Study the Effect of Etching Time on the Characteristics of the Porous Silicon that Prepare from N-Type Silicon by Photoelectrochemical Etching Method

Israa Akram Abbas[1a], Salah Qaddoori Hazaa[2]
[1] Mustansiriyah University, College of Education, Physics Department
[2]Al-Karkh University of Science, College of Science, Department of Medical Physics
***Email:* israa.akram.78@gmail.com**

Abstract:
In this paper, samples of porous silicon were studied and prepared using n-type silicon with directionality (111) using photoelectrochemical etching method with current density (20 mA/cm^2) and with different etching time (5, 10, 15, and 20 min). The results of the structural properties tests of porous silicon using (XRD) showed an increase in the width of the mid-top of the curve with the increase of the etching time and thus the grain size decreases from (46.99 nm to 4.36 nm), from the (SEM) examination, the results showed that the pore depth increases with the increase in the etching time, from the (AFM) examination found that the grain size rate increases from (63.55nm to 75.68nm) and the surface roughness also increases from (2.2nm to 17.9nm) with the increase in the etching time. The porosity is within the visible light region and as the etching time increases, the curve shifts towards short wavelengths, thus increasing the optical energy gap (1.99eV to 2.02eV).
Keywords: Porous silicon, n-type, XRD, Photoelectrochemical, Etching time.

دراسة تأثير زمن النقش على خصائص السيليكون المسامي الذي يتم تحضيره من السيليكون من النوع n بطريقة النقش الكهروكيميائي الضوئي

اسراء اكرم عباس[١]، صلاح قدوري هزاع[2]
[١]قسم الفيزياء ـ كلية التربية ـ الجامعة المستنصرية
[٢]قسم الفيزياء الطبية – كلية العلوم – جامعة الكرخ للعلوم

الخلاصة
في هذا البحث تم دراسة وتحضير عينات من السليكون المسامي باستخدام سليكون من النوع (n-type) وباتجاهية (111) باستخدام طريقة التنميش الكهروكيميائي ضوئي بكثافة تيار($20\ mA/cm^2$) وبزمن تنميش مختلف (5, 10, 15, and 20 min). اظهرت نتائج فحوصات الخصائص التركيبية للسليكون المسامي باستخدام فحص (XRD) زيادة عرض منتصف القمة للمنحني مع زيادة زمن التنميش وبالتالي يقل الحجم الحبيبي من (46.99mm الى 4.36 nm)، ومن فحص (SEM) اظهرت النتائج ان عمق المسام يزداد مع زيادة زمن التنميش، ومن فحص (AFM) تبين ان معدل الحجم الحبيبي يزداد من (63.55nm to 75.68nm) وكذلك خشونة السطح تزداد ايضاً من (2.2nm to 17.9nm) مع زيادة زمن التنميش، اما فحص مطياف اللمعان (PL) بين ان طيف السليكون المسامي يقع ضمن منطقة الضوء المرئي وبزيادة زمن التنميش فأن المنحني يزاح نحو الاطوال الموجية القصيرة وبالتالي تزداد فجوة الطاقة البصرية (1.99eV to 2.02eV).

Introduction

In the mid-1950s, the Uhlirs, a husband and wife pair based at Bell laboratories, made an unintentional discovery of porous silicon. Using aquatic or non-aquatic electrolytes containing HF to etch crystalline of Si, porous silicon is formed [1]. The diameter of the pore can be used to classify porous silicon. Micropores are pores with a diameter of fewer than 2 nanometers. Mesopores are pores with a diameter of between 2 and 50 nanometers. Macropores are pores with a diameter greater than 50 nanometers [2].

Porous silicon (P-Si), a nanostructured substance, has gotten a lot of recognition as a way to improve silicon's optical properties (Si) [3]. P-Si layers formed by electrochemical etching (ECE) on crystalline Si (c-Si) wafers have photoluminescent and electroluminescent characteristics like semiconductors with an immediate energy gap. Because of its large bandgap, high optical transmission range (700 – 1000 nm), squab absorption spectrum, surface roughening, and a strong anti-reflection coating, P-Si has become a popular material in electronics and optoelectronics (ARC). The key reasons that boost P-Si relative to c-Si are the surface roughness and reduce effective refractive index, which may minimize the loss of sunlight radiation reflection [4][5].

