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Investigating the Role of Hydrofluoric Acid Concentration in Tailoring the Morphology and Enhancing the Photonic Properties of Nanoporous Silicon Wafers

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ABSTRACT

At This research used an electrochemical method to convert bulk silicon wafers into porous silicon (PS). The wafers, chosen with a (100) orientation and (3-8) Ω.cm resistivity, the time of etching was 25min and the current density of etching 25 mA/cm². It was carried out nanoscale surface morphology on the PS substrates by modify the hydrofluoric acid (HF) to ethanol ratio (1:3, 1:6, and 1:9). In the compositional aspect it was used (AFM) to show that higher hydrofluoric: ethanol concentricity augment the porosity and particles density of wafer surface. subsequently, the etching depth given changeful directions with changing HF concentration, and the nanodimensions were clearly showed within the porous silicon layers were they produced. The anatomy of Photo luminescence (PL) specified that the energy gap E.G. was widened with increasing the porosity of wafers and the density of particles, as seem by a shifting to the blue in the PL spectrum.

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دراسة دور تركيز حامض الهيدروفلوريك في التصميم الطبوغرافي والخصائص الضوئية لشرائح السليكون المسامي النانوي

أمجد حسين جاسم

قسم الفيزياء، كلية العلوم، جامعة تكريت، تكريت، العراق

الملخص

في هذا البحث تم استخدام طريقة التنميش الكهروكيميائية لتحويل شرائح السيليكون الكتلي إلى سيليكون مسامي. خضعت الشرائح، ذات الاتجاهية (100) والمقاومية (8−3) اوم. سم، للتخديش لمدة (25) دقيقة عند كثافة تيار تبلغ 25 مللي أمبير/سم². ولقد تم الحصول على تراكيب سطحية نانوية لشرائح السليكون المسامي عن طريق تغيير نسبة حمض الهيدروفلوريك إلى نسبة الإيثانول (1:3، 1:6، و1:9). كما اظهرت فحوصات مجهر القوة الذرية أن ارتفاع تراكيز الهيدروفلوريك: الإيثانول زاد من المسامية وكثافة الجسيمات السطحية. بالإضافة إلى ذلك، أظهر عمق الحفر اتجاهات متغيرة مع تغيير تركيز الحامض وقد تم الحصول على ابعاد نانوية ضمن الطبقة المسامية المنتجة. في حين وُجد من خلال تحليل التألق الضوئي (الفلورة)، أن فجوة الطاقة ازدادت مع زيادة المسامية وكثافة الجسيمات، كما يتضحُ ذلك من خلال الازاحة الى الأزرق في طيف الاستضائية.

1. Introduction

The materials were feature like porous silicon (PS) as a worthy interest in essential physics and many technological applications [1]. The PS properties which was individual led to use in several fields, Like physical, diodes, biological, chemical sensors, and photo electronic of solar cells [2]. Porous silicon and its versatilities can be referred to its structural properties and optical characteristics, which were important in its operation toward these different scopes.

A hydrofluoric acid (HF) was a critical aspect of involve and reinforce with PS using. It’s known the HF was intensive acidic nature, It plays a multifaceted functions in the application and processing of porous Silicon. In the reproduction of semiconductors, HF is fundamental for cleaning the surfaces of silicon wafers, It was take off the oxides and impurities manufacturing. This important cleaning for clarity and efficiency of the devices of semiconductor [3].

Beyond the cleaning of surface, hydrofluoric role extend to the etching by chemical method of PS. This chemical etching was very important for controlling the type of pores and depth on porous silicon surfaces, which clearly affects the work of semiconductors electronic wafers and their applications. HF acid was also used to remove nano-oxide layers from PS surfaces, which improves the fabrication and operation of devices in nanoelectronic applications. The ability of HF to vary the surface properties also

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makes it useful in applications like sensing and photodetectors that demand specific adherence characteristics or modulation in surface properties [4-7]. Given the global use of HF in several stages of PS processing and its important impact on the final properties of PS, the purpose and the aims this study is to scour deeper into understanding how changing concentrations of HF impact the structural and optical properties of PS. By studying the effects of vary HF: ethanol ratios on the porosity, surface morphology, and photoluminescence of PS, the study examine to optimize the application of HF in consolidate porous Si execution and applicability in a wide range of technological and manufacturing scopes [8].

