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EFFECT OF ULTRASONIC FREQUENCY ON CHEMICAL ETCHING PROCESS

Yasmeen Z. Dawood[1], Ali H. Al-Hamdani[2] and Mehdi Q. Zayer[3]
[1]Department of Physics, Collage of Education, University of Mustansiriya, Baghdad, Iraq
[2]Department of Laser and Optoelectronic Engineering, University of Technology, Baghdad, Iraq
[3]Department of Applied Science, University of Technology, Baghdad, Iraq
E-Mail: ali_alhamdani2003@yahoo.com

ABSTRACT

In this work, ultrasonically enhanced chemical etching was employed to fabricate porous silicon layer. Porous silicon layer was fabricated in p-type (111) orientation silicon by using HF solution, and HNO_3. It was found the structure of porous silicon layer on p-type Si was improved by ultrasonic. Porous silicon micro cavities with much higher quality factors can be fabricated by this method. The improved quality induced by ultrasonic etching can be ascribed to increased rates of escape of hydrogen bubbles and other etched chemical species from the porous silicon pillars' surface. The effect is attributable to effective change in the concentration of free holes carriers. Ultrasound has led to indicating probably a change in bonding configuration, and increase in oxidation. Also, a correlation was established between the ultrasonic treatment and the microstructure.

Keywords: porous silicon, electrochemical etching, ultrasonic treatment, structure properties.

INTRODUCTION

Porous silicon (PS) is a new material which has attracted attention for use in silicon based optoelectronic devices. Efforts are going on worldwide to exploit its unique properties of visible photoluminescence (PL) and electroluminescence (EL) for new applications. An important property of PS, which needs to be studied in detail, is its high reactivity with chemicals due to its large surface area and surface defects. The surface area per unit volume in this material can range from a few m^2/cm^3 to 200 m^2/cm^3, depending on the fabrication conditions. The surface can adsorb gases, liquids or chemical vapours, resulting in drastic changes in its properties [1-3].

Studies on PS properties for various applications have been undertaken by many researchers. The fact that efficient EL is observed when liquid contacts are used suggests that electrical properties are affected by the presence of liquids [4]. Another interesting aspect is the remarkable electronic passivation of silicon surfaces achieved using various techniques [5]. Very low values of surface recombination velocities have been achieved by simple immersion of bulk silicon in hydrogen fluoride (HP), leading to surface recombination centers < 10^8 cm^{-2}. This has been ascribed mainly to complete hydrogen termination of surface with no dangling bonds [6-7].

The objective of this work is to investigate the effect of ultrasound (US) on the formation of porous semiconductors. The effect of US on semiconductor processing could play an important role in determining the size of micropores in porous semiconductor. The US, on the other hand, can have similar effects such as the changes in density and crystal size through the process of sono cavitation [8, 9]. There have already been successful applications using the US cavitation to the synthesis of materials.

In this work, we report on the structural properties of porous silicon layers grown on a variety of wafers by electroless etching technique under the effect of ultrasonic treatment. We have carried out experiments in a systematic way in order to determine their effect on the formation of porous Si. AFM (Atomic Force Microscope) and FTIR measurement have been used for the subsequent analysis of the samples.

EXPERIMENTAL WORK

For chemical etching p-type (111) oriented silicon (sheet resistivity 5.25Ω/□) was used. Porous silicon layers were prepared in (HF: HNO_3: H_2O) at (1:1:2) respectively, solution using ultrasonically enhanced (frequency 22 kHz, US power 30W or 50W) chemical etching. Etching time was 20 min. PS nanostructures were investigated by atomic force microscope (AFM) JEOL JSM-IC25S. Transmittance FTIR spectra of the PS layer were measured by using a double beam Perkin-Elmer 850 spectrometer. It was shown that; the ultrasonic power of 30W and 50W resulted in a considerable increase in both the hydrogenation and the oxidation amounts in p-type Si.

