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Unraveling the Influence of Hydrofluoric Concentration on the Morphology of Porous Silicon Surfaces Fabricated through Photochemical Etching using Sunlight

Samples of n-type porous silicon samples with negative conductivity, low resistivity ($4.3x10^{-4}$ Ω.cm) and crystalline orientation (100) were prepared by photochemical etching method using sunlight as a light source. The intensity of the incident sunlight was collected and focused on the surface of the sample through a telephoto lens with a diameter of 7.5 cm and a focal length of 30 cm. The effect of changing concentrations of hydrofluoric acid (20%, 30%, and 40%) when using etching time of 30 min and illumination intensity of 6181 mW/cm^2 was studied. The results of surface morphology showed forming porous layers with thicknesses 527.7, 594.7, and 663.4nm and mean grain diameters of 104.9, 121.1, and 99.80 nm, respectively.

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1. Introduction

The discovery of the phenomenon of photoluminescence in porous silicon prepared from crystalline silicon wafers at room temperature led to increasing interest in porous silicon structures that are characterized by an indirect energy gap [1,2], in order to give it a broad spectrum that extends from infrared radiation, and continues to the entire visible spectrum and may reach near ultraviolet spectrum by controlling the porosity of their surfaces and their atomic dimensions [3-5].

The processes of reducing the sizes of the pores and decreasing them to extremely small sizes and dimensions during the processes of preparing porous silicon will form complex and isolated networks of pores that lead to their separation and independence from each other with thin walls and the creation of pits and trenches between them [6-8], forming very small and patterned areas in the form of different nanostructures with semi-spherical or irregularly shaped heads to achieve quantitative confinement. Then, what is called nanoporous silicon is formed [9,10].

As a result of the photoluminescence processes that occur on the surfaces of porous silicon, its porous structures are stimulated to increase its ability to absorb light, which is used in the applications of photodetectors [11-13], which leads to an increase in the amount of light energy, and thus reduces the losses resulting from recombination, enabling us to convert the absorbed solar energy into electrical energy for use in solar cell applications and generating renewable energy [14-16]. Because of their porous surfaces of different sizes and distributions it provides large areas for contribute to processes of storing and preserving electrical charges, and works to rearranging them to be highly efficient in applications of energy storage systems such as electrical capacitors and batteries [17,18].

The changes which occur in the concentrations of chemicals used in their preparation processes, including the change in hydrofluoric acid concentration, which produces their porous structures using the photochemical etching technique occurs without applying any external effort to provide their surfaces with the gaps [19,20]. It is processes opposite to the preparation processes using the electrochemical etching technique, which requires an applied external effort on it and which makes it of great importance in optical sensing applications [21,22].

This article seeks to shed light on the importance of changing the concentration of hydrofluoric acid in light of the stability of other influences and its effective role in shaping porous silicon surfaces and the changes that occur to them when they are prepared using the photochemical etching technique, by taking advantage of the energy of sunlight that is absorbed by the prepared porous silicon surfaces because It is considered one of the most important sources of renewable energy.

2. Experimental Part

Based on the photochemical etching system and using sunlight as a light source, as shown in Fig. (1), n-type single-sided silicon slices were prepared with electrical resistance of 10^{-4} Ω.cm. Their surface is completely polished with crystalline orientation of (100). The material is cut into small samples with dimensions of 1.0x0.5 cm. It is then placed in a solution of acetone and ethanol for 5 minutes to remove the impurities stuck to it and get rid of the remaining diluted HF solution on it. After that, the samples are left to dry in order to configure them for the preparation process.

Fig. (1) Photochemical etching system of this work using sunlight as a light source

Through the light source (sunlight), the optical power of the lens with a diameter of 7.5 cm and the illumination intensity is calculated by multiplying the total lens area by the intensity of solar radiation. The average radiation intensity of 140 mW/cm^2 was adopted. So the value of both the optical power and the illumination intensity per (cm^2) are 6181 mW and 6181 mW/cm^2, respectively.