2. Materials and methods

In this research, bulk silicon wafers which were used with a (100) orientations and its resistivity (3−8) Ω.cm, the electrochemical method used to etch wafers, the time of etching 25min at a 25 mA/cm² density of current. It was obtained nano- scale surface morphology on the PS samples by changing the hydrofluoric acid (HF) to ratio of ethanol (1:3, 1:6, and 1:9). The topography of surfaces and inner structure of the samples which were used also studied using an (AFM), and photoluminescence was used to study the energy gap of the samples after treatment with HF: Ethanol.

3. Experimental part

Porous silicon is of great importance in many applications, especially electronic photo applications and electronics in general, as it is possible to manufacture porous silicon by cutting crystalline silicon, or what is called bulk silicon, into samples with specific dimensions called silicon wafers [9]. The wafers were cut into dimensions of (1.5) cm^2. The etching process is completed, especially the electrochemical etching used in this experiment, in the presence of a Teflon cup, the etching concentrations of acid HF: Ethanol (1:3), (1:6) and (1:9) and the figure below is the electrochemical etching system.

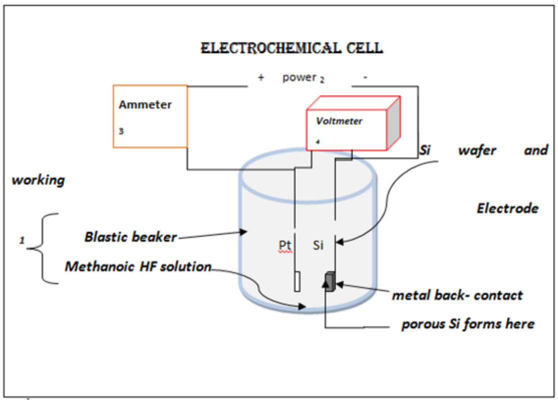


Fig. 1: The porous silicon fabrication system (electrochemical cell) [10]

The etching process is carried out through some equations and mechanisms, The equations of the processes during the porous silicon formation can be expressed as follows:

$$Si + 2HF + 2h^{+} \quad \rightarrow \quad SiF2 \ + 2\,H^{+} \quad \ldots\ldots(1)$$

$$SiF_2 \ + 4HF - \quad \rightarrow \quad H_2 \ + \ H_2\,Si\,F_2 \quad \ldots.(2)$$

The rate of etching is resolve by the holes (h+) pilling up in the close region of the HF electrolyte and Si atoms [11]. The form of the pores can be tubular or in the shape of triangles, squares, etc. This was became from the type of wafers or according to the intensity of light if the experiment used photochemical etching method.

4. Results and Discussion

Through AFM examination of the samples, it was found that the thickness of the porous layer increases with increasing concentration of HF acid, but to a certain extent, and then decreases with increasing HF acid concentration as in fig (3). This is because the etching processes will not be limited to depth only, as the etch works on the peaks produced on the surface of the wafer. Thus, the thickness decreases in-depth, sometimes with an increase in the concentration of HF acid [12], as was evident in figures of samples 2, 3, and 4 respectively.

