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Investigation of Structural Properties of Gradient -Porosity Porous Silicon Layer Produced by Laser- Assisted Etching

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Abstract

Laser-assisted etching process with a step-gradient illumination intensity of 630nm laser wavelength was conducted to produce high porosity and minimum thickness of gradient – porosity porous silicon layer (GPSi). The structural properties were studied with the aid of scanning electron microscopy. The porous surface consisted of complex network of deep and shallow cylindrical pores. The x-ray investigation of the gradient-porosity porous silicon revealed a conversion of the native orientation of silicon wafer from (100) to poly - crystalline phase with new (101, 002, 111 and 211) orientations having nanocrystallite sizes of 15, 15.7, 20 and 15 nm respectively.

Keywords: laser, gradient etching, porous silicon, x-ray.

Introduction

Porous silicon (Psi) is a complex network of silicon regions surrounded with a void space fabricated by electrochemical , chemical and laser – assisted etching of silicon wafer in a chemical solution containing hydrofluoric acid (HF) [1]. Gradient porosity – porous silicon (GPsi) is a special form of porous silicon in which the pore cross section and structure varies with depth [2, 3]. The porosity of (Psi) and hence the structural properties can be controlled either by varying the etching current density or the laser illumination intensity [1, 4]. In previous studies [5], the gradient porosity porous silicon was prepared and discussed as efficient anti reflection layer for solar cell applications. The dynamic electrochemical etching process steadily decreases anodization current density which is applied for etching. With etching time, less than 10 sec, and current density varying between 0–100 mA/cm^2, (GPsi) layer was prepared and studied [5]. For solar cell applications, the optoelectronic properties of gradient – porosity porous silicon layer was investigated [6] for gradient porosity (psi) devices in which electrochemical etching with step-gradient current was applied to form the porous layer. Much work has been carried out using visible and infrared CW lasers to produce a Conventional single single-layer (psi) [7-10, 4]. The aim of this work is to produce a gradient porosity (psi) layer on n-type silicon substrate using CW, 630 nm diode laser assisted etching with a step-gradient illumination intensity between 20-150mW at variable etching period. Scanning electron microscopy (SEM) images and x-ray diffraction charts were utilized to investigate the morphological and structural properties of the gradient - porosity (psi) layer.

Experimental work

Gradient-porosity porous silicon layer was fabricated by etching of n-type silicon wafer of (100) orientation and (10Ω.cm) resistivity by using a mixture of 48% HF acid, ethanol and distilled water with mixing ratio of H_2O: HF: C_2H_5OH = 1:1:1. The gradient -porosity layer was fabricated using laser-assisted etching process employing CW 630nm diode laser at different illumination steps in the range between 20 - 150 mW/cm^2 at fixed etching current density of 16mA/cm^2 and fixed 8 min etching time for single porosity samples and 2-8 min for gradient – porosity layer. With 1cm^2 irradiated areas, the etching process was materialized in specially designed cell consisted of a two – electrode combination: a silicon substrate as an anode and a 2*2 mm aperture gold mesh as a cathode. The experiment was conducted at ambient temperature and is shown in the figure (1).