RESULTS

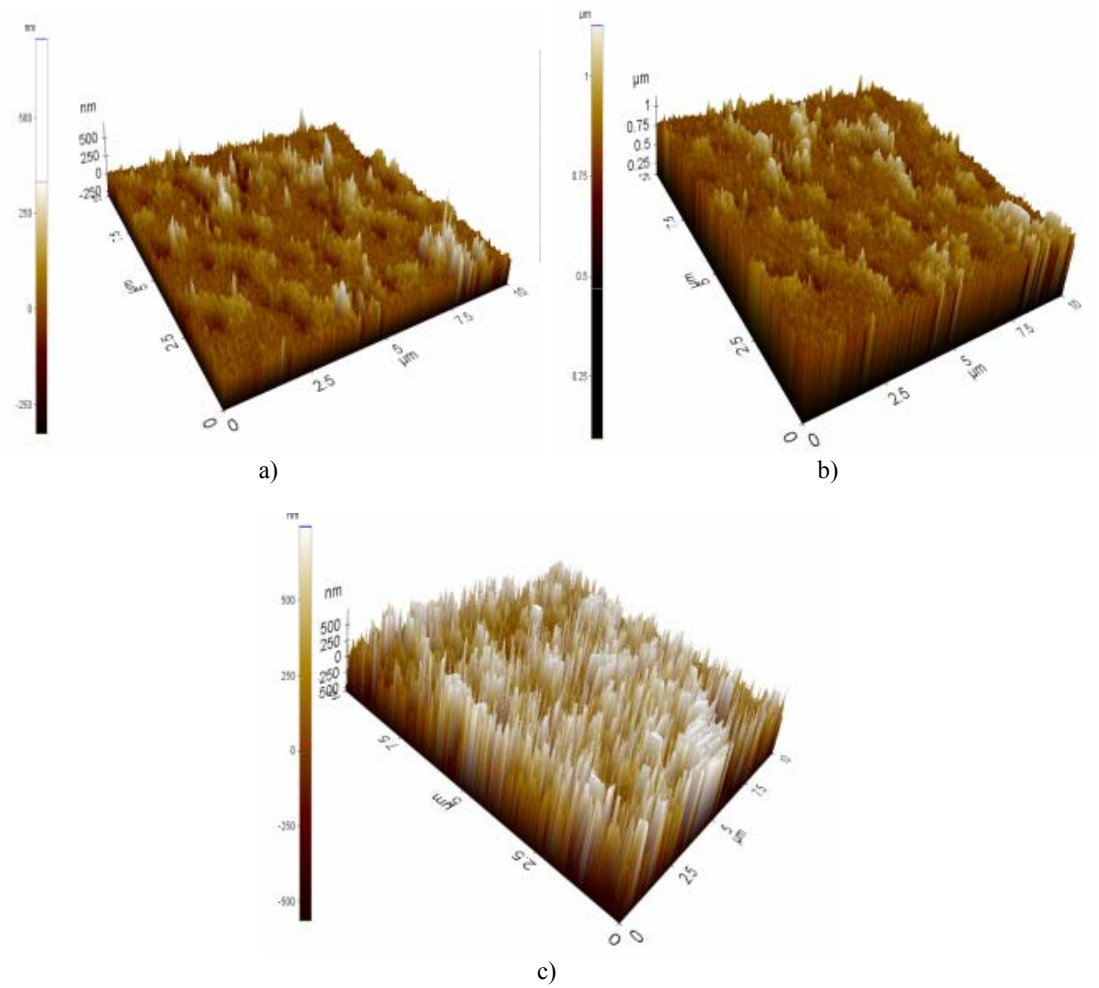
The porous layer of silicon was fabricated by means of the chemical etching in (HF and HNO_3) solution using different US excitation from 30 to 50 W. Ultrasonically enhanced etching process causes the reaction between the etchant and the silicon wafer to proceed more rapidly along the vertical in the silicon pores than laterally (coefficient of anisotropy (average depth of pores/average width of pores) increases from 7.31 to 158.4).

The AFM images of their samples are shown in Figure-1 (a) - (c). The PS layer thickness of samples A, B and C are 500, 1000 and 1250 nm, respectively. In the same effective etching time, two obvious conclusions can be obtained: (1) the PS layer thickness of samples

prepared by ultrasonic etching (samples B and C) are larger than that of samples prepared by usually technique (non-ultrasonic) etching (sample A). (2) The silicon pores of sample C are the most continuous in the surface-normal direction and have both the uniform distribution and the smallest diameters.

A sample has more uniform PS layer with smaller silicon pores and the etching efficiency is also higher than those prepared by usually technique (non-ultrasound). The reason is believed to be that when employing simply the chemical etching method, the chemical reaction products will deposit at silicon pores, mostly at pore tips, and prevent the dissolution of silicon wafer, consequently enlarging the lateral etching. A lot of micro-bubbles will appear in the electrolyte solution when the ultrasonic wave acts on it. These bubbles will shrink and expand repeatedly with the variety of sound pressure and result in desorbing of the chemical products from silicon pillars. If the bubble is broken, an extreme high pressure will be produced. This pressure will bring the dissolved species out of the silicon pores. In addition, the other ultrasonic effects, such as vibration, will also speed up the diffusion of chemical products. All these reasons cause the chemical reaction to concentrate on the pore tips, thereby reducing the lateral etching and improving the uniformity and etching efficiency.