Porous silicon's growing utilize in electronic implementations such as light-emitting diodes, light-exam instruments, solar cells photoelectric, gas exam instruments, microdevices, biological exam instruments, and essential physics has resulted in an especially wealthy field of research into its physical and chemical characteristic. [6]

Porous silicon manufacture is a fairly easy method needing single a limited amount of instrument. There are four main techniques of manufacturing of P-Si layer: electrochemical, photo-electrochemical, and photochemical and stain etching methods [7].
The difference between the photoelectrochemical etching technique and electrochemical etching technique just needs to utilize a photon source like intensive light or lasers, where it is utilized to supply the desired holes in the irradiated area of the Si wafer to begin the etching process [8]. In the n-type semiconductor, the majority of carriers are electrons; to create an appropriate amount of holes to perform the reaction of corrosion, the semiconductor should be illuminated. Light is generated an electron-hole couple at a nigh of the interface between semiconductors, and the holes are sweeping to the top by the built-in area [9]. The limitations of the photoelectrochemical etching technique are irregular lighting distribution and the etching process is considered relatively slow compared to the electrochemical etching technique [10].
The structure, pores diameter, porosity, and thickness of the shaped porous layer all play a role in the physical characteristic of P-Si. The P-Si physical properties can vary relies on parameters of etching such as density of current, concentration of HF, or substrate doping form and degree. Furthermore, where the function size of P-Si pores is lower than a little nanometer, numerous quantum-size impacts arise, making P-Si much more intriguing [11] [12].

Experimental Work

P-Si samples are prepared using (PECE) anodization etching of n-type element (111) orientated with a resistivity (10 Ω.cm) at a current density (20 mA/ cm^2) and etching time is (5, 10, 15 and 20 min) and using the etching cell made up of Teflon since Teflon does not interact with HF acid. Used the Halogen lamp at the power of 120 W. The wafers are then turning over items with dimensions of (2×2) cm^2.

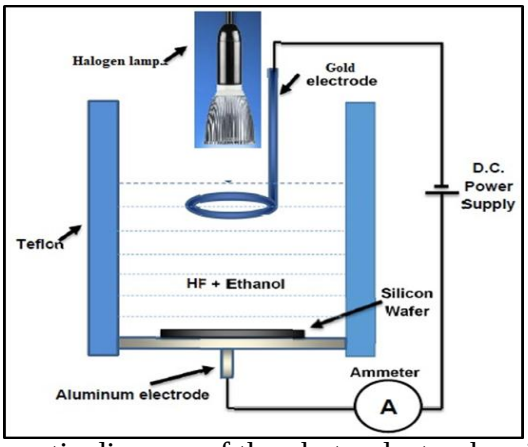

Fig. (1) Schematic diagram of the photo-electrochemical etching.

The etching solution containing 1:1 of HF (48%): Ethanol (99.99%) severally and therefore the engraved space of sample is (1.3677 cm^2), the solution feature prevents hydrogen molecules from clumping together and ensures that the Halogen lamp enters the sample. In this process, a gold electrode (immersed in solution) was used as a cathode, while an anode made of aluminum was used as an anode, and it was put in the lowest of the Teflon and the Silicon was place on it as shown in Figure (1).
Four samples are obtained. A series of structural and optical characterizations are made using X-ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), Atomic force microscopy (AFM), and Photoluminescence (PL).

Results and Discussion

The X-ray diffraction patterns of the Si substrate before and after etching at different times were shown in Figure (2) and (3). All samples showed the (111) peak located around $2\theta = 28.5°$ according to JCPDS (Card No. 96-901-3108). The peak start as sharp feature for crystalline Si before etching, with high intensity. Increasing the etching time cause to increase the peak broadening due to formation of nano particles for porous silicon. It is also observed that the peak intensity declines with rising the processing time due to reducing the crystallinety. Lattice constant

is slightly affected by porous time. Table (1) shows the peaks parameters for (111) direction at different etching time.

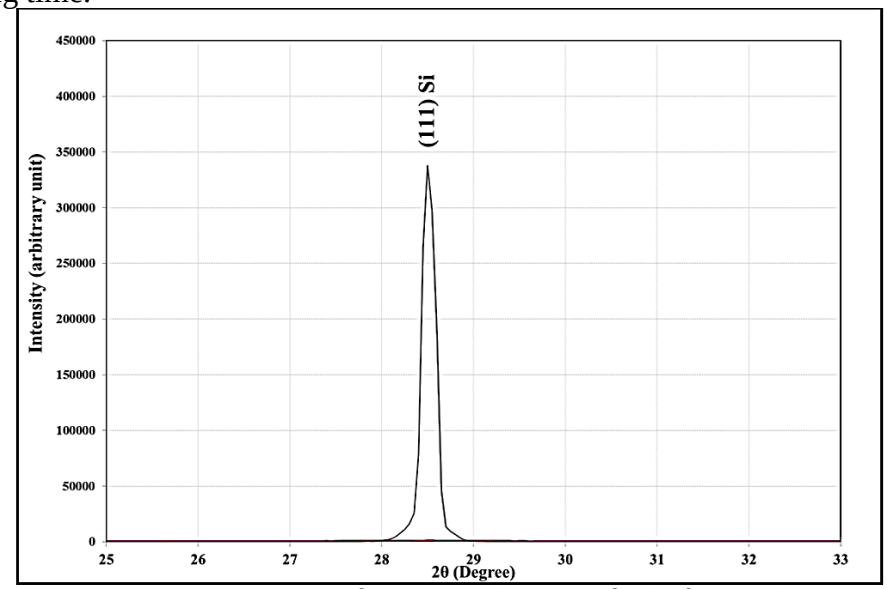

Fig. (2): XRD patterns for (111) silicon wafer before etching.

