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Spectroscopic Aspects of Gradient-Porosity System

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Abstract

Laser-assisted etching process with the illumination of short laser wavelength of 405nm has been used to prepare efficient and thin layers of gradient- porosity porous silicon (GPSi) by employing two techniques; a step-gradient etching current and step- laser power density. From the spectroscopic aspects of (GPSi), it has been found that a very low reflectivity at wavelengths 400 nm and 850 nm was obtained as compared with a single layer –porous silicon. The photoluminescence study aided by scanning electron microscopy has revealed multi- peak photoluminescence (PL) emissions spectra of (GPSi) with peak intensity higher than that of Psi due to the gradient porosity inside the porous layer. These (PL) peak positions refer to porous system with multi energy band gaps compared with single energy band gap of the (Psi) layer. The SEM images indicated a pore-like structure of the surface of the etched layer with different pore sizes and porosities.

Keywords: Gradient Porosity System.

Introduction

Porous silicon is a very promising material in the fields of solar cells and optoelectronics devices. It is a complex matrix of nanostructured silicon and void spaces [1]. Porous silicon films can be prepared by using laser-assisted etching process of crystalline silicone in hydrofluoric acid solution, with possible control of porosity by the etching current density or by the laser illumination intensity [2, 3] leading to in – depth profile of porosities. Porous structures are classified into macro porous, mesoporous and nanoporous; according to pores dimensions [4]. Gradient porosity porous silicon (GPSi) is a special form of porous silicon in which the pore cross section and structure varies with depth [5, 6]. By controlling the pores profile, it is possible to prepare (GPSi) which has a controllable gradient refractive index across the porous layer thickness. This property will facilitate using it as broad band anti-reflection coatings (ARC) employed in solar cells [7] instead of silicon nitride. In the current study, a gradient porosity porous silicon (GPSi) layer was formed on an n-type silicon using laser - assisted step- gradient etching current and step - (405 nm) laser power density, as a function of etching time. Optical properties of the gradient-porosity porous layers were extracted using photoluminescence spectra (PL), reflectivity and scanning electron microscopy (SEM).

Experimental work

Gradient-porosity porous silicon layers were fabricated by etching of n-type silicon wafer of (100) orientation and (10 Ω.cm) resistivity by using a mixture of 24% HF acid and ethanol with mixing ratio of $HF:C_2H_5OH=1:1$. Gradient - porosity layer was achieved using 405 nm diode laser-assisted etching in two methods. In the first one, two laser illumination intensities; 100mW/cm^2 and 20mW/cm^2 were utilized with steadily decreasing laser intensity for a period of 2 min at a fixed etching current density of16 mA/cm^2. The etching time was then increased from 2 min to 8 min in four steps. In the second method, the laser - assisted etching process was demonstrated by step - gradient etching current density from 2 to 16 mA / cm^2 for two minutes under 405nm, 60 mW/cm^2 diode laser illumination. The etching process was materialized in specially designed cell; consists of two silicon combination electrode as an anode and a gold mesh as

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cathode, see figure (1). The experiment was conducted at room temperature with an irradiated area of about $1cm^2$**.**

