

## Morphological Aspects of Oxidized Porous Silicon Prepared by Photo Electrochemical Etching

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### Abstract

This paper reports morphological properties of porous silicon and oxidized porous silicon, prepared by photo electrochemical etching from n-type silicon wafers as a function of experimental parameters. Scanning electron microscopic (SEM) Observations of porous silicon layers were obtained before and after rapid thermal oxidation process under different preparation and oxidation conditions .The surface morphology, Pore diameter, wall thickness, pore shape and porosity values were, studied based on microstructure analyses of (SEM) images.

**Keywords:** Porous Silicon, Thermal Oxidation, SEM.

### جوانب طوبغرافية للسليكون المسامي المؤكسد المحضر بطريفة (التنميش الفوتو-كهروكيميائي)

#### الخلاصة

في هذا البحث تم دراسة الخصائص الطوبغرافية لنماذج من السليكون المسامي والسليكون المسامي المؤكسد المحضرة من السليكون المانح بطريفة الفوتو- كهروكيميائي كدالة للعوامل التجريبية بالاعتماد على صور المجهر الالكتروني الماسح لطبقات عينات السليكون المسامي قبل وبعد عملية الاكسدة الحرارية السريعة تحت ظروف أكسدة مختلفة . ولقد تم دراسة المتغيرات التالية(طوبغرافية السطح ، قطر المسامه، شكل المسامه، سمك الجدار بين مسامتين، وقيم المساميه بالاعتماد على تحليل صور المجهر الالكتروني الماسح.

## Introduction

Uhlir and Turner [1], first described the formation of porous silicon layers (PSLs) on silicon electrodes in hydrofluoric acid electrolytes under anodic bias in 1956. The discovery of a form of Porous Silicon with photoluminescence efficiency much higher than that of bulk Si has led to a flurry of research activity [2]. Therefore this material has become popular between scientists and enters in various important applications. Canham [3], reported that the bulk Si can be made micro porous (pore width  $\leq 20$  nm), meso porous (pore width 20-500 nm) or macro porous (pore width  $> 500$  nm), depending upon etching conditions. The photo electrochemical etching takes advantage of the rectifying nature of the semiconductor/liquid junction; illumination increases the etching rate at n-Si [4]. Thönissen et al [5] illustrated that illumination of the Si sample during or after the etching process known to be a further free etching parameter, which can be used to modify the P-Si layer morphology. In this work, we report the influence of oxidation temperature on the structural properties of n-type porous silicon.

## Experiment

Crystalline wafer of n-type Silicon with resistivity of  $10 \Omega \cdot \text{cm}$ ,  $508 \mu\text{m}$  thickness, and (111) orientation were used as starting substrates. The substrates were cut into rectangles with areas of  $(1 \times 2 \text{ cm}^2)$ . The native oxide was cleaned in a mixture of HF and  $\text{H}_2\text{O}$  (1:2). After chemical treatment,  $0.1 \mu\text{m}$  thick Al layers were deposited, by using an evaporation method, on the

backsides of the wafer. Photo electrochemical etching then performed in a mixture 48% (1:1) HF-Ethanol at room temperature by using a Pt electrode. Current of  $40 \text{ mA/cm}^2$  was applied for 10 min; green laser with  $514.5 \text{ nm}$  illuminated Samples and power  $30 \text{ mW}$ . The etched area of sample was  $0.5 \text{ cm}^2$ . The rapid thermal oxidations experimental system is shown in fig. (1), the oxidization occurs at  $750 \text{ }^\circ\text{C}$  by using tungsten halogen lamp (OSRAM type 64575), with power  $1000\text{W}$  at different oxidation times 50 and 25 sec. The morphological properties which include, surface morphology, layer thickness, pore diameter, wall thickness, pore shape, porosity and surface area. These structural properties measured by scanning electron Microscopy (SEM). Measurements were carried out in the School of Physics/ Nanostructures and ptoelectronics Research Center (NOR)-lab, University Sian Malaysia (USM).