According to Table (4.2) the values of d_{hkl}, lattice parameters and cell volumes are nearly equal to the standard values in the JCPDS standard card. The effect of etching time strain, crystalline size C.S, dislocation density δ and number of crystallites per area are calculated by using the following equations.

$$C.S = \frac{0.9\lambda}{\beta \cos\theta} \quad \ldots\ldots\ldots (1)$$

$$\varepsilon = \frac{\beta \cos\theta}{4} \quad \ldots\ldots\ldots (2)$$

$$\delta = \frac{1}{(C.S)^2} \quad \ldots\ldots\ldots (3)$$

$$N = \frac{t}{(C.S)^3} \quad \ldots\ldots\ldots (4)$$

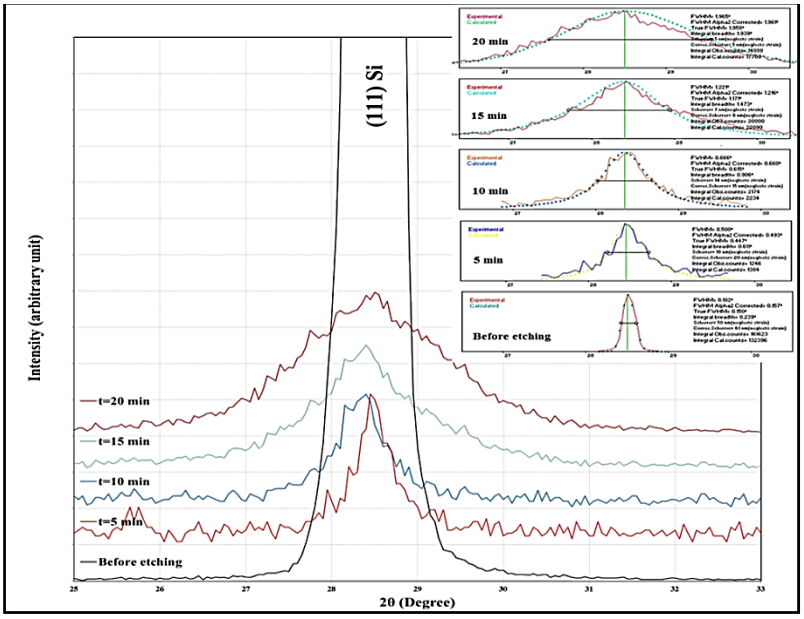

Fig. (3) XRD patterns for (111) Si substrate and porous Si at different etching times and their Gaussian fitting.

Table (1) The XRD results for (111) direction and the influence of etching times on some structural parameters for porous silicon.

Samples	Etching time (min)					Standard values
parameters	0	5	10	15	20	
2θ (degree)	28.50	28.45	28.35	28.40	28.50	28.352
FWHM (Deg.)	0.182	0.500	0.666	1.221	1.965	-
dhkl (Å)	3.1294	3.1347	3.1456	3.1401	3.1294	3.1454
Lattice parameter(Å)	5.42019	5.42952	5.44828	5.43889	5.42019	5.448
Unit cell volume ($Å^3$)	159.2	160.1	161.7	160.9	159.2	161.7
C.S (nm)	46.99	17.12	12.85	7.01	4.36	-
Strain	0.00077	0.00211	0.00281	0.00516	0.00831	-
δ *1015 (m^{-2})	0.45	3.41	6.06	20.35	52.60	-
No *1016 (m^{-2})	0.19	3.99	9.43	58.06	241.31	-

Figure (4) illustrates the difference of crystalline size and lattice strain with porosity time. The crystalline size decreases while the lattice strain increased due to reducing the crystals volume. In addition, the dislocation density within the lattice also increased as shown in Figure (5).

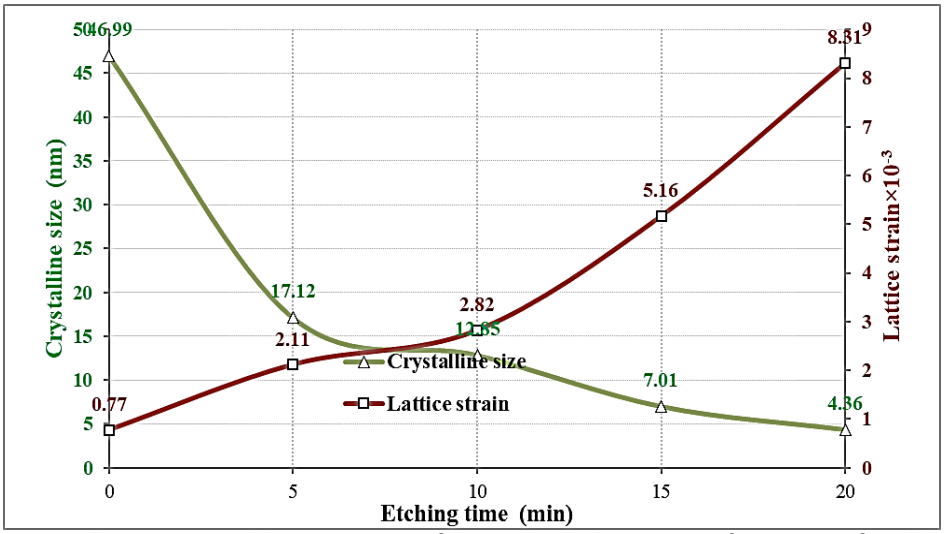

Fig. (4) Crystalline size and lattice strain for porous silicon as a function of etching time.