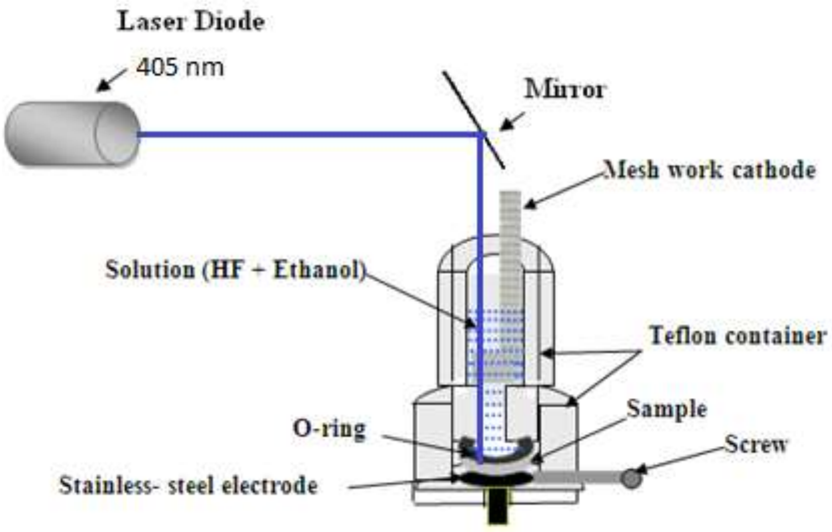


Figure (1): Schematic diagram of the Laser assisted etching system.

The cell can provide porous silicon layers of uniform cross sectional area. This uniformity is recommended for the application of (Psi) in the field optoelectronics applications. Gravimetrical method was used to determine the porosity size and thickness. The SEM and x-ray diffraction measurements were carried out in the school of material engineering at the University Sains Malaysia in Penang.

Results and discussions

Porosity and layer thickness

The etching process was carried out at four steps using laser intensities of 150, 100, 50 and 20 mW / cm^2. The samples prepared at different laser illumination steps are referred to S_1, S_2, S_3, and S_4. S_1 was etched with fixed illumination intensity of 150 mW / cm^2 for 8 min (single porosity sample). GPsi samples were subjected to multiple etching steps, each step for two minutes. S_2 was etched with laser intensities of 150 mW / cm^2 and100 mW / cm^2, S_3 was etched with laser intensities of 150 mW/ cm^2, 100 mW / cm^2 and 50 mW / cm^2 and sample S_4 was etched with laser intensities of 150, 100, 50and20mW/cm^2. The porosity γ(%) of the gradient porosity porous silicon and the porous layer thickness (d) were determined gravimetrically and calculated by using equations (1) and (2) respectively [5].

$$\gamma(\%) = \frac{m_1 - m_2}{m_1 - m_3} \qquad \text{.............................} \quad (1)$$

Where m_1 is the weight of silicon wafer before etching, m_2 is the weight just after etching, and m_3 is the weight of the sample after removing the porous layer. The porous layer thickness (d) is determined by using gravimetric measurements.

$$d = \frac{m_1 - m_2}{A \times \rho} \qquad \text{.............................} \quad (2)$$

Where A and ρ correspond to the illumination area (cm^2) and (ρ = 2.33 g/cm^3) to the density of bulk silicon. The etching rate of laser-assisted etching process describes the etching process speed and depends on the formation parameters and governed by the diffusion rate and drift velocities of holes to the surface. As a result, the etching rates could be estimated from the layer thickness and etching time. Etching rates were calculated for all samples by taking the ratio between porous layer thickness and the etching time. The depth of the porous layer was obtained by gravimetric measurements. Porosity, porous layer thickness and etching rate of the gradient porosity porous silicon samples for different laser illumination steps are presented in table (1).

Table1. Porosity, porous layer thickness and etching rate for (GPsi) porous silicon samples.

Sample	Porosity %	Porous layer thickness µm	Etching rate µm/min
S1	79	11.8	1.45
S2	23	4.1	1.02
S3	38	4.1	o.63
S4	75	4.2	0.52

It is found, for single porosity sample S_1, that both porosity and layer thickness increase with increasing etching time, and are 79% and 11.8µm respectively. For the gradient porosity porous silicon samples S_2, S_3 and S_4, the porosity of (GPsi) increases with increasing the laser illumination steps and approaching a high value, very close to that of single porosity sample 79%. The layer thickness of (GPsi) is approximately fixed to a very small value of 4.1 µm which is lower than that of single porosity sample. The larger porosity with lower layer thickness was obtained for S_4 sample. Photons of the laser light create electron–hole pairs in the illuminated area. Holes move towards the Si wafer surface due to the band bending at the Si/HF interface [4, 7]. These holes participate in the chemical reaction taking place at larger number of sites on the surface which therefore, facilitates etching.

