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# Study the Effect of Etching Time on the Morphology of Porous Silicon Surfaces Manufactured via Photochemical Etching

Given the importance of silicon nanocrystals in many applications of microelectronics, energy storage, and biomedicine, porous silicon was prepared from a n-type silicon wafer with a crystal orientation (100), negative conductivity, and low resistance (4.3 x 10^-4 ohm*cm) by photochemical etching technique in the presence of a halogen lamp (1000 W) and concentrated hydrofluoric acid (HF 40%). The effect of changing the etching time (70 minutes, 80 minutes, and 90 minutes) on the morphology of their surfaces was studied, and the results of atomic force microscopy (AFM) showed the formation of porous layers (392.8 nm, 491.3 nm, and 566.3 nm) and average diameters of the grains and nanoparticles (101.4 nm, 106.9 nm, and 44.85 nm) respectively. The results indicated that the surface roughness and thickness of the porous layer of the samples prepared increases when the etching time increases and decreases when the etching time decreases.

***Keywords:*** Porous Silicon; Etching Time; Photochemical Etching; Nanoparticles
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## 1. Introduction

The importance of silicon nanofabrication technology has emerged through the great efforts that have been made to organize the structures of atoms and the compositions of materials that fall within the nanoscale [1], in order to benefit from them in many laser [2] and optoelectronic applications [3], in addition to their nanoscale optical properties [4], which led to the appearance of a quantum confinement effect on its crystals through the movement of electrons and holes on its surfaces inside the crystal [5], which in turn led to an increase in its efficiency of electrical conduction, and the effectiveness of its light radiation resulting from the processes of controlling its wavelengths [6].

Through the multiple modifications made by researchers to the properties to develop silicon to produce optical and electronic properties completely different from the properties of the parent silicon material, what is called porous silicon appeared [7], which is forked and complex networks of isolated pores that are separated from each other by thin walls [8]. As a result of material reduction and miniaturization processes that lead to very small dimensions and sizes, we have the formation of nanoporous silicon [9].

The formation of porous silicon has given new dimensions to technologies based on crystalline silicon [10], as it has become of wide and great interest as a result of the changes and transformations that occur in the nature of its indirect energy gap, which turns into an energy gap direct, leading to improving the efficiency of its photoluminescence [11]. Enlarging the energy gap brings about changes in the resistance of the material, that increases with a decrease in the size and dimensions of the pores [12], in addition to the depletion processes of charge carriers accompanying the preparation process [13].

There are many techniques for preparing porous silicon, such as electrochemical etching [14], photoelectrochemical etching [15], spot etching [16], and photochemical etching technique using different light sources, such as using types of lasers or using spherical or flat halogen lamps [17-19]. It is possible to control its porosity and atomic dimensions [20,21], in order to work in a wide range of the electromagnetic spectrum which extends from infrared to the entire visible spectrum and even near ultraviolet [22-25].

We will show in this article the extent of time effect on the morphology of the porous surface of silicon produced through the process of preparation by the photochemical method, relying on a halogen lamp as one of the light sources to melt random areas of the silicone surface that determined through the atomic force microscope (AFM). Thus improving its properties and developing it to benefit from it more widely in applications of integrated circuits and electronic devices.

## 2. Experimental Part

The experiment is carried out on a single-sided n-type silicon chip whose surfaces are completely polished, with a resistivity of 4.3x10$^{-4}$ Ω.cm and a crystalline orientation of (100), so the slice is cut into dimensions of 0.7x0.5 cm to be prepared for preparing porous silicon samples through using the photochemical etching system.

The samples are washed in diluted hydrofluoric acid (HF 10%) for 8 minutes to remove the layers of oxide stuck on it. Then, the samples are immersed in acetone and ethanol for 6 minutes to wash and clean them of the impurities stuck on them and to remove the remaining diluted hydrofluoric acid (HF 10%) from their surfaces. The samples are then left to dry.

The preparation system consists of a Teflon container, which is a solid polymeric material characterized by its high resistance to acids. The diameter of the container ranges 5.5 cm, its height is 3.5 cm, and the drilling depth from the inside is 1.5 cm. In the middle of container from the inside is a circular protrusion with a diameter of 1.5 cm, and the height of the protrusion ranges 0.7 cm from the surface of the drilling depth. The circular protrusion contains a support engraved in its face in the shape of the letter (U) to place the sample on it, while the Teflon container is filled with hydrofluoric acid (HF 40%) and the sample to be prepared is placed on the support so that it is covered by the HF solution, and a halogen lamp is shined (1000 W) on it vertically.