## Results and discussion

The measured characters of RTO (rapid thermal oxidation) system were shown in fig. (1). In figure (2) we can see that the curve consist of three regions. The first region (heating region) shows the heating degree increased with irradiation time. Second region (oxidation cycle) where the temperature remains constant and rapid thermal oxidation occurred at this region. Third region (cooling region) is obtained at moment lamp is stopping to supply the wafer by heating energy. The pours layer thickness is about  $20 \mu\text{m}$  this value was measured by using optical microscopy have resolution down to 600 X. figure (3, 4) shows SEM images of surface for

samples prepared at etching time 10 min with Green laser and current density 40 mA/cm<sup>2</sup>, figure (3) represent fresh sample without oxidation ,while in figure (4,a,b) represent sample after oxidation process of 750 °C at oxidation time 25 and 50 sec respectively. The structure properties of fresh and oxidized porous silicon can be described into the following sentence:

#### **Pore diameter and wall size**

The pore diameter and wall size estimated based on the SEM image, and oxidized samples were measured from SEM images in figure (3) and (4) respectively, from two figures we can see that the pore diameter and wall size were decreased with increasing oxidation time, the decreasing in pore diameter due to growth oxide layer within pore lead to replace unstable hydrogen and oxygen by stable and pure oxygen which is appear like cloudy covered PSi layer .The pore size and wall thickness can be shown in Table (1).

#### **Surface roughness and Pore shape**

Figure (4, a, b) shows lower roughness rather than before oxidation process in figure (3).The decreasing in roughness after oxidation was also observed by A.E. Pap et al. [7] and Cherrier et al.[8],that decreasing in roughness after oxidation is an indicator of lower with dislocations and lower point defect density [9] By comparing the SEM image for fresh sample with SEM images after oxidation time 25 sec in figure (4,a) ,we can see that after oxidation the pore shape conserved in spite of size reduction .Finally, in figure (4,b) we could observed that the pore shape tends to round shape that due to oxide during oxidation, a certain fraction of Si Skelton into SiO<sub>2</sub> which has circular

shape[10].The Surface roughness and pore shape could be observed in Table ( 1).

#### **Porosity**

From SEM image ,we could founded that after oxidation the pore density is the same it is about  $11 \times 10^8$  pore/cm<sup>2</sup>and the pore size is decreased so the porosity after oxidation is lower than before oxidation ,this is due to decrease voids between wall(pore)due to transformation of silicon crystallite into silica which is compeered by the volume expansion[9,11].Table(2) shows the value of porosity before and after oxidation process.

#### **Specific Surface area**

The SEM image, show that the porous silicon consisted of a complicated network of pores and columns separated by a very thin walls in nanometer sized structures having very large surface area which usually varies from 3-600 m<sup>2</sup> /cm<sup>3</sup> depending on experimental conditions. A number of properties of material composed of micrometer sized grain, as well as those composed of nanometer-sized articles depend strongly on the surface area .For example, the electrical resistivity of a granular material is expected to scale with the total area of the grain boundaries [12,13].The surface-volume ratio (specific surface area) in m<sup>2</sup>/cm<sup>3</sup> could be measured as the following equation [14]:

**Surface Area (m<sup>2</sup>/cm<sup>3</sup>) = Area of one pore × No. of pores /Area of PSi structure × Depth).....1)**

The pore geometry was considered as cylindrical in shape and thus the area of one pore is [14]:

**The area of one pore = 2π rpsi hpsi..... 2)** where hpsi is the height of pore measured in (m), rps, is the radius

of the pore measured in (m). By taken the maximum value of pore width and the density of pore was constant before and after oxidation process where it is about  $11 \times 10^8$  pore/cm<sup>2</sup>. That values was applied in equation (1) we obtained on the surface area values represented in Table (2). We can observed that after oxidation the surface area will be decreased that due to, after oxidation porous surface will be saturated and the stable oxygen-Passivated surface will replace unstable Hydrogen-Passivated surface which caused to decrease pore size this will be lead to decrease the surface area [2,15].

