

Effect of HF Concentration on the PS Structures Prepared by Photoelectrochemical Etching

Dr. Ali H. AL-Hamdani  Dr. Bassam G. Rasheed**
& Yasmeeen Z. Dawood***

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Abstract

Porous silicon was fabricated at p-n junction wafer by photoelectrochemical (PEC) etching. Silicon wafer with various electrolyte containing different HF concentrations was used to explain PS formation by the reaction at the Si/ electrolyte interface. An investigation of the dependence on HF concentration to formed PS layer was made. The surface morphology of PS layer was study as a function of HF concentration. Pillar like structures are formed at low HF concentration and pores structures are obtained a at higher HF concentration (40%). The etching rate increases with increasing HF concentration causing faster silicon dissolution. Thus the total pillar volume would increase by increasing the HF concentration.

Keywords: Porous silicon, Photo electrochemical etching, Etching rate, HF concentration.

تأثير تركيز حامض الهيدروفلوريد على طبقة السليكون المسامي المحضر
بطريقة التنميش الكهروكيميائي الضوئي

الخلاصة

تم انتاج طبقة من السليكون المسامي بطريقة التنميش الكهروكيميائي الضوئي باستخدام قواعد سليكونية ثنائي الوصلة. ودراسة تأثير تركيز حامض الهيدروفلوريد على تكوين طبقة السليكون المسامي من خلال التفاعل الحاصل بين الحامض وسطح السليكون. نلاحظ ان التركيب السطحي لطبقة السليكون المسامي دالة لتركيز الحامض المستخدم. طبيعة السطح ذات تركيب اشبه بالاعمدة عند التراكيز القليلة بينما عند استخدام تراكيز عالية (40%) يكون التركيب السطحي على شكل حفر. كما تم ملاحظة زيادة في معدل التنميش بزيادة تركيز الحامض نتيجة لزيادة في عملية التفاعل والذي سيأثر على عدد الاعمدة (التركيب السطحي) والذي يزداد بزيادة تركيز الحامض.

Introduction

Porous silicon (PS) has attracted great interest both from fundamental physics point of view as well as its technological applications in biological and chemical sensors, light emitting diodes, microdevices, and solar cells [1-4]. The PS can be prepared by the electrochemical anodization etching technique [5],

PEC etching [6], stain etching processes in a hydrofluoric acid-based solution, and a hydrothermal etching technique in a hydrofluoric acid free solution[7] and laser induce etching LIE) [8]. Depending on the etching parameters, for example, current

*Laser and Optoelectronic Engineering Department, University of Technology/ Baghdad

**Applied Science Department, University of Technology /Baghdad

***Collage of Education Department, University of Al-Mustansiriya/ Baghdad

(density, HF concentration, substrate doping type, and level, the physical properties of PS can be varied. Therefore, porous silicon is also particularly suitable in order to study the influence of spatial confinement on fundamental properties of pore condensed matter as a function of pore geometry parameters. The conditions for the formation of PS on all types of substrates in terms of current density and HF concentrations were reported by Zhang et al [9], where they have shown that the formation of PS occurring during anodization was found to be dependent on the nature of electrochemical reactions.

The electroluminescence property of PS was reported by Lehmann and Gosele, where they have shown that the red color of PS changes to yellow color by an increase in applied current density during etching and this change in color was attributed to quantum confinement effect in silicon nanocrystalline between the pores. There is much theoretical evidence that quantum confinement due to nanoscale-sized crystallites of Si results in the occurrence of PL in PS layers. Quantum size effects lead to an increase in the band gap of the nanocrystals compared to single-crystal silicon which could explain the visible luminescence properties. To further explore the occurrence of PL in PS, we have systematically studied the quantum confinement effect in three different pore diameter PS samples [10].

The first application of photoelectrochemically formed PS layers grown on Si wafers as an ARC was reported by Prasad et al. They have shown that the PS layers are formed on n+ region of a p-n⁺

junction in concentrated hydrofluoric acid under white light illumination. By carrying out ellipsometric measurement they found that the PS layers had the refractive index $n=1.9$, which meets the first condition ($n^{1/4}=(n_{Si})^{1/2}$) for PS to act as an ARC on Si. Here n_{Si} is the refractive index of Si. Solanki et al. developed a PS layer transfer process, which provides an opportunity to grow monocrystalline epitaxial Si films of thickness 20 μm on low-cost substrates such as glass. In most studies for applications of PS as ARC on Si solar cells, the PS layer is required to be formed on the n+ heavily doped phosphorus diffused emitter [11]. Recently PS ARC on multicrystalline Si (mc-Si) is gathering accelerated momentum to produce inexpensive Si solar cells [12]. Key parameters determining the morphology of the porous silicon layer during anodization are electrolyte type, HF concentration in electrolyte, doping type and level in Si substrate and current density.

In the present study modifications in Si surface morphology are studied by PEC etching by different HF concentration. The etching time, laser wavelength and its power density were fixed, effect of etching rate on the surface morphology reconstruction is investigated.