As the laser power density increases, the number of the photo-generated *e-h* pairs increases too. Therefore, more holes result in more Si dissolution in the HF solution [11]. The laser intensity in laser assisted etching is responsible for the photo-generated holes rate [12]; these holes accumulate at the surface and inside the etched sample. Fast etching rate and **large** layer thickness were observed when the illumination time is fixed during etching. Increasing the laser illumination intensity can form a complex silicon nanowire matrix system of different size. The morphological nature of the etched surfaces will then show different pores sizes and shapes. Our results agree well with those published elsewhere [4], where the etching process depends on the photo-generation of *e-h* pairs (G) in the silicon wafer and is given as:

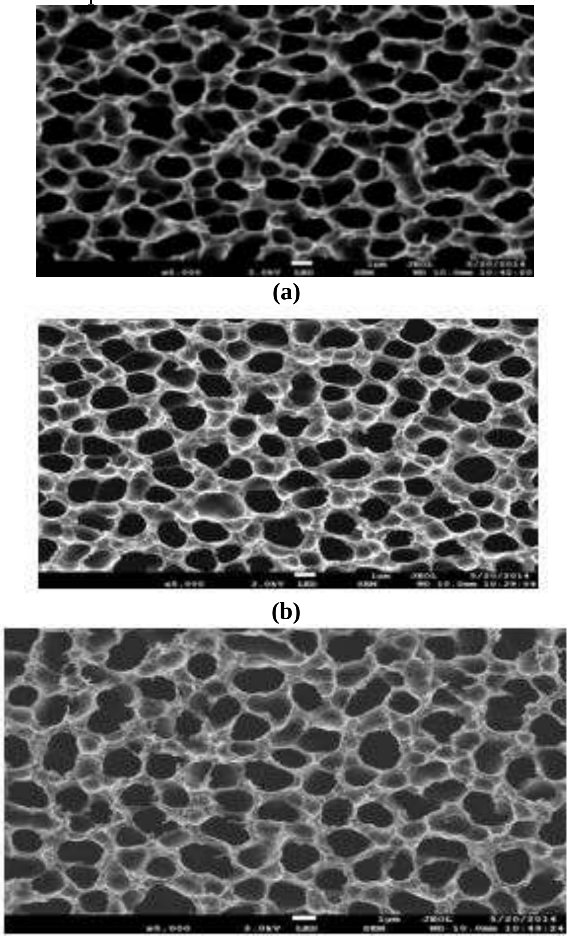
$G = Q_E\,(P/h\upsilon)$ ………………………… (3)

Where P is the power of the laser, hυ is the energy of the incident photons and Q_E is the quantum efficiency. The increasing incident laser intensity will speed up the etching process in three different rates $x_1.x_2$ and x_3. The x_3 rate occurs in z-direction deeply through the silicon wafer and is responsible for increasing the porous layer thickness whereas the x_2 and x_3 refer to etching rates occurring at the surface of the porous layer. These two rates are mainly responsible for increasing the porosity rather than the porous layer thickness. The use of laser intensities in steps decreasing steadily from higher to lower values will enable a suitable control of the photo-generated holes, i.e. the porosity and layer thickness, and produce the (GPsi) layer.

Surface morphology

Porous silicon is a special morphological form of Si characteristics through the presence of highly developed network in silicon crystal. It is very difficult to characterize the morphology of PSi because of its extremely rich details with respect to the range of variation in pore size, shape and distribution. All morphological properties of single-layer and gradient-porosity PSi layer such as pore width, pore shape and the wall thickness between two pores are strongly dependent on the etching conditions. These features of PSi have been studied by direct imaging of its structure by scanning electron microscopy.