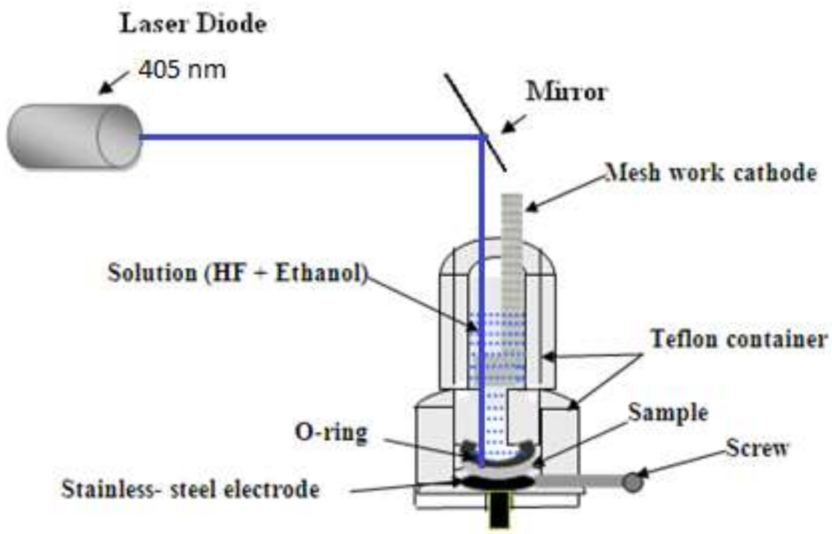

Figure (1): Schematic diagram of the Laser assisted etching system.

The cell provides us a porous silicon layer of uniform cross sectional area. This uniformity is recommended for the application of porous silicon in optoelectronic applications. **A** cross section of the home-made cell is shown in figure (1), in which a mesh gold cathode with aperture size of (2*2mm) was used. **P**orosity **size** and the thickness of the porous layer **we**re determined gravimetrically. The PL spectrum was obtained from a PL system (HR 800UV, Jobin Yvon) by exciting the synthesized layer with low power density 10 mW/cm^2 (He-Cd) laser operating at 325nm**.** SEM, reflectivity and PL measurements were carried out in the school of material engineering at the University Sains Malaysia in Penang.

Results and discussion

A) Reflectivity studies

The reflectivity of crystalline single layer porous silicon and gradient- porosity porous silicon were studied as a function of wavelength in the range 400nm - 850nm. The gradient behavior in refractive index was confirmed by examining the reflectivity of the gradient porosity samples. It is widely accepted that variation of refractive index within porous layer is responsible for the reflectivity of porous silicon layer.

1) Reflectivity of crystalline silicon and single layer porous silicon

The reflectivity of mirror – like silicon surface and n-type single layer porous silicon; prepared in laser-assisted etching process at laser illumination intensity of 80 mw/cm^2 and fixed etching time (8 min) and etching current density (16 mA/cm^2), were studied. Figure (2), illustrates the reflectivity – wavelength relation of the reference sample (mirror-like) silicon surface. It shows a maximum value of about 47% at wavelength of 400nm but decreases at longer wavelength reaching its minimum of about 23% at 850nm. This relatively high reflectivity is due to the large reflective index discontinuity which exists at the air-silicon interface.

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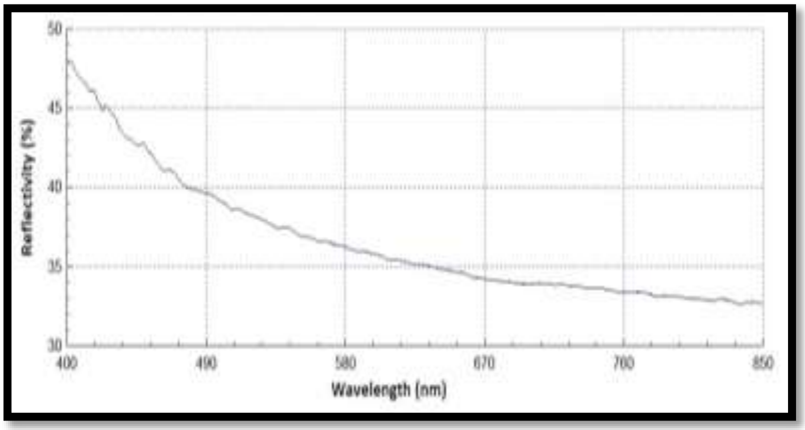

Figure (2): presents the reflectivity of reference (mirror-like) silicon sample as a function to spectral range wavelengths.

Figure (3) shows the reflectivity of the single layer porous silicon sample prepared with illumination laser intensity of 80mw/cm^2. This figure shows a much lower reflectivity of porous silicon surface than that of the reference sample. The etching process led to a change in surface reflectivity of the porous silicon sample to 12.8% for 400nm and to only 4% for the 850 nm wavelengths. This variation in reflectivity refers to a dramatic change in refractive index of the porous silicon sample.