Experimental work

Single-crystal silicon wafers (p-n junction) used in the experiment was of n-type (phosphorus-doped) of 0.002 $\Omega\cdot\text{cm}$ resistivity, 300 μm thick, and (100) orientation were cut into rectangles with areas of (1 \times 1) cm^2 . A good ohmic contact on the back side of the wafers was obtained by Al evaporated. The wafers were cleaned prior to formation of PS layer in

ethanol solution, followed by rinsing in deionized water. Porous silicon layer was formed by photoelectrochemical etching of silicon in mixture of (1:1) diluted HF:C₂H₅OH. The wafers were fixed in a single tank electrochemical cell, where the wafer stands horizontally. The porous silicon is formed within 1×1 cm² area through Teflon holder. During electrochemical process the anodization current density was 75 mA/cm² for 15 min in under light exposure with 130 mW/cm² laser light (532nm). The HF concentration various (10-40) %. After the photoelectrochemical process the wafer was rinsed with deionized water and blown dried.

The surface morphology of PS layers scanning by optical microscopy and the surface structure investigation. Fourier transform infrared (FTIR) spectrum of the PS layer were measured using a double beam Perkin-Elmer 850 spectrometer within the range (400-4000) cm⁻¹.

Result and discussion

The surface morphology of PS samples produced by PEC at different HF concentrations have been studied . The surface morphology of n-layer on p-n junction etched with 532 nm laser at power density of 130 mW/cm² for 75 mA/cm² and 15 min is shown in figure (1). Two different surface morphologies have been observed, which were affected by the HF concentration.

Irregularly shaped pore structure is clearly seen. At low HF concentrations (20-30)%, as shown in figure (1-a), the observed pillar structures have homogeneity form and the pillars are nearly perpendicular to the Si wafer with diameter of about 30µm and the distance between pillars

is in the range (9-12)µm. For the sample with higher HF concentration (40%), a pore-like structure appeared with large number of pores distributed within the porous structure shown in figure (1-b), and the number of these pores would be around 25 pores with diameter of 30µm. Highest concentration, there is more electron acceptor in the solution resulting in an increased band bending for further etching as the etching process is very fast in case of using high HF concentrations.

Under potentialstatic conditions (75mA/cm²), the dependence of pore density on HF concentration was investigated with a fixed illumination (130mW/cm²). Anodizing with a 20% HF concentration, approximately 8 µm² average pillars dimensions could be obtained. If enhancing the HF concentration to 30%, 25µm² pillar average dimensions occur (figure 2). In this case, the pillars dimensions also markedly decrease with an enhanced HF concentration with respect to the positive correlation between pore density and HF concentration, concerning the relation between pore density and HF concentration remain the same.

Consequently, enhancing the HF concentration will strengthen direct dissolution by HF acid and suppress indirect dissolution. Therefore, maintaining an equal current density and increasing the concentration of HF can result in a reduction of pillar dimensions, a higher HF concentration will lead to a smaller diameter and a higher density of macropores via self organization. A higher HF concentration and a stronger focusing power materialize a smaller pillar size and a mighty penetrating power makes for the

dense arraying of pillar. Note that both focusing and penetrating power originate from the etching current density: for a given electrolyte and illumination [13]

Total pillars volume can be calculated from the diameter and depth of the pillars (by using optical microscope) and number of pillars in a unit area. Variation of total pillar volume with the change of HF concentration is shown in Fig. (3). Increase in HF concentration, increases the total pillar volume and the curve obeys Faraday's law, in that the mass produced at an electrode during electrolysis is proportional to the number of moles of electrons transferred at the electrodes [14].

The observed Fig.(1) results show that deeper porous layer are formed on increasing the HF concentration while keeping the etching time fixed for 15min. This means the etching becomes faster at higher HF concentration. Quantitatively, the etching rate can be calculated by the ratio between maximum etching depth to etching time [8].

The etching rate increases with the increase of HF concentration. The etching rate is $0.3\mu\text{m}/\text{min}$ with HF acid concentration of 10%, and this value increases to $0.46\mu\text{m}/\text{min}$ till 30% the etching rate was $0.6\mu\text{m}/\text{min}$, then decreases of $0.21\mu\text{m}/\text{min}$ with increasing the HF concentration (40%). This is because as the concentration of HF acid increases, there are more electrons accepters in the solution and this leads to increase the rate of charge transfer between the semiconductor surface and the electrolyte. Thus, etching rates are calculated as a function of HF concentration and shown in Table (1). The band bending is reduced by

formation of ion complexes in the solution besides the increase detachment of silicon atoms by the fluorine ion, then the etching rate get increased due to the fluorine ion increment.

The chemical composition of the surface of macroporous was investigated by means of transmission spectra in FTIR spectroscopy. Figure (4) shows the IR transmission of PS layer that etched by PEC etching, the PS layer shows Si-H absorption bands at $905\text{-}910\text{ cm}^{-1}$ and $2087\text{-}2400\text{ cm}^{-1}$. These modes are related to groups adsorbed at the extended PS surface. 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 bands Si-H refers to the structure of porous layer in the macroporous silicon. Indeed, the PEC based PS is rich in passivating Si-H_x species and hence could be of great interest for the improvement of silicon solar cells performances.