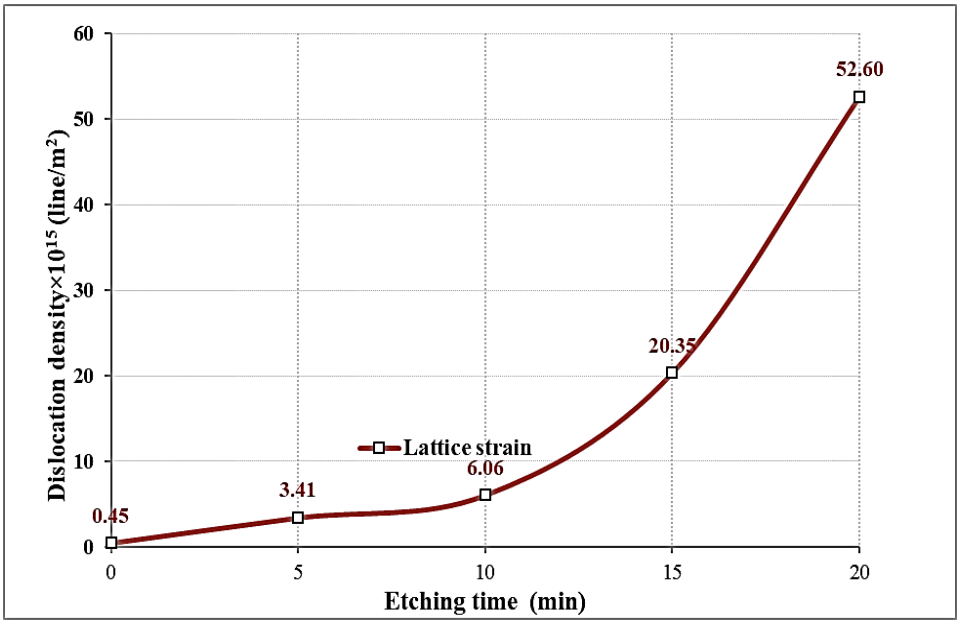

Fig. (5) Dislocation density as a function of etching time.

Figures (6) to (9) illustrate the surface and cross-section images of the scanning electron microscope (SEM), at different magnification powers, for porous silicon prepared using photoelectrochemical etching at different times, starting from (111) n-type Si wafer. The sample prepared in five minutes appears to form grooves and pores to a depth of 6.18 μm. The images with high magnification power show that the outside surface layer and the area of the pores are covered with a layer consisting of small nanoscale spheres around 50 nm diameter. Increasing the preparation time to 10 minutes led to form of hexagonal holes with a depth of 11.25 μm. The increase in preparation time to 15 min cause to increase in the diameter of these holes larger than 1 μm and increased the depth of the porosity depth to about 12.28 μm. Whereas, the samples prepared in 20-minute time crated as a porous substance with adjacent cavities, of very thin walls, and a penetration depth of 21.27 μm. All sample surfaces, as well as the walls separating the pore spaces, were covered with a layer of spherical nanoparticles with a size of about 50 nm.

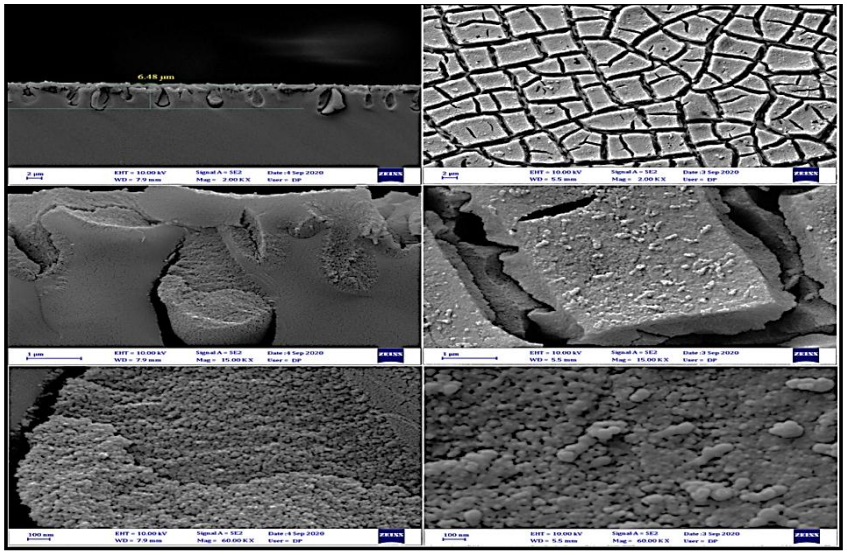

Fig. (6) SEM images for porous silicon at different magnification powers prepared at 5 minutes etching time (surface view to the right and cross-section view to the left).