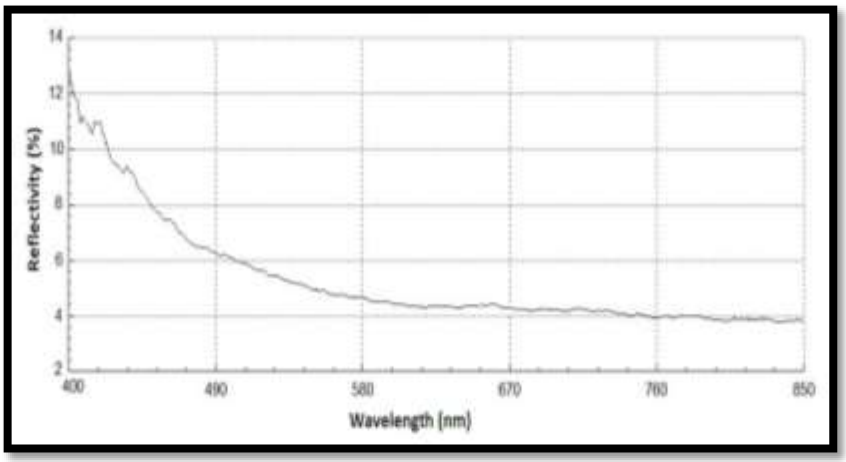

Figure (3): shows the reflectivity of single layer (n-type) porous silicon of porosity (87%) prepared by laser-assisted etching at illumination intensity of (80mw/cm^2) with etching conditions (16mA/cm^2) and (8 min).

2) Reflectivity of gradient-porosity porous silicon

The gradient-porosity (GPSi) samples were fabricated on silicon substrates using two methods: the laser - assisted etching with step-gradient current and fixed 60 mw/cm^2 laser intensity, and the laser - assisted etching with step-gradient 20 -100 mW/cm^2 laser intensity with fixed etching current density of 16mA/cm^2 and 2 min etching period for each laser intensity. The reflectivity measurements of these two methods are presented in figures (4 and 5). In figure (4), the reflectivity curve of porous silicon prepared by step-gradient current starts with maximum value of 4.5% at the short wavelength region and reaches its minimum value of 1.3% at the long wavelength

region. Similarly, higher reflectivity of (3.5%) was measured at the short wavelength region and lower value of (2.5%) was seen at the longer wavelength region, as shown in figure (5). The obtained data indicate lower reflectivity of the (GPSi) samples for all wavelengths than those of the single – layer porous silicon samples.

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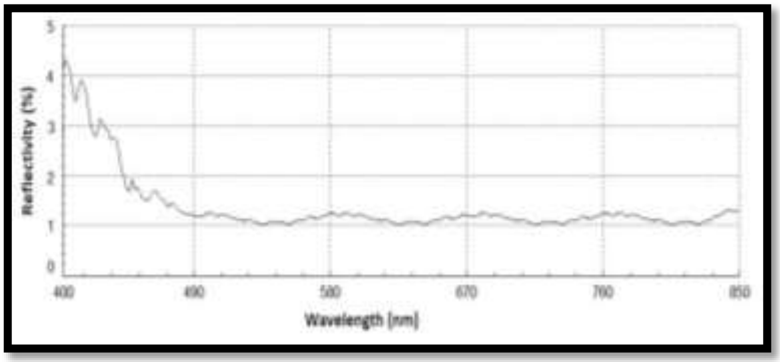

Figure (4): reflectivity of (GPSi) porous silicon sample prepared by laser illumination intensity of (60mw/cm^2), under step-gradient current density.