Silicon samples are prepared with variable etching times (70, 80, and 90 min) and constant resistivity (4.3x10$^{-4}$ Ω.cm) as well as constant concentration of HF (40%) using light source (halogen lamp 1000 W). This ensures that the process of etching, dissolving, and formation of pores has occurred on the upper surface of the sample facing the light source, by observing the appearance of hydrogen bubbles on the surface of the sample resulting from chemical reactions leading to the dissolution of the silicon, or through the change in the color of its surface approaching the reddish-brown color that indicates the formation of the porous layer [26,27].

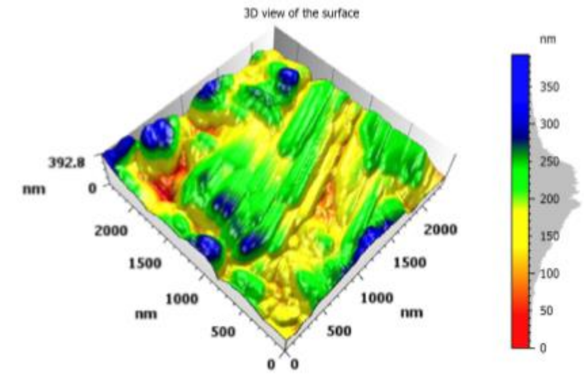
After the etching process is completed, we lift the sample with iron tweeze and place it in a tightly closed plastic container filled with methanol to prevent oxidation and preserve its properties.

The fine details of the surface morphology and the structures of the nanoparticles formed on the surface of the prepared samples are studied through an atomic force microscope (AFM) for the purpose of analyzing them and knowing the nanostructure of the porous layer, its thickness range, and roughness rate of its surface and particle sizes.

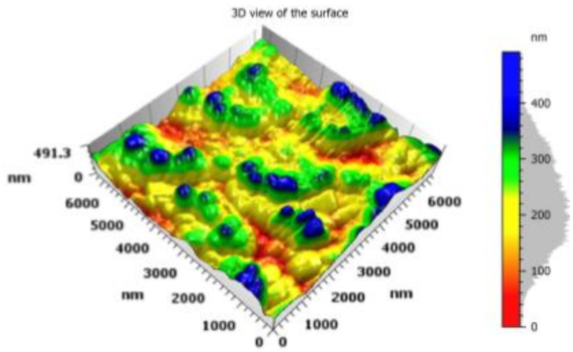
### 3. Results and Discussion

The process of decomposition of silicon molecules takes place as a result of the rapid exchange of silicon-fluoride bonds Si-F, which interact with water molecules $H_2O$, when placed in a dilute HF acid solution to form strong and stable covalent bonds. As a result, dense groups of silicon-hydroxyl bonds Si-OH, are formed that lead to formation of bridges and stable structures from Si-O-Si bonding to reveal oxide nuclei [28,29].

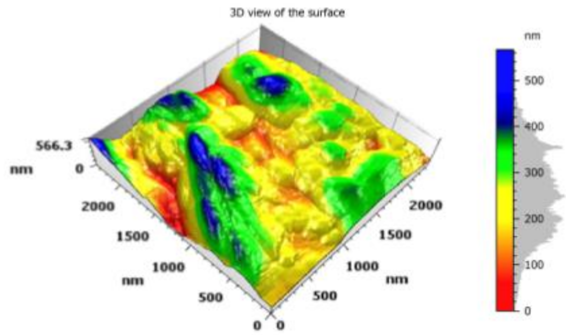
The precise dissolving mechanism of silicon occurs through the presence of important gaps for electronic polishing and etching to occur. When samples are immersed in a concentrated HF acid solution at different etching times (70, 80, and 90 min), porous layers of nanoporous silicon are formed, which is shown by 3D imaging of the morphology of silicon surfaces through the AFM examination shown in Fig. (1), where the silicon surface is saturated with hydrogen.