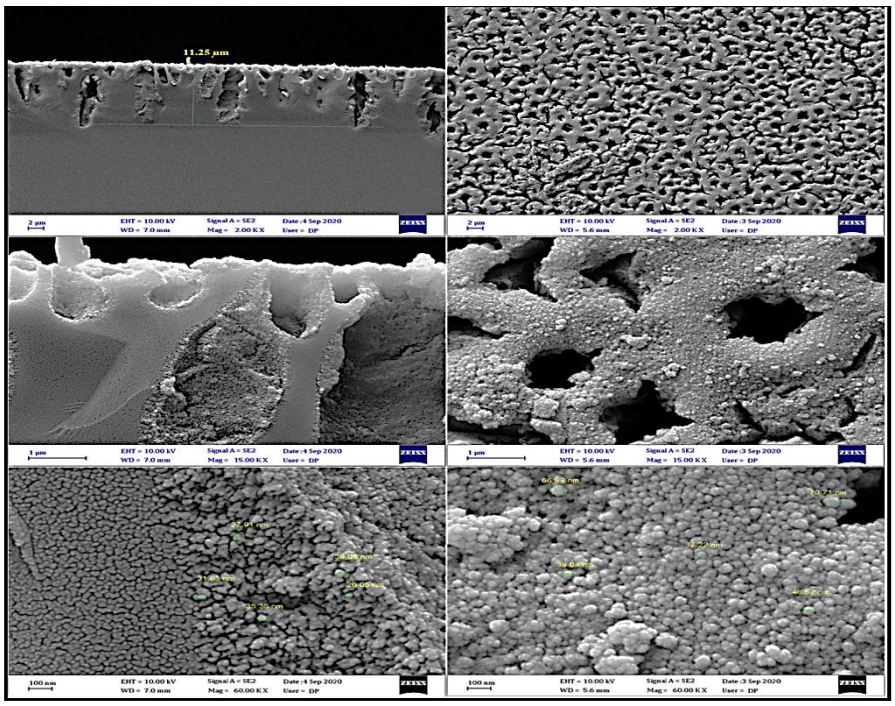

Fig. (7) SEM images for porous silicon at different magnification powers prepared at 10 minutes etching time (surface view to the right and cross-section view to the left).