Smoothness of the three samples was measured by AFM and is shown in Figure-1. The most obvious phenomenon displayed in the micrograph is that the silicon pillar dimension increases from sample C to sample A while the uniformity decreases. The surface roughness root mean square (RMS) value for each of the four samples is 17.324 nm (sample A), 9.505 nm (sample B) and 3.779 nm (sample C).



a) b)

c)

Figure-1. AFM image of PS layer at 20min in a) chemical etching b) US (30W) + chemical etching c) US (50W) + chemical etching.

Table-1 shows thickness; etch rate, average size and roughness of PS layer after etching time 20min and power of US. Increase of US power leads to produce deeper pores (average depth 1250nm) as compared to ones produced with low (30W) US excitation (average depth 1000nm). On the other hand if the US power is high (50W), the cavitation process is strong evidence.

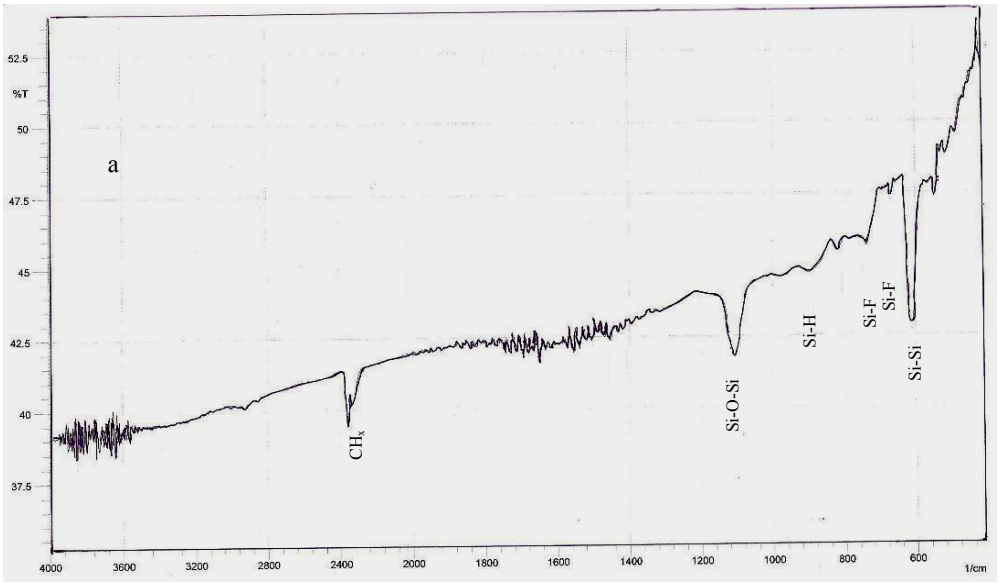
Table-1. Parameters of PS layer.

	Thickness (nm)	**Etching rate** (nm/min)	**Average size** (nm)	**Roughness** (nm)
Chemical etching only	500	25	100	2.42
Chemical etching + US (30w)	1000	50	70	3.12
Chemical etching + US (50W)	1250	62.5	280	3.78

The chemical composition of the surface of the macro porous was investigated by means of the transmission spectra in the FTIR spectroscopy. The FTIR transmission spectrum on freshly prepared PS layer which prepared by chemical etching at different wavelength from 400 to 4000 cm^{-1} is shown in Figure-2.

The ultrasonic treatment during PS layer formation resulted in the Microstructural features in p-type (111) Si. As can be seen from this Figure, the freshly prepared PS layer showed Si-H absorption bands at 2400 cm^{-1}. These modes are related to groups adsorbed at the extended PS surface [4]. It is already well known that Si - H_x content is necessary for the passivation quality, as hydrogen may easily diffuse at the PS/Si interface as well as inside the Si wafer itself.

The FTIR spectra of the samples, where the peaks 1108 cm^{-1} corresponds to the stretching modes of the Si-O-Si bridges in SiO_x. As this peak dose not undergoes important changes when the samples are processed, it can be argued then this mode is related to the Si substrate. Otherwise, the mode at 1108 cm^{-1} appear only in PS layer with some oxidation degree, the frequency can be related to the highly stressed SiO_2-Si interface of defective Si oxide at the PS surface. These modes are the symmetrical and antisymmetrical vibrational modes of the Si-O-Si bridges [9]. The decrease in Si-H and Si-O band intensities indicates probably that there is some etching activity induced by ultrasonic cavitation. The relative decrease of hydrogenation compared to oxygen is also confirmed by the Si-H is stronger in ultrasonic cavited sample as estimated from the relative band intensities. The peak at 613cm^{-1} belongs to Si-Si stretching mode, while the peak at 818-889 cm^{-1} is O-Si-O bending mode. The peak at 663 and 739 cm^{-1} to SiF. The existence of Si-F bond is a characteristic of the chemical etching technique [11]. While peak at 1460, 846 and 831 cm^{-1} are corresponds to hydrocarbon vibration mode which is related to the wash of the sample in ethanol [1].