The SEM images for single porosity sample S_1 prepared at fixed illumination intensity of 150 mW/cm^2 and 8 min etching time, and the (GPsi) samples S_3 and S_4 prepared with step - gradient laser illumination intensity are shown in figures (2a), (2b) and (2c) respectively. We can note from this figure that the pore width has different sizes. The increase in pore width may be attributed to the increased holes number on the surface of silicon electrode with the progress of etching process leading to preferential dissolution between nearest - neighbor pores, thereby promoting pore-pore overlap. However, the etching rates may be different and leads to non-uniformity in values of pores width. Compared to the sample with constant - illumination intensity etching, Figure (2a), the SEM image figure (2b) and (2c) of step-gradient etching sample demonstrate gradient pore-size from small to large pore with the increasing laser illumination intensity step. For S_1 sample, the structure of the surface consists of complex network of rectangular and cylindrical pores aligned in random direction. The black regions represent deep pores inside the pores structure, and the overall structure is pore- like structure. The gradient laser illumination modifies the surface morphology. The surface structure of the S_3 sample is a complex network of cylindrical pores aligned in random directions, with pores having two colors; black deep pores and nearly white shallow pores. Therefore the pores have nearly two depths a cross the layer thickness (gradient- porosity porous silicon layer). Increasing the illumination step as in sample S_4, has increased both; the average pore width and pore width to a value very close S_1 with porous structure consisting again of black deep pores and nearly white shallow pores.



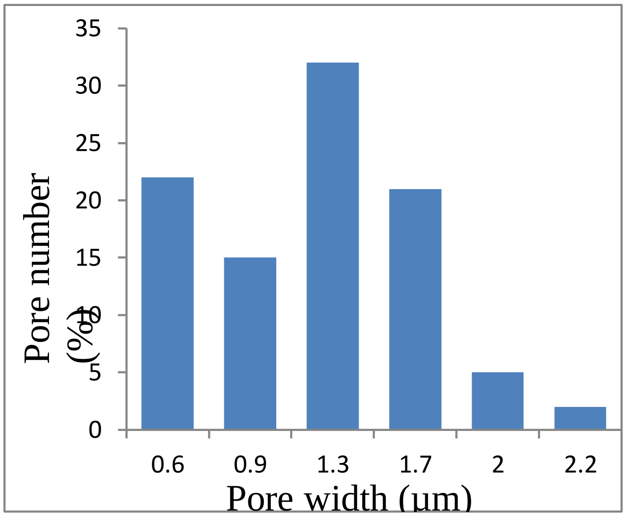
(a)

(b)

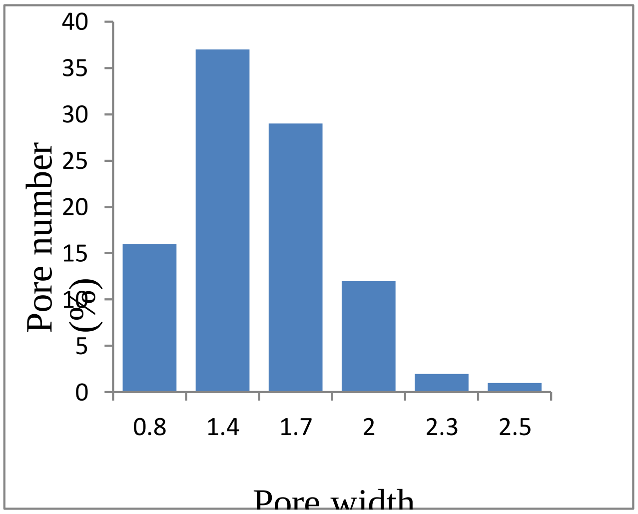
(c)

Figure (2): SEM images of (a) single-layer porous silicon sample (S1), (b) gradient-porosity porous silicon sample (S3) and (c) gradient-porosity porous silicon sample (S4)

