensitive to the surrounding ambient air and it is possible to oxidation spontaneously. The chemical bonds and infrared transmittance peak of PS prepared at different current densities (20, 30, 40, 50 and 60 mA/cm^2) and 16% HF concentration for 10 minutes are shown in Fig. 4 and listed in Table 3.

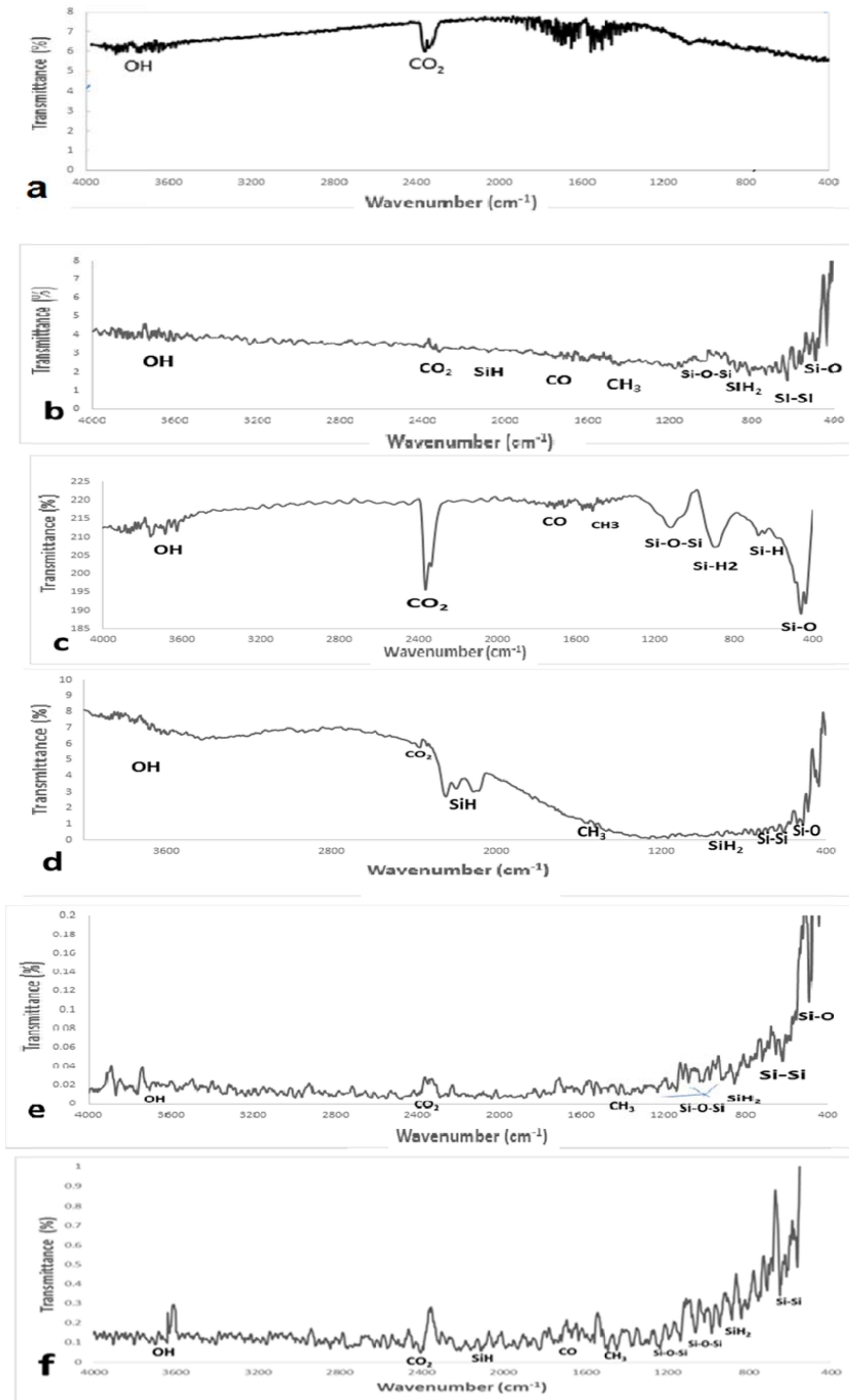

Fig. 4: FTIR transmission spectra of (a) bulk Si (111) and PS for different etching current densities (b) 20, (c) 30, (d) 40, (e) 50 mA/cm^2 and (f) 60 mA/cm^2.

Table 3: Wavenumber positions and attributions of the transmittance peaks are observed in the PS samples for different etching current densities (b) 20, (c) 30, (d) 40, (e) 50 and (f) 60 mA/cm^2.

Peak Ref. (cm^{-1})	B peak (cm^{-1})	C peak (cm^{-1})	D peak (cm^{-1})	E peak (cm^{-1})	F peak (cm^{-1})	Bonds
495[10]	494	475	486	489	-	Si-O
610[10]	618	-	605	620	619	Si-Si stretching
661[11]	-	672	-	650	653	SiH wagging
856[12]	866	-	852	856	-	SiH_2 wagging
880-910[12]	-	880	-	914	882	SiH_2 scissoring
980-1050[10]	1005	-	-	1078	985	Si-O-Si antisymmetric stretching
1150-1240[11]	1205	1118	-	1228	1230	Si-O-Si symmetric stretching
1448.54[13]	1442	1460	1459	1435	1446	$C-H_3$ asymmetric deformed
1705[13]	1701	1710	-	-	1711	C-O
2087[12]	2077	-	2081	-	2090	SiH stretching in Si_3-SiH
2360[13]	2350	2360	2345	2345	2380	CO_2
3610[12]	3610	3609	3605	3620	3620	OH stretching is SIOH

Conclusions

PS layers prepared by PECE for five n-type silicon wafer at different etching current densities with constant etching time 10 min. from the measurement of PS, It can be concluded that: The XRD properties showed a very sharp peak indicating the single crystalline nature of the Si wafer and peak becomes a broadening with increasing the current density. The AFM investigation shows PS has sponge like structure of PS and when increasing current density pores with maximum diameter are formed and when the current density increased pore walls are broken exposing the next lower surface. The FTIR properties shows in PS samples oxygen is normally absent, the dominant bonds being Si-H_1, Si-H_2 and Si-H_3 groups. In addition, it is very sensitive to the surrounding ambient air and it is possible to oxidation spontaneously. Moreover, there were other peak appeared which might be attributed to C=O and C-H where these carbon peaks were attributed to the organic trace residues from the process.

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