Porous silicon samples are prepared at different hydrofluoric acid concentrations (HF 20%, HF 30%, and HF 40%) at constant etching time (30 min), resistivity (10^{-4} Ω.cm), and illumination intensity (6181 mW/cm^2). Therefore, the samples are placed inside a cylindrical Teflon container known for its high resistance to acids and corrosion. The diameter of the Teflon container is 5.5 cm, an external height of 3.5 cm, and an internal drilling depth of 1.5 cm. In the middle of its internal design is a cylindrical protrusion with an engraved face in the shape of the letter (U) to hold the samples, where a container is filled with HF 40%, so that immersed of the surface of the sample, and then sunlight is shined on it, which in turn produces a light intensity of 6181 mW/cm^2 to contribute to the formation of the porous layer.

The formation of pores and the etching processes are confirmed through the chemical reactions that occur on the upper surface of the samples, since we notice the appearance of small hydrogen bubbles as a result of the dissolution of the silicone and their surface reddening in a color close to brown as a result of the continuing etching processes on their surface [23,24].

After the preparation process is completed, the sample is lifted with iron forceps to preserve its surface morphology. It is then placed in a plastic container filled with methanol and closed tightly to preserve its nano-porous structure. Its characteristics of the formed pores and the compositions of its particles are analyzed through an atomic force microscope (AFM), which shows us the shape of the porous layer and its thickness, its nanoparticles, their particle sizes, and their surface roughness.

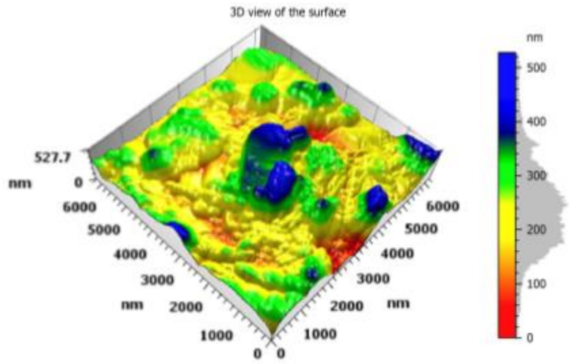
3. Results and Discussion

The precise dissolution process occurs on silicon surfaces through the presence of gaps when sunlight is shed and focused on them to complete the process of electronic polishing and the formation of pits whose molecules dissolve when they interact with water (H_2O) molecules by placing them in HF acid solution. So, Si-F bonds are formed, which leads to the formation of stable and dense bridges from the Si-OH bond, to reveal the oxide nuclei emerging are formed from the Si-O-Si bonds [25-27].

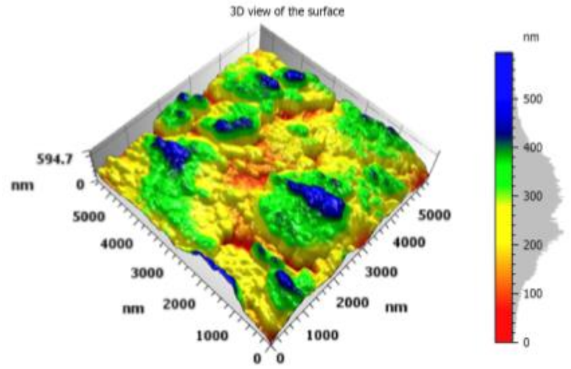
The effect of changing the concentrations of HF acid (20%, 30%, and 40%) is evident on the morphology of their surfaces at an etching time of 30 min and an illumination intensity of 6181 mW/cm^2, porous layers of nanoporous silicon are formed with structures separated by grooves, pits, and semi-spherical heads, which is shown by the 3D AFM images shown in Fig. (2).

The thickness of the porous layer of the etched samples increases as the concentration of HF acid increases and decreases when the concentration decreases. The surface roughness rate is proportional to the root mean square (RMS) roughness in the form of a Gaussian distribution, due to the occurrence of agglomerations of nanoparticles due to the continuity of etching and removal processes on their surfaces, which leads to change the sizes and dimensions of nanostructures.