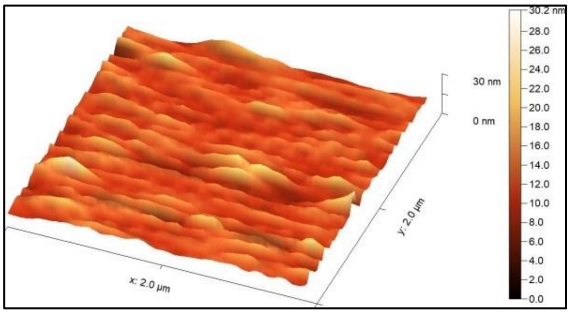


Fig. 2: AFM image of PS prepared by ECE technique with a constant time of 25 min. and constant density of current 25 mA /cm2 with HF: ethanol mixing A: (1:9)

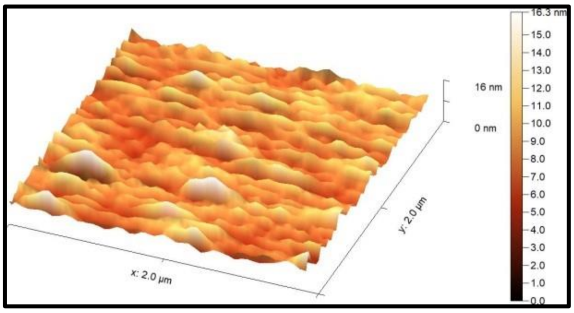


Fig. 3: AFM image of PS prepared by ECE technique with a constant time of 25 min. and constant density of current 25 mA /cm2 with HF: ethanol mixing B: (1:6)

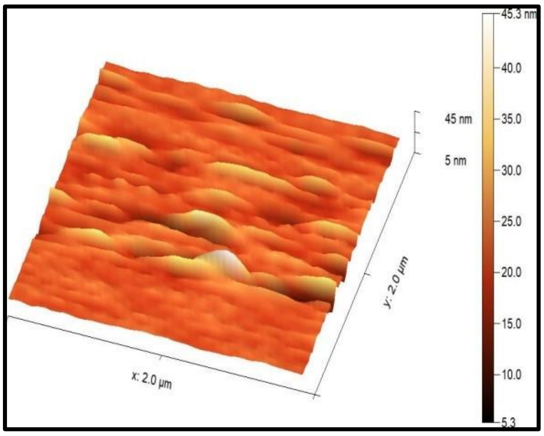
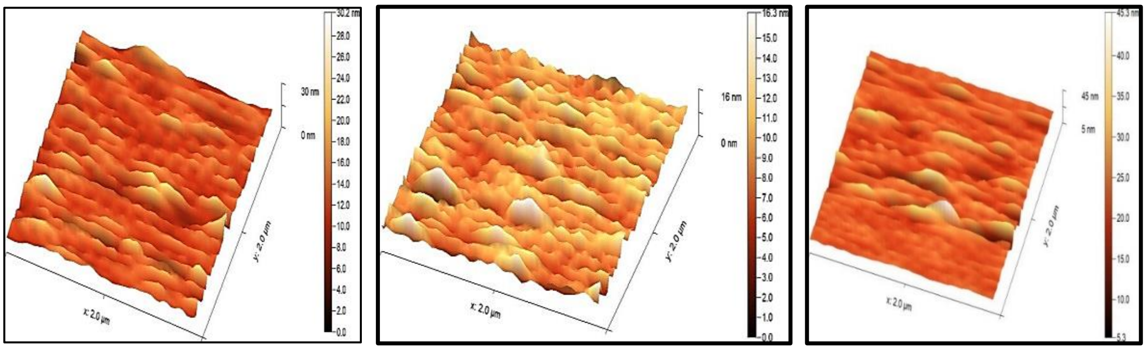


Fig. 4: AFM image of PS prepared by ECE technique with a constant etching time of 25 min. and constant density of current 25 mA /cm2 with HF: ethanol mixing C: (1:3)



A **B** **C**

Fig. 5: AFM images of PS prepared by ECE technique with a constant etching time of 25 min. and constant density of current 25 mA /cm^2 with HF: ethanol mixing (A-1:9, B-1:6, C-1:3)

Table 1: The calculated topography characteristics of PS samples prepared by the ECE technique with a constant etching time of 25 min. and constant density of current 25 mA /cm2 with HF: ethanol mixing (1:3), (1:6) and (1:9).