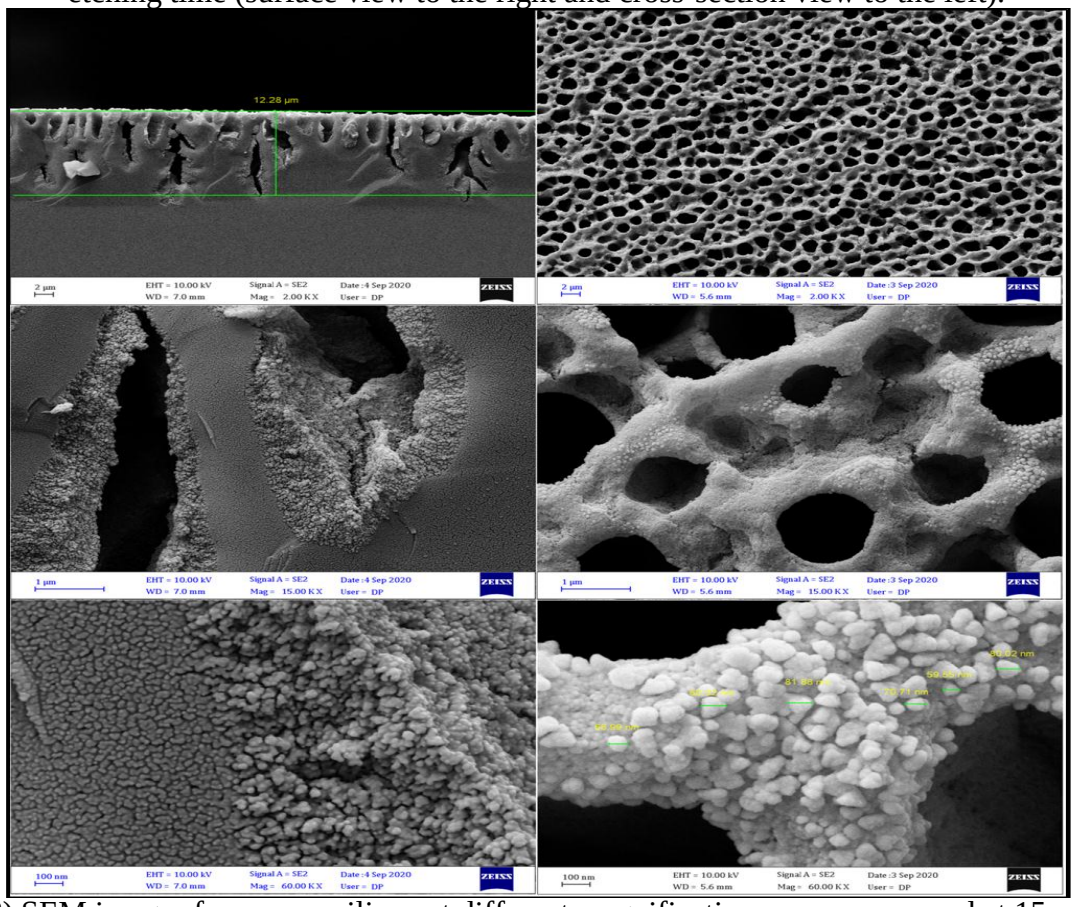

Fig. (8) SEM images for porous silicon at different magnification powers prepared at 15 minutes etching time (surface view to the right and cross-section view to the left).

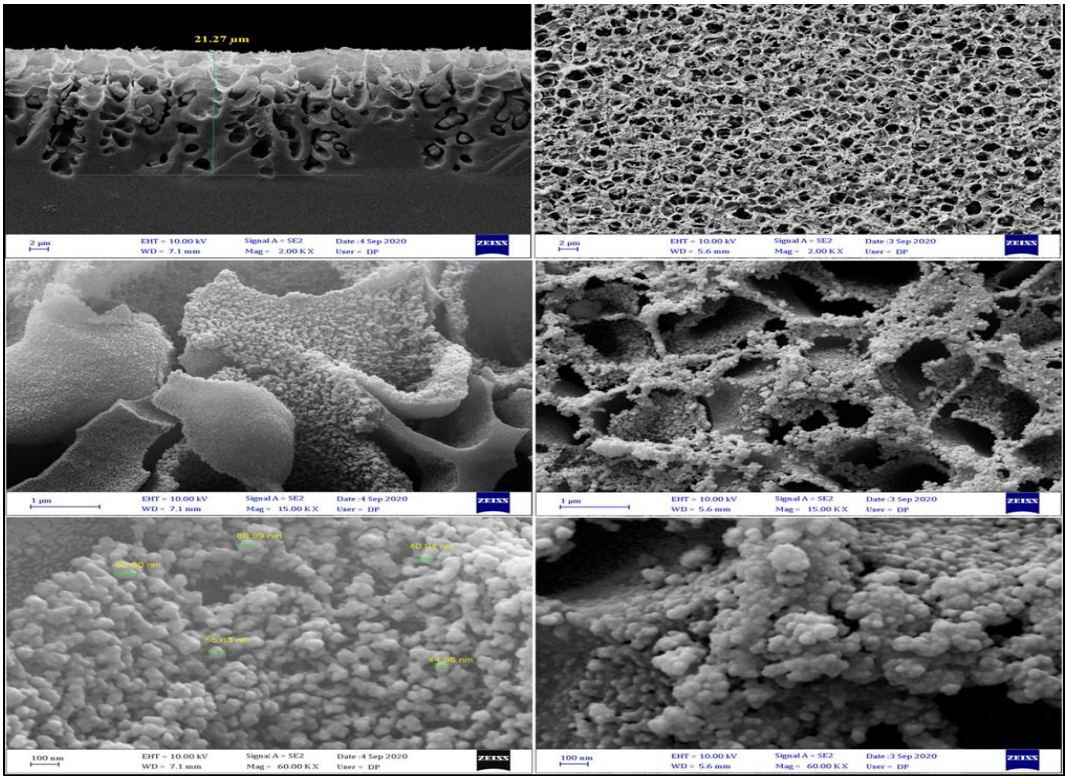

Fig. (9) SEM images for porous silicon at different magnification powers prepared at 20 minutes etching time (surface view to the right and cross-section view to the left).

The 2D, 3D AFM images and the cumulating histogram for porous silicon (P-Si) prepared at different times were shown in Figure (10). The sample appeared with many halls separated by walls. The separation walls become thinner and finely become removed with increasing the etching time. The particle size has narrow distribution at 5 min etching time and become of wide distribution, especially at 20 min etching time.