#### Conclusion

The obtained results show that the structural properties of P<sub>Si</sub> layer depends upon the oxidation time, the surface roughness, layer thickness, porosity, and pore diameter are lower than these measured in the case of fresh sample (without oxidation treatment).

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Table (1) Shows the pore diameter and wall size of fresh and oxidized sample

Oxidation time(sec)	Pore diameter( $\mu\text{m}$ )	Wall size( $\mu\text{m}$ )	Pore roughness	Pore shape
Fresh sample(without oxidation)	1.4-6	0.014-0.25	Medium	Triangular
25	1.2-3.5	0.011-0.22	Low	Triangular-Cylindrical
50	1.2-5	0.009-0.2	Smooth	Cylindrical

Table (2) Shows porosity and surface area before and after rapid thermal oxidation process.

Oxidation time(sec)	Porosity %	Pore diameter ( $\mu\text{m}$ )	Surface area-volume( $\text{m}^2/\text{cm}^3$ )
Fresh sample(Without oxidation)	72	4	300
25	66	3.3	228
50	64	3	207

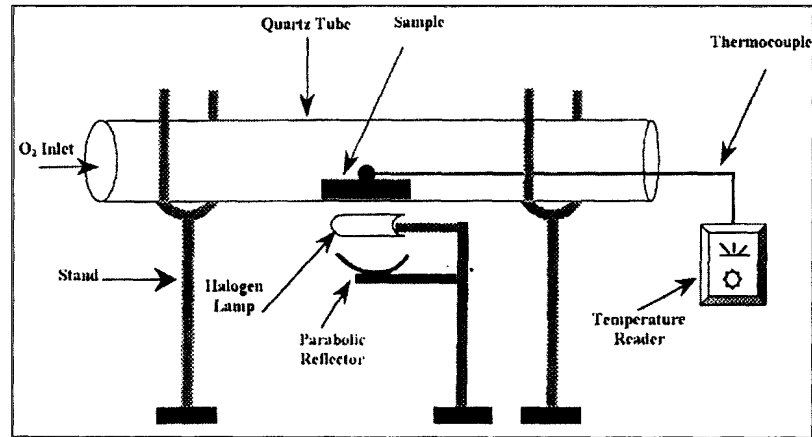


Figure (1) shows the manufactured system of rapid thermal oxidation.