HF: ethanol concentration	Density (Particles/mm^2)	Mean roughness (nm)	Cross section (nm)
1:3	1000000	1.75531	174.2
1:6	450000	1.61757	256.4
1:9	110000	1.52325	95.1

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From table (1), It has been noticed that Density (Particles/mm²) indirectly proportional to the increase in the concentration of HF acid concerning ethanol. This indicates that the density of the formed particles depends entirely on the increases in drilling and uprooting operations, which are mainly based on the presence of fluorine ions and their density, which increases uprooting operations and thus increases the density of the particles formed on the surface, As for both mean roughness and cross section, they depend on the same variables because the roughness principle is the sum of the decreases and rises in the excavation operations. The cross section is the amount of what was excavated and the depth of that uprooting. Therefore, they behave similarly with the same variables, directly proportional to increasing acid concentration.

Cross-section tests found that the etching behavior was the same and enhanced what appears in Figures 2,3 and 4, as tests 6, 7, and 8 showed the cross-section of the etched wafers. The etching processes increased with the increase in the concentration of HF acid relative to ethanol to certain limits. After that, the thickness of the porous layer decreased with increasing concentration. This is because the fluorine ions were not limited to uprooting the silicon atoms only from the depth; they also worked on uprooting those atoms from the surface.

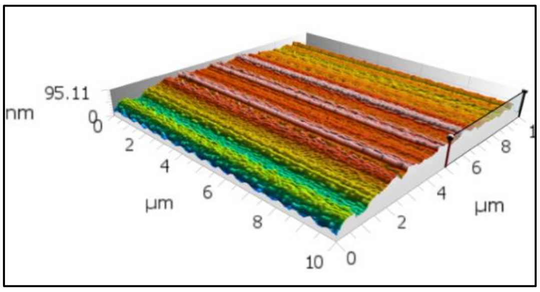

Fig. 6: Cross-section image of PS prepared by ECE technique with a constant time of 25 min. And constant density of current 25 mA /cm2 with HF: ethanol mixing A: (1:9)

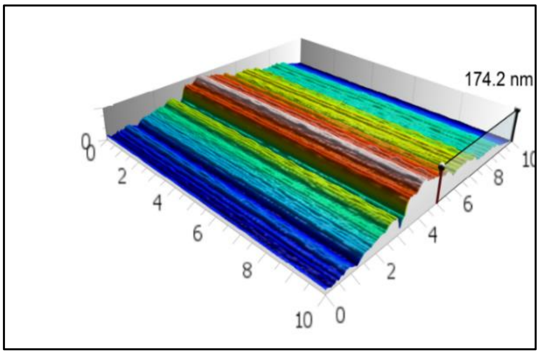

Fig. 7: Cross-section image of PS prepared by ECE technique with a constant time of 25 min. And constant current density 25 mA /cm2 with HF: ethanol mixing B: (1:6)

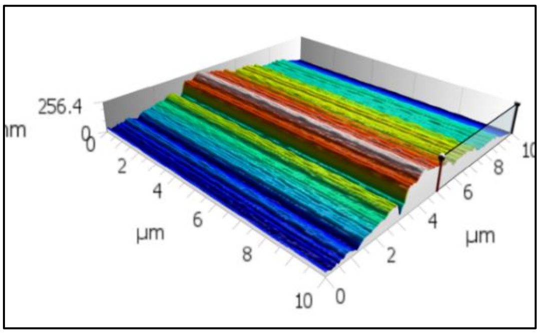

Fig. 8: Cross-section image of PS prepared by ECE technique with a constant time of 25 min. And constant current density 25 mA /cm2 with HF: ethanol mixing C: (1:3)