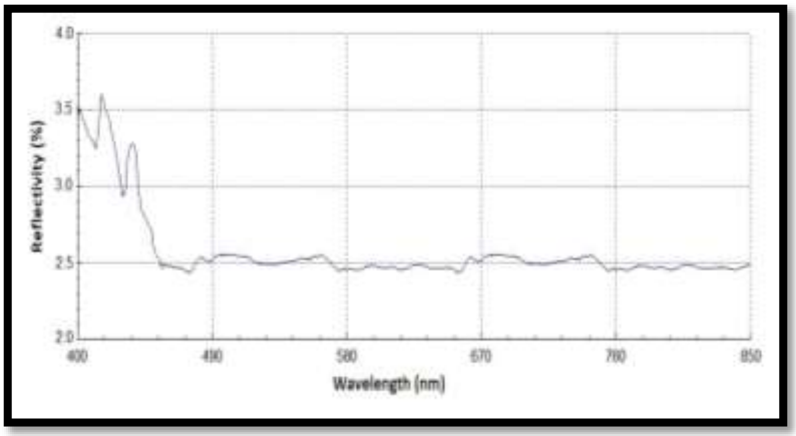

Figure (5): reflectivity of (GPSi) porous silicon sample prepared by step-gradient laser illumination intensity between 20 - 100mW/cm^2 and etching current density of 16mA/cm^2.

The variations of reflectivity are generally attributed to the nature of porous layer, where this layer contains light scattering voids and large surface-area to volume ratio, which enhance the optical absorption and hence, a low reflectivity is obtained [8]. The effect of porosity values on the reflectivity may be due to the effective dielectric constant of the porous material system. This can be expressed as:

$$\mathbf{P}\left(\frac{\epsilon_1-\epsilon_{eff}}{\epsilon_1+2\epsilon_{eff}}\right)+(\mathbf{1}-\boldsymbol{P})\frac{\epsilon_2-\epsilon_{eff}}{\epsilon_2+2\epsilon_{eff}}=\mathbf{0} \quad \text{..........} \ (1)$$

Where (P) is the porosity, $\epsilon_1$and ϵ_2 are the complex dielectric of host material and filling material andϵ_{eff} is the effective dielectric function of mixed material (porous). The refractive index of porous silicon is expected to be lower than that of bulk silicon. It decreases with increasing porosity, simply because porous silicon is a mixture of silicon and air. The refractive index is calculated from the square root of the effective dielectric function [5]:

$$n_{psi}=\sqrt{\epsilon_{psi}} \quad \text{.........................} \ (2)$$

Based on the results presented above, the gradient-porosity porous silicon samples can act as broad band antireflection coating.

The decreasing reflectivity results are in good agreement with those published by C. C. Striemer, et al. [5] and J. D. Hwang et al. [2]. This explanation is illustrated in in figure (6a). Placing a single-layer PSi of intermediate refractive index onto the silicon surface will result in large index discontinuity broken into two smaller steps; see figure (6b), leading to a lower reflectivity. Step-gradient current density or step-gradient laser intensity was applied to break the air–silicon index discontinuity into smaller and smaller steps, leading to a step-gradient refractive index, figure (6c), hence achieving a broadband antireflection property.

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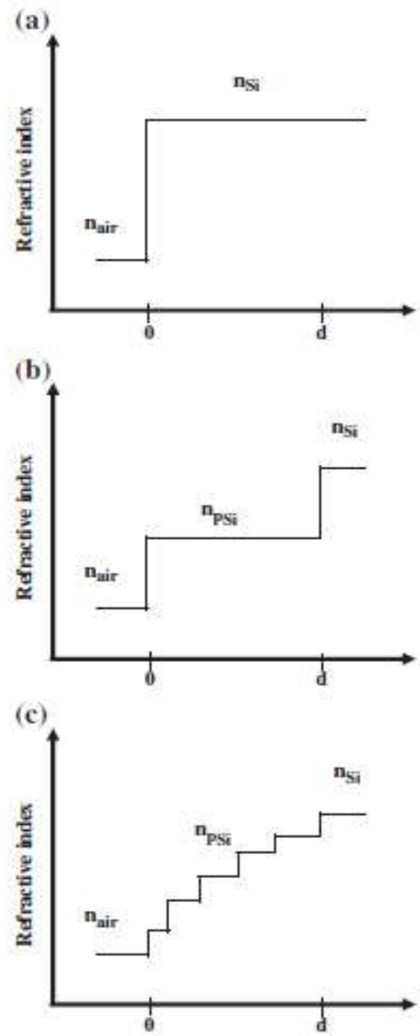

Figure (6) : Three basic spatial refractive index profiles of thickness d. (a) No antireflection layer, (b) standard antireflection of single-layer PSi, and (c) antireflection layer with step-gradient refractive index [5].