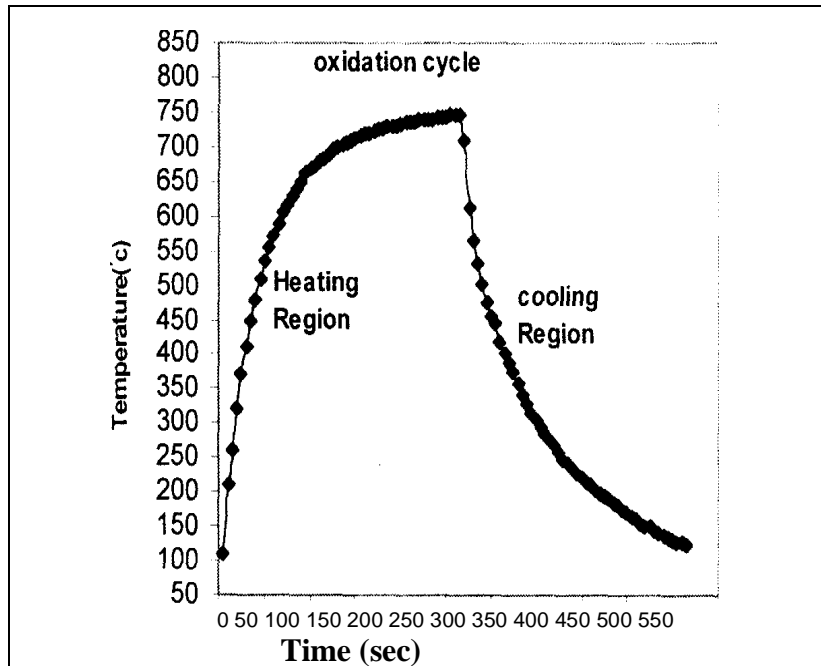


Figure (2) shows the calibration system of rapid thermal oxidation

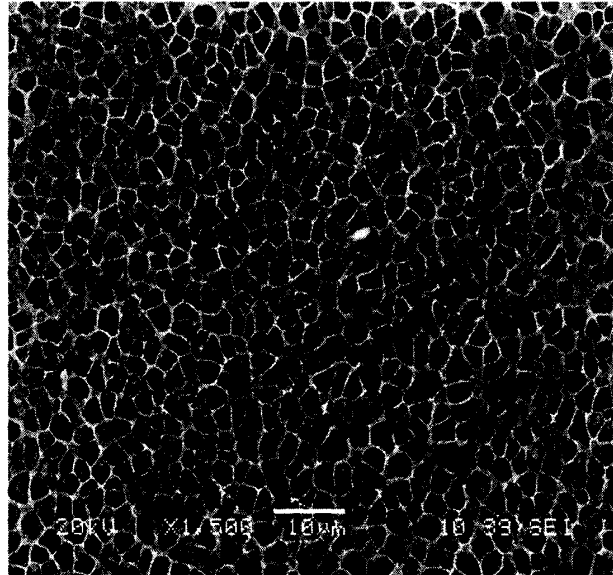
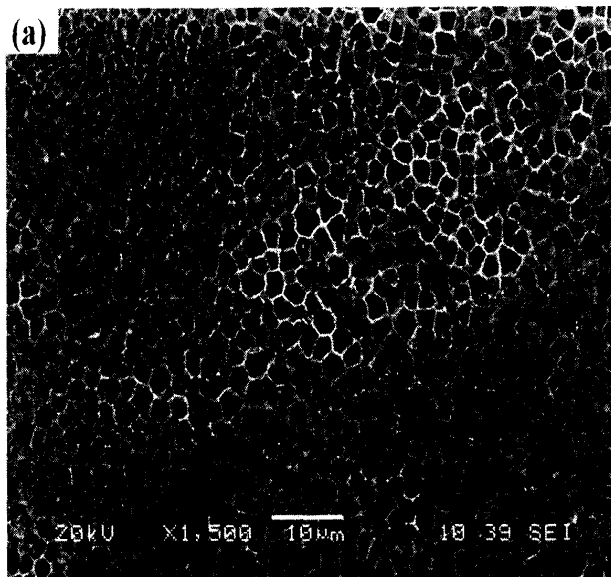
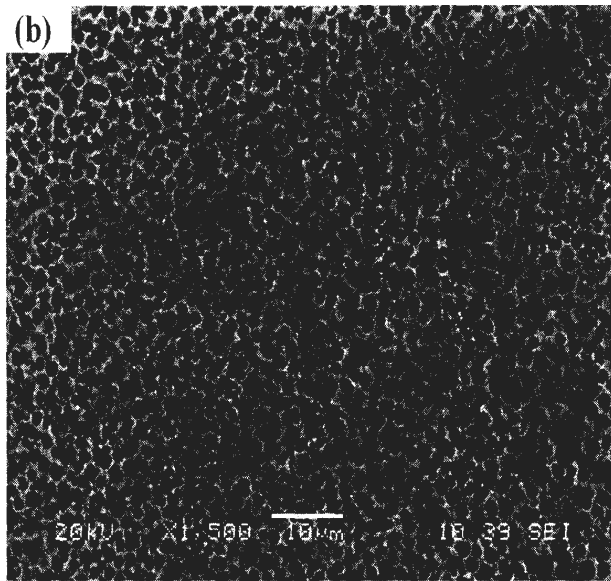


Figure (3) Shows SEM image of fresh sample porous silicon





**Figure (4) Shows SEM image of oxidized porous silicon, (a) at 25sec, (b) at 50 sec.**