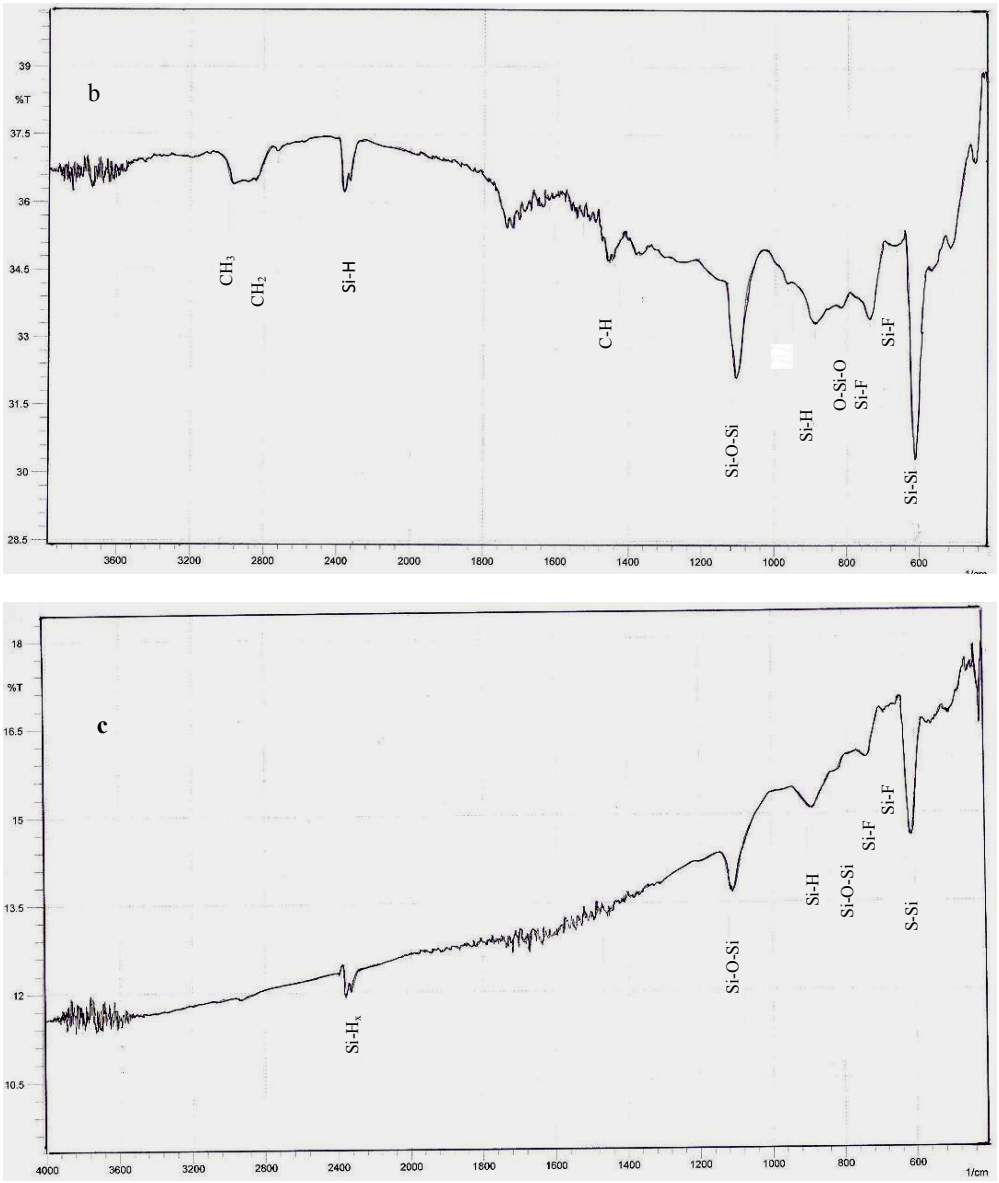


Figure-2. FTIR spectra show the effect of ultrasonic treatment. a) chemical etching, b) chemical etching + US (30W) and c) chemical etching + US (50W).

CONCLUSIONS

In summary, we have presented an ultrasonic enhanced chemical etching method for fabricating PS layer. Surface investigations atomic force microscopy (AFM) reveal that when other etching parameters are constant, the ultrasonic etching creates a thicker and more uniform PS layer, with smaller silicon pores than non-ultrasound chemical etching.

AFM observations further confirm the improved structural properties, which can be explained by the PS formation mechanics, especially by ultrasonic cavitation. The studies of both PS single layer and PS micro cavity show that ultrasonic etching optimizes the sample's characteristics. The best quality sample has been acquired by combining the ultrasonic etching with usually technique. This new etching method is very efficient technique to fabricate PS materials, especially PS multilayer, and opens a feasible way to realizing the application of PS materials.

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