The statistical distributions of pore diameter size of the single-layer porous silicon sample (S_1) and gradient-porosity porous silicon samples are shown in figure (3). As seen, the distribution is nonsymmetrical for both types of samples. For $S_{1,}$ the pore size varied from 0.6 to 3.3 μm with an average pore diameter of (1.3) μm. For gradient-porosity porous silicon sample S_3 the pore size varied from 0.6 to 2.2 μm with an average pore diameter of 1.3 μm. For gradient-porosity porous silicon sample (S_4) the pore size varied from 0.8 to 2.8 μm with an average pore diameter of (1.4) μm



(a)



(b)

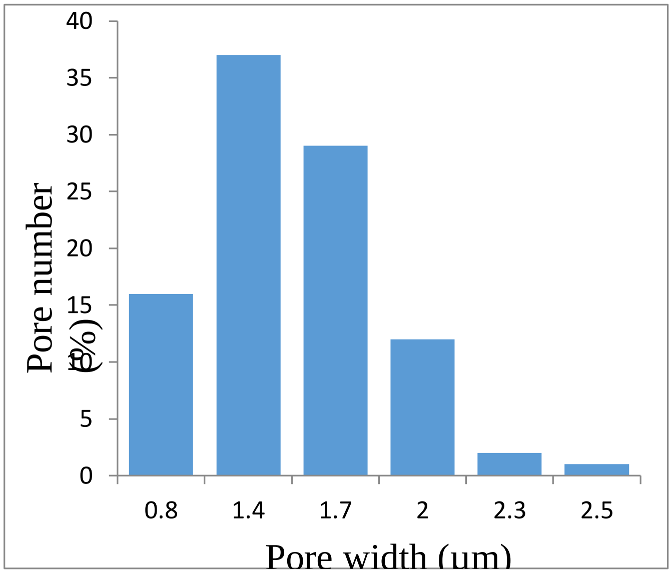


Figure (3): Statistical distributions of pore diameter size for (a) single-layer porous silicon sample (S_1), (b) gradient-porosity porous silicon sample (S_3) and (c) gradient-porosity porous silicon sample (S_4).

The pore shape change from nearly circular to rectangular cross-section has resulted from excessive etching at the pore wall which increased the silicon dissolution in HF solution [10]. As etching process proceeds with step – gradient laser illumination intensity, extra holes cannot reach sufficiently the surface of silicon; therefore further dissolution of silicon will occur in low rate leading to the formation of shallow pores inside the porous structure.

In summarized framework, we can deduce several facts from figure (2) and (3).

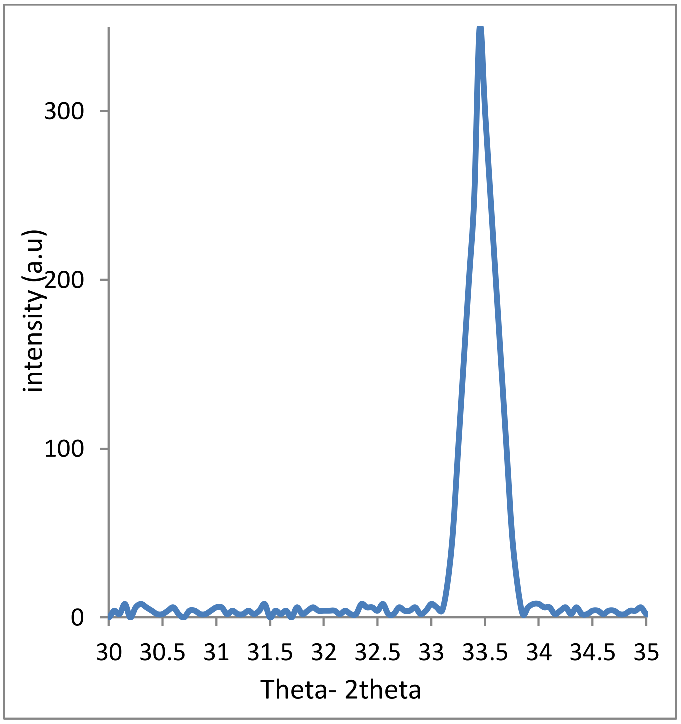
1. The pore width of single – layer PSi is higher than that of gradient – porosity GPSi layer.
2. The growth of the imaged pores in figure (2-a) for single – layer porous silicon is nearly complete, while the opposite is true for pores in figure (2,b and c) for gradient – porosity porous layer.
3. In figure (7), when the etching progresses steadily, the photo-generated carriers confined within thin walls which increase the etching of these walls and completely removing the PSi layer.