In our dynamic etching study, the obtained data for the (GPSi) reflectivity in laser - assisted etching is much lower than what had been obtained (3.7%) for short wavelengths by (C. C. Striemer, et al.) [5]. The results of J. D. Hwang et al., [2] who employed (PEC) with step-current density techniques showed a reflectivity reduction of less than (1%) for the gradient-porosity sample within the spectral range 300-400nm. We demonstrate here a reduction of (6.5% to 7.5%), indicating our efficient approach and its possible use as brood band AR for solar energy collection and other optoelectronics applications.

B) Surface morphology.

Porous silicon layer exhibits dramatic and very special structure characterized by the presence of interconnected pores in a single crystal. All morphological properties of single-layer and gradient-porosity layer such as porosity, layer thickness, pore width, pore shape and the wall thickness between two pores are strongly dependent on the etching conditions. These features of porous silicon have been studied by direct imaging by scanning electron microscopy.

Single - layer porous silicon

The surface morphology of the single - layer PSi is shown in figure (7). The SEM image shows (top - view) of single - layer of PSi produced at illumination intensity of ($80mw/cm^2$) with etching current density of ($16mA/cm^2$) and (8 min) etching time. In this figure, e can easily notice the different size pore width.

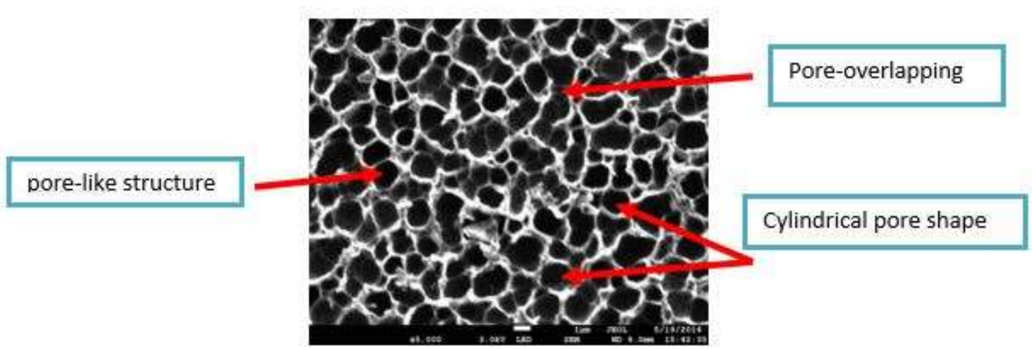

Figure (7): SEM images for the single layer porous silicon prepared by laser-assisted etching using ($80mw/cm^2$) intensity, ($16mA/cm^2$) current density and (8 min) period

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This increase in pore width may be attributed to the increasing of holes number on the surface of silicon electrode with etching process progressing in preferential dissolution between nearest-neighbor pores, thereby promoting pore-pore overlap. Etching rates, however, may be different and could lead to non-uniform pore widths, (0.4 to 2.2) µm. This variation may be due to the non-uniform spatial laser intensity distribution, Gaussian [9] resulting in non-uniform hole-photo-generation and therefore different pore widths.

Gradient – porosity porous silicon layer

The surface morphology of the gradient – porosity porous silicon was examined by SEM. Figure (8-a) shows SEM top-view images of (GPSi) layer obtained with step-gradient current density and laser illumination intensity of (60mw/cm^2). The (GPSi) layer with step-gradient laser illumination intensity from 20-100 mW/cm^2 and etching current density of 16mA/cm^2 is shown in figure (8 b). Figure (8 – a, and b) shows a pore- like structure with variable pores sizes. Pore width and shape values are clearer in (8 b) than in (8 a). One can note that pore shapes depend on the separation between them.