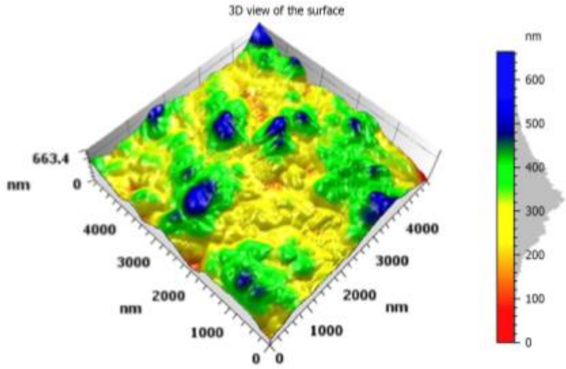
The surface kurtosis and surface skewness of the produced samples are shown in a logarithmic distribution because it contains low valleys and grooves extending with a certain homogeneity in relation to the distribution of surface heights and in a curved pattern that is close to the average values and gradually decreases when moving away from them. This distribution is used in many electronic industries related to technologies surface because it resists corrosion and reduces pressure and stress on the surface.



(a)



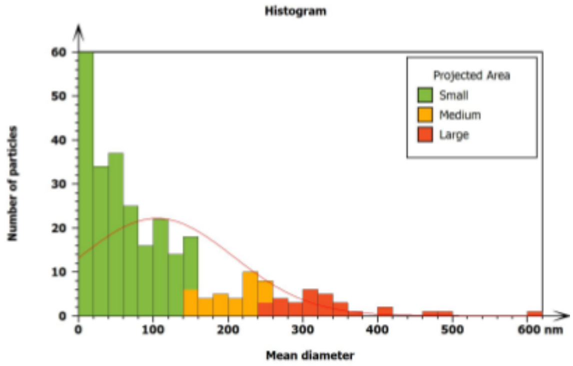
(b)



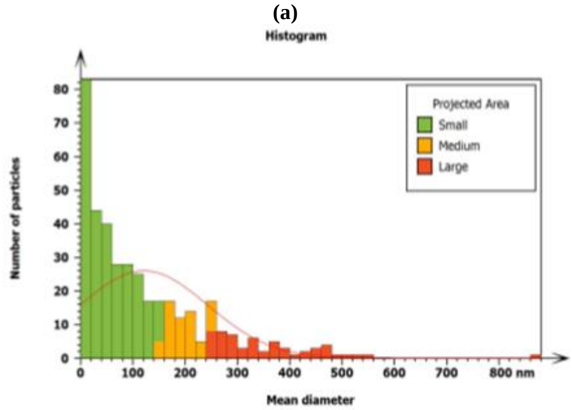
(c)

Fig. (2) 3D AFM images of silicon surfaces produced at different HF acid concentrations: (a) 20%, (b) 30%, and (c) 40%

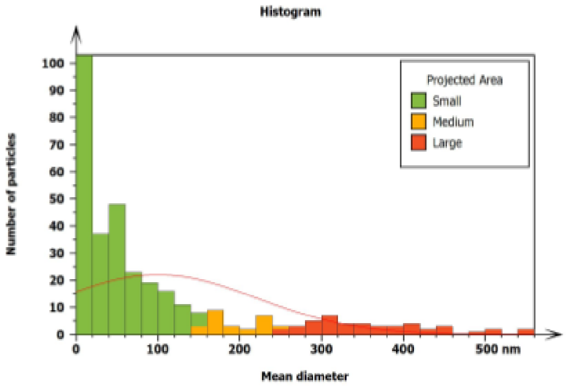
Figure (3) shows that etching operations occur randomly on the surface or on the walls or sides, leading to a significant increase in the number of flowing gaps, so different nanoparticles with multiple compositions are formed along the surface of the sample by mean diameters 104.9 nm, 121.1 nm, 99.80 nm, which increases the surface area and generates high photovoltaic to emit spectral emissions within the visible region, which can be utilized in many materials science, optoelectronics, and nanotechnology applications.



(a)



(b)



(c)

Fig. (3) Statistical distribution of the numbers of particles formed on the surfaces of the produced samples with their mean diameters nanoscale at different HF acid concentrations: (a) 20%, (b) 30%, and (c) 40%

4. Conclusion

Sunlight is one of the most promising and effective light sources in the process of preparing porous silicon slices using the photochemical etching method. It is one of the most important renewable and environmentally friendly sources of energy, and is considered as a successful alternative to other industrial sources. The results showed that increasing the concentration of hydrofluoric acid will lead to an increase in the thickness of the porous layer, and reducing it will lead to reducing the thickness of the porous layer when the etching time, resistivity, and illumination intensity are constant. It is considered useful in the applications of sensors and photodetectors, improving the efficiency of solar cells, and sensing diodes.

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