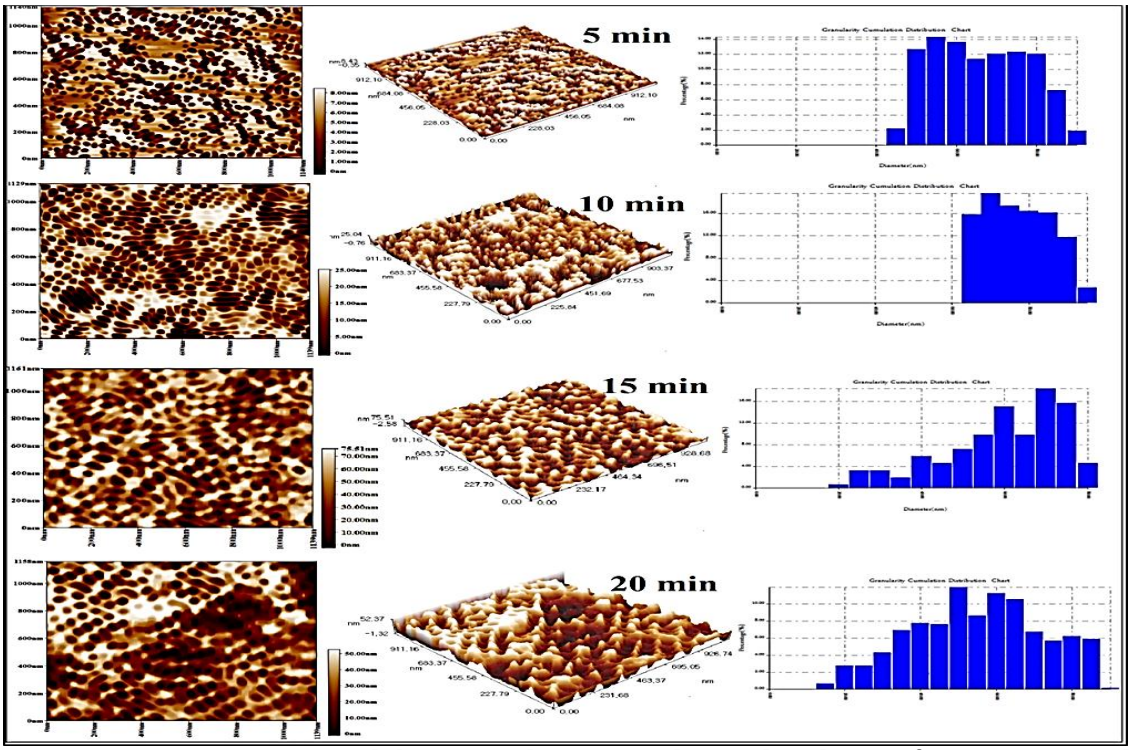

Fig. (10) 2D, 3D AFM images and their granularity cumulating distribution for P-Si prepared with different times.

Table (2) AFM parameters (Average Diameter, Average roughness and RMS roughness for P-Si prepared with different times.

Etching time	Average Diameter (nm)	Average roughness (nm)	RMS roughness (nm)
5	63.55	2.2	2.54
10	74.78	6.45	7.45
15	75.55	12.2	15.2
20	75.68	17.9	20.1

The porous silicon can emit a red visible luminescence at room temperature by photoluminescence measurements. The real cause for the luminescence probably is the fine microporous in the silicon layer which is present at the pore walls, as shown by the SEM images. It can be seen from Figure (11) that the emitting light of peak at 622 nm for the sample prepared at the time of 5 min. It is noticed from the spectra, for the same excitation, that nearly the same photoluminescence peak intensity with the increase of the preparation time, and a simple move in the peak wavelength of photoluminescence toward shorter wavelengths, as shown in Table (3). a simple move in the peak location wavelength of photoluminescence to shorter wavelength as rising the etching time could be explained by the quantum imprisonment phenomena, due to reducing the nanocrystallites and the increase of porosity, which causes to increase the band-gap and the corresponding peak will blue shifted.