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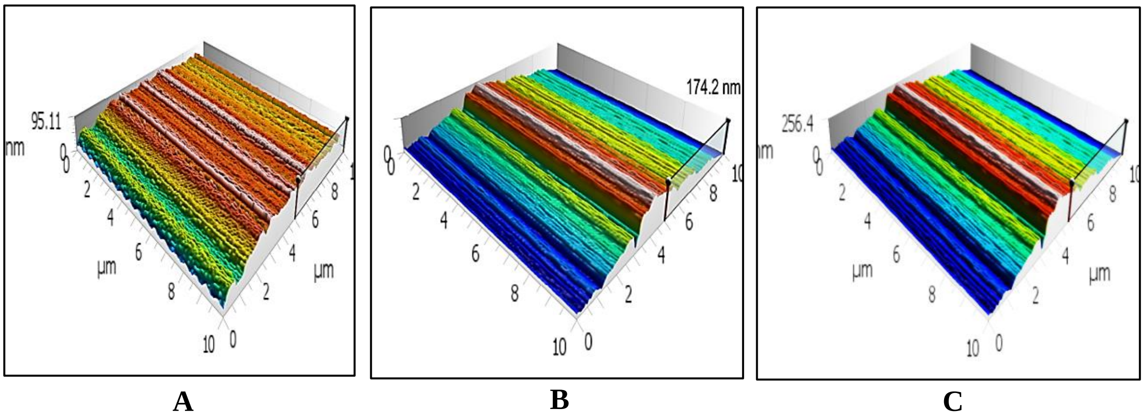

Fig. 9: Cross-section image of PS prepared by ECE technique with a constant etching time of 25 min. and constant density of current 25 mA /cm^2 with HF: ethanol mixing (A-1:9, B-1:6, C-1:3)

The values of the concentrations of particles on the surfaces for all wafers A, B and C showed that with an increase in the concentration of HF acid, the density of the surface particles decreased, which was reflected in the reduction in roughness in all samples and HF concentrations. This was clearly shown in Fig. (10, 11).

By examining photoluminescence, it was found that increasing the concentration leads to the appearance of a blue shift, and this is because agglomerates were formed that led to the appearance of a smaller crystal size, which in turn led to an increase in the energy gap that led to the appearance of this shift so this agreement with [13].

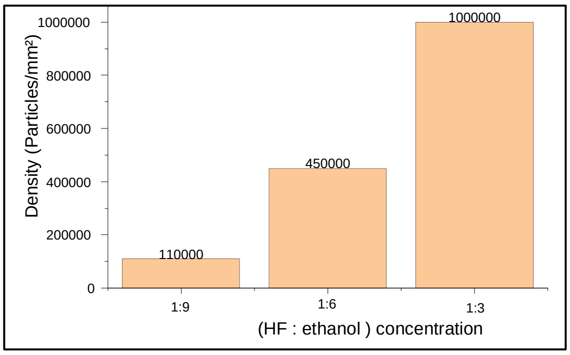

Fig. 10: The mixing aggregation on the density of particles formed on the surface

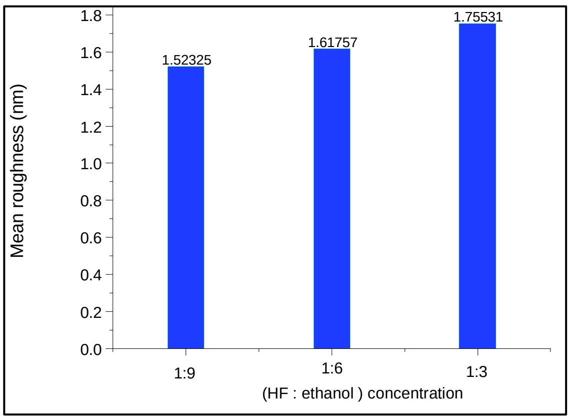

Fig. 11: The mixing aggregation on the surface's Mean roughness (nm).