For single – layer porous silicon samples, the charge carrier has better opportunity to initiate and grow pores. The contrary is true for gradient – porosity porous silicon samples.

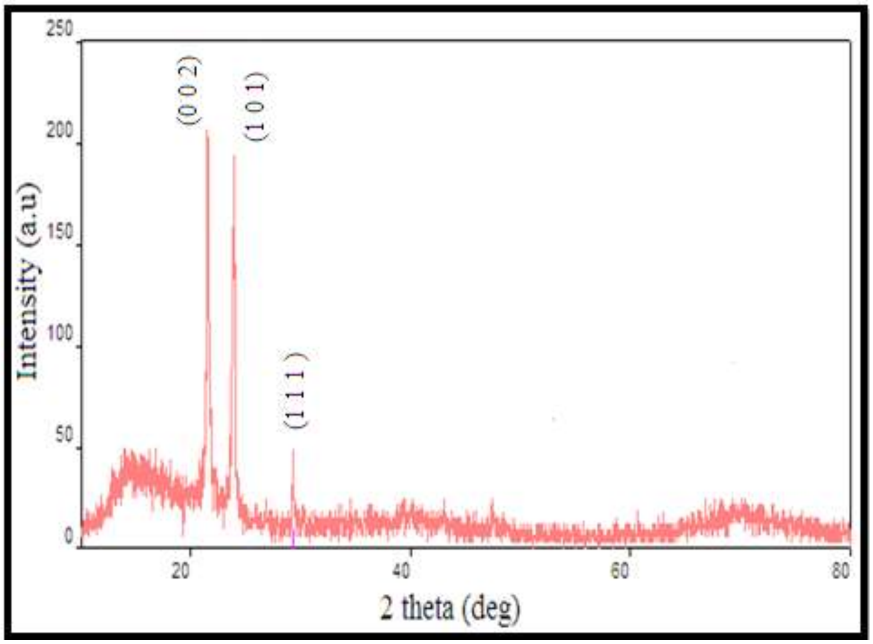
X-ray characteristics

The x - ray diffraction test provides an important view on the morphological nature of single porous silicon and gradient-porosity porous silicon. The silicon Nano crystallites size and morphology of porous layer (crystalline or amorphous) give us excellent concepts for the behavior of porous silicon in different application fields. The Nano crystallites sizes was calculated by using Scherer's formula and the structural properties were analyzed based on the x-ray diffraction measurement of porous samples. The x-ray diffraction pattern of S_1 with fixed illumination intensity of 150 mW/cm^2 and 8 min etching time and the (GPsi) samples S_3 and S_4 prepared with step - gradient laser illumination intensity are shown in figure (4-a), (4-b) and (4-c) respectively. The x-ray diffraction pattern for the S_1 sample, figure (4a) the single - porous silicon layer has a single peak at (33.3) 2ϴ angle. The results shows that the morphological phase of single porous silicon remains single-crystalline phase with (100) crystalline orientation.