**(a)**




**(b)**




**(c)**

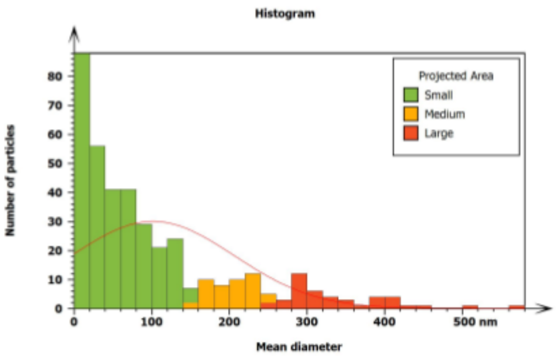
**Fig. (1) 3D AFM examination of the morphology of silicon surfaces prepared at different etching times: (a) 70 min, (b) 80 min, and (c) 90 min**

As soon as the surface is illuminated by the light of the source directed at it, it will begin to generate electron-gap pairs as a result of the absorption of light inside the chip, which in turn helps in the formation of the depletion layer in the illuminated area that It removes the silicon atom from its surface, leaving behind a hole or freckle to change the surface geometry and distribution of the electric field, which causes irregularities in its surface and the formation of holes [30,31].

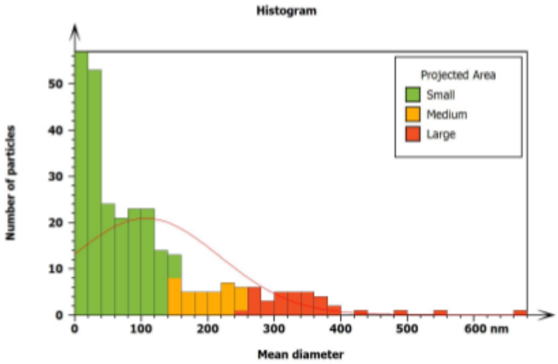
The thickness of the porous layer and the average roughness surface of the prepared samples increase as the etching time increases and decrease when the etching time decreases, which leads to an increase in the root mean square (RMS) roughness, and shows the surface shape of the sample in the form of a semi-squishy structure and they are separated from each other by empty pore grooves and contain structures with pointed heads as shown in Fig. (1). This is a result of agglomerations of nanoparticles due to the continuation of etching processes, which leads to a change in the sizes and dimensions of the nanostructures of the prepared samples.

The surface kurtosis ($S_{sk}$) of the prepared samples shows a Gaussian distribution containing high peaks and low valleys that reflect the homogeneity of the surface skewness ($S_{ku}$) that gives a logarithmic distribution to show the differences of nanostructures in the distributions of surface heights.

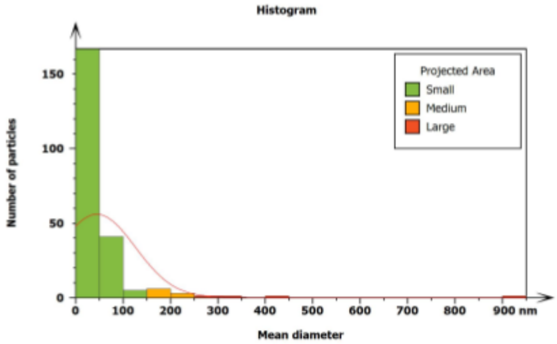
Figure (2) shows the number of particles formed on the surface of the prepared sample due to the large transfer of positive charges accompanying the increase in etching time, which leads to a process of etching and gouging in multiple directions on the surface, sides and walls, and randomly, leading to an increase in the movement of the gaps and their numbers, and thus the production and formation of nanostructures particles of different compositions distributed with a certain homogeneity along the surface of the sample. The average diameters of the formed nanostructure are 101.4 nm, 106.9 nm, and 44.85 nm, which contributes to increasing the surface area, which in turn helps in increasing photovoltaic generation, enabling us to obtain spectral emissions within the visible region. These variables related to the distribution of the formed particles, the sizes of the surface pores, and the diameters of their nanostructures are used in many applications of nanotechnology, materials science, and micro-optoelectronics.




(a)




(b)




(c)

**Fig. (2) Statistical distribution of the numbers of particles formed on the surfaces of the prepared samples with their mean diameters nanoscale at different etching times (a) 70 min, (b) 80 min, and (c) 90 min**

## 4. Conclusion

Photochemical etching using a 1000W halogen lamp as the light source is an effective way to obtain porous silicon layers with multiple structures and properties. The results showed that increasing the etching time in the preparation processes when the concentration of hydrofluoric acid, the resistivity, and the light source are constant will lead to an increase in the sizes and diameters of the nanoparticles, which is useful in photodetectors, energy storage, and the manufacture of diodes.

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