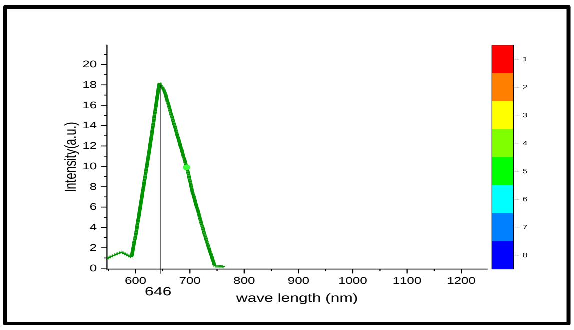

Fig. 12: PL image of PS wafer prepared by ECE technique with a constant time of 25 min. And constant density of current 25 mA /cm2 with HF: ethanol mixing A: (1:9)

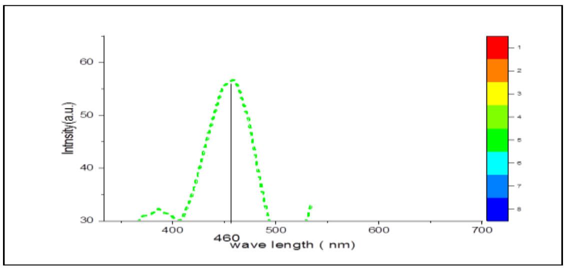

Fig. 13: PL image of PS wafer prepared by ECE technique with a constant time of 25 min. And constant current density 25 mA /cm^2 with HF: ethanol mixing B:(1:6)

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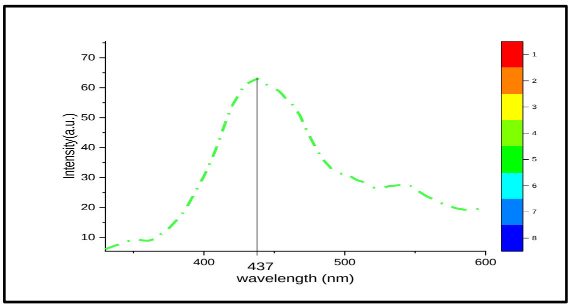

Fig. 14: PL image of PS wafer prepared by ECE technique with a constant time of 25 min. And constant density of current 25 mA /cm^2 with HF: ethanol mixing C: (1:3)

The variation in the apparent intensity of the figures (12,13,14) due to luminescence indicates a variation in the distances between one pore and another, as the surface topography resulting from the drilling operations varied and led directly to affect the properties of quantum confinement. It may be tiny, so traces of quantum confinement appear in it, making some peaks of PL wide, and this agreement with [14]. The latter mechanism originated the observed luminescence [14, 15]. The absence of photo luminescence from the sample (C) observes that porous silicon with a pore diameter of (30 nm) or less behaves as bulk silicon where the silicon crystallite size between two pores is too large to lead to an efficient quantum confinement. The absence of a PL signal from sample (C) and a strong signal from sample (A) indicates that the quantum confinement effect in a narrow silicon regime between two pores results in a strong PL signal.

5. Conclusion

In this study, the focus was on knowing the effect of hydrofluoric acid (HF) concentration on some properties of porous silicon (PS). The increasing concentration of HF leads to a higher density of surface particles due to more intense uprooting and drilling processes. In addition, the surface roughness, a vital aspect of PS topography, increases with increasing HF concentrations. Interestingly, the depth of porous wells does not necessarily correlate with the acid concentration, indicating a compound interaction beyond mere acid strength. The observation significant was the widening in the energy gap E.G. with Increasing HF concentrations, attributed to the lessening in particle sizes from ongoing particle reduction processes. This result supports the direct effect of non-structural changes on some electronic properties of PS. These insights clarify HF's role in modifying PS with implications for its application in semiconductor and nanotechnology.

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