The peaks $1050\text{-}1150\text{ cm}^{-1}$ corresponds to the stretching modes of the Si-O-Si bridges in SiO_x. The peak at 1150 cm^{-1} is generated by the asymmetrical stretching of Si-O-Si bridges in stoichiometric SiO₂. In the range of $1021\text{-}1100\text{ cm}^{-1}$, the O-Si-O (Si=O) stretching mode is related to SiO_x ($x < 2$), and with increase of x this peak shifts to be nearer to 1100 cm^{-1} . In a recent study of Si=O (O-Si-O) [14] clusters formed on the surface nanometer scale silicon crystallites due to oxidization, it was also demonstrated [15] that silicon nanocrystallites that are fully passivated by Si=O bonding.

Conclusions

The surface morphology study of the photoelectrochemical etching Si reveals that different surface morphology reconstructions of Si wafer surface take place as a function of HF concentration when other parameters of etching process were fixed. Depending upon the HF concentration, pores and pillars like structures can be formed on the Si wafer. Pillar like structures are formed at low HF concentration. Etching rate on the Si wafer is formed to be as a function of HF concentration. Etching rate increases by increasing the HF concentration because of the holes required for etching, increases with HF concentration. The pillar width and deeper can be controlled by controlling the HF concentration and thus the etching rate.

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Table (1) Etching rates of PS samples prepared with different HF concentration

HF concentration	Etching rate $\mu\text{m}/\text{min}$
40%	0.53
30%	0.66
25%	0.46
10%	0.21

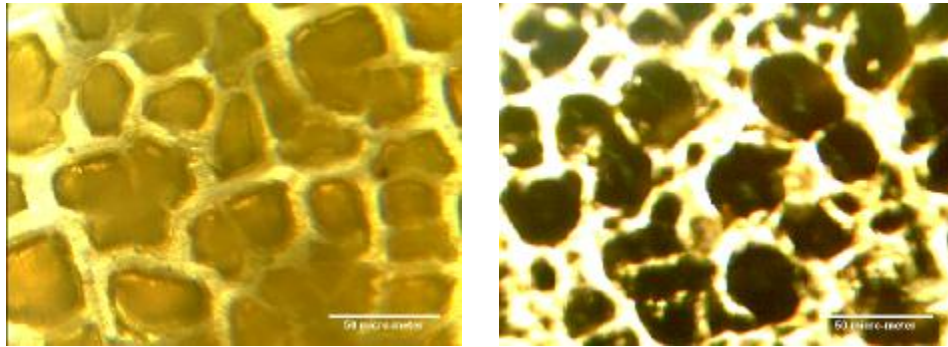


Figure (1) surface morphology of PS layer produced by PEC etching with (a) 25% and (b) 40% HF concentration

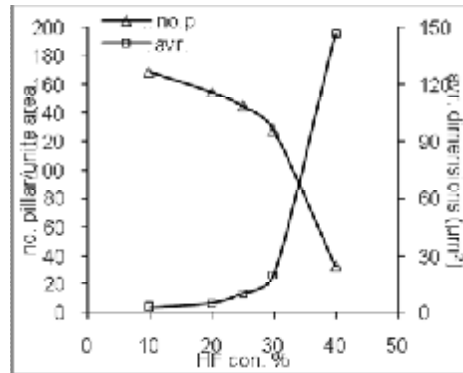


Figure (2) Effect of HF concentration on the structure (no. of pillar and average dimensions) of porous layer

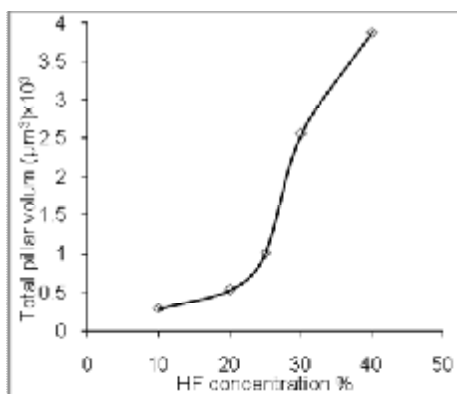


Figure (3) Variation of total pillar volume as a function of HF concentration

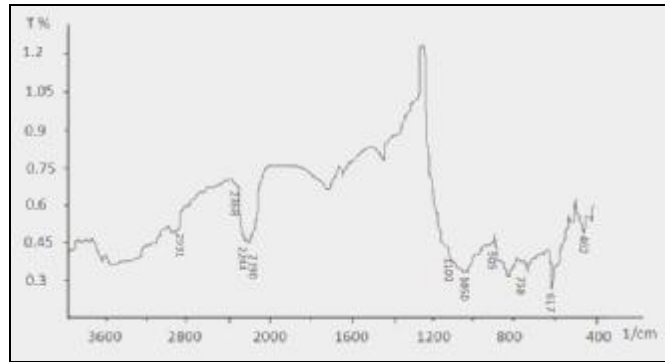


Figure (4) FTIR spectra of PS layer prepared by PEC etching