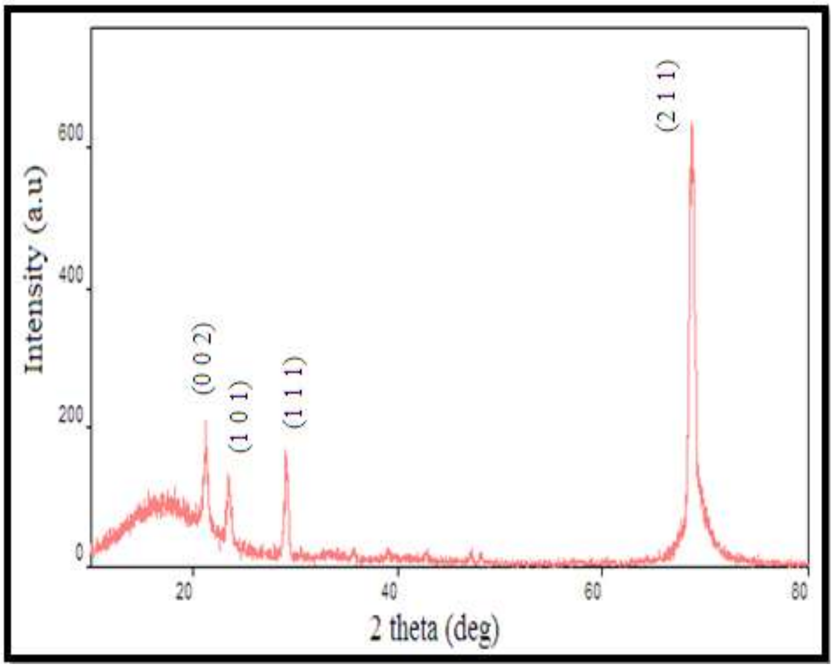
Multi peak characteristics at different angles 2ϴ (33.85, 21.5 and 29.2) is shown for S_3 in figure (4b) and (23.5, 21, 29 and 68.5) is shown for S_4 for figure (4c). These results indicate that the X-ray curve is showing a conversion of the native orientation of silicon wafer from single-crystalline phase to a poly - crystalline phase with (101), (002), (111) and (211) crystalline orientations.


300
200
100
0
intensity (a.u)
30
30.5
31
31.5
32
32.5
33
33.5
34
34.5
35
Theta- 2theta

(a)


250
200
150
100
50
0
Intensity (a.u)
(0 0 2)
(1 0 1)
(1 1 1)
20
40
60
80
2 theta (deg)

(b)



(c)

Figure (4): X-ray characteristics of the (a) single-layer porous silicon sample (S_1), (b) gradient-porosity porous silicon sample (S_3) and (c) gradient-porosity porous silicon sample (S_4)

The nanocrystallite size can be calculated from x-ray diffraction pattern by employing Scherer's formula shown in equation (4).

L=0.9 λ/ BCos θB …………………….. (4)

Where L is the nanocrystallite size of porous layer in (nm), λ is the wavelength of laser radiation in nm, B is the full width half maximum (FWHM) in radians, θB (radians) is the diffraction angle and 0.9 is the value of shape. The average nanocrystallite size of silicon of single-layer porous silicon sample (S_1) is around (12.8) nm, while for gradient-porosity porous silicon sample (S_3) are (29, 27 and 61) nm corresponding to the crystalline phases (002, 101 and 111) respectively. For gradient-porosity porous silicon sample (S_4), the average nanocrystallite sizes of silicon are (15, 15.7, 20 and 15) nm corresponding to the crystalline phases (002, 101, 111 and 211) respectively. From these data, we can deduce that the single-layer porous silicon has a minimum nanocrystallite sizes compared with that of gradient-porosity porous silicon layer. Increasing the illumination steps from sample S_3 to S_4 has decreased the silicon nanocrystallite sizes. It turned out that etching with laser intensity steps decreases steadily from higher to a lower value can facilitate a suitable control of the photo-generated holes for making porous silicon [12].

Conclusions

Gradient - porosity porous silicon layer produced by laser- assisted etching provides simple way to prepare high porosity with low layer thickness of GPSi. Structural and other porous silicon characteristics were modified into different orientations with different nanocrystallite sizes. The single crystalline silicon was converted to poly-crystalline silicon without the native orientation.

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