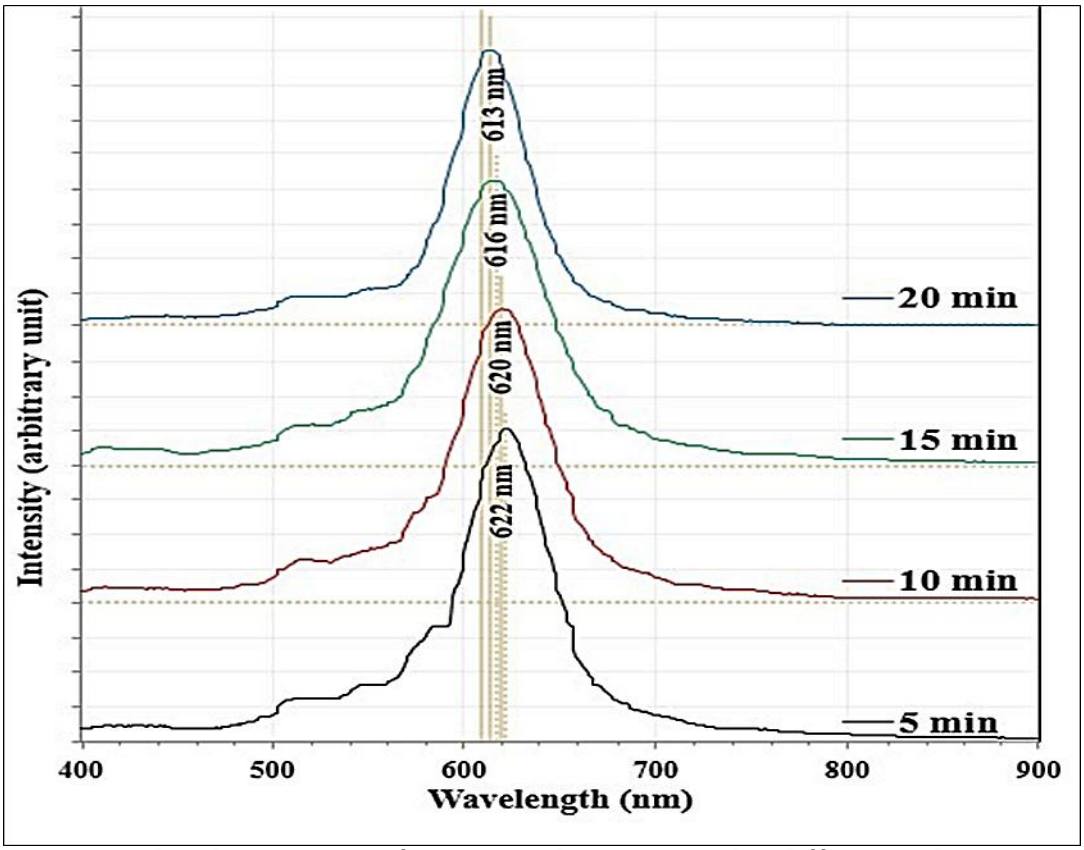

Fig. (11) Photoluminescence for porous silicon prepared at different etching time.

Table (3) The PL peak and the calculated energy gap for different porosity times.

Etching time (min)	λ (nm)	Energy gap (eV)
5	622	1.99
10	620	2.00
15	616	2.01
20	613	2.02

Conclusions

1. Through examinations of the porous silicon chips, it was revealed that the depth of the pores increases with increasing the etching time, thus the surface roughness and surface area increases and the particle size decreases, also noted that the best substrate at an etching time (10 min).
2. The PL test showed a shift of the curve apex towards short wavelengths when increasing the etching time. The spectrum of porous silicon falls within the visible spectrum of the red color region.

References

[1] M. J. Sailor, *"Porous Silicon in Practice: Preparation, Characterization and Applications"*, First Edit. Wiley-VCH Verlag GmbH & Co. KGaA, 2012.
[2] J. N. Bugayong, "Electrochemical etching of isolated structures in p- type silicon", Msc. thesis, Louisiana State University and Agricultural and Mechanical College, 2011.
[3] M. S. Almomani, N. M. Ahmed, M. Rashid, M. A. Almessiere, and A. S. Altowyan, "Broadband visible emission from photoelectrochemical etched porous silicon quantum dots containing zinc", *Mater. Chem. Phys.*, vol. 258, 2021.
[4] K. A. Salman, Z. Hassan, and K. Omar, "Effect of Silicon Porosity on Solar Cell Efficiency", *Int. J. Electrochem. Sci.*, vol. 7, pp. 376–386, 2012.
[5] M. Kopani *et al.*, "Effect of etching time in hydrofluoric acid on the structure and morphology of n-type porous silicon", *Appl. Surf. Sci.*, vol. 532, 2020.
[6] B. Pratama, I. Syahidi, E. Prayogo, K. Triyana, H. Susanto, and R. Suryana, "Porous silicon

fabrication on N-type Si (111) electrochemical anodization technique with HF: methanol solution", *Mater. Today Proc.*, vol. 44, pp. 3430–3436, 2021.
[7] P. R. Malempati, "Surface-enhanced Raman spectroscopy substrates based on nanoporous silicon and pattern transfer", M.Sc thesis, Louisiana State University and Agricultural and Mechanical College, 2011.
[8] N. A. Abdulkhaleqa, A. K. Hasanb, and U. M. Nayef, "Enhancement of photodetectors devices for silicon nanostructure from study effect of etching time by photoelectrochemical etching technique", *Opt. Int. J. Light Electron Opt.*, vol. 206, 2020.
[9] V. Lehmann, *"Electrochemistry of Silicon: Instrumentation, Science, Materials and Applications."* Wiley-VCH Verlag GmbH, 2002.
[10] S. Carrillo, L. Gayou, G. Salgado, D. Macuil, and C. Ramírez, "Structural properties of porous silicon obtained with laser photoetching assisted by computerized numeric control", *J. Laser Appl.*, vol. 33, no. 2, 2021.
[11] P. Kumar and P. H. Faculty, "Effect of Etching Parameter on Pore Size and Porosity of Electrochemically Formed Nanoporous Silicon", *J. Nanomater.*, vol. 2007, pp. 1–5, 2007.
[12] H. K. Abood and F. A.H. Mutlak, "Structural, Morphological and Optical properties of n-type Porous Silicon-effect of Etching Current Density", *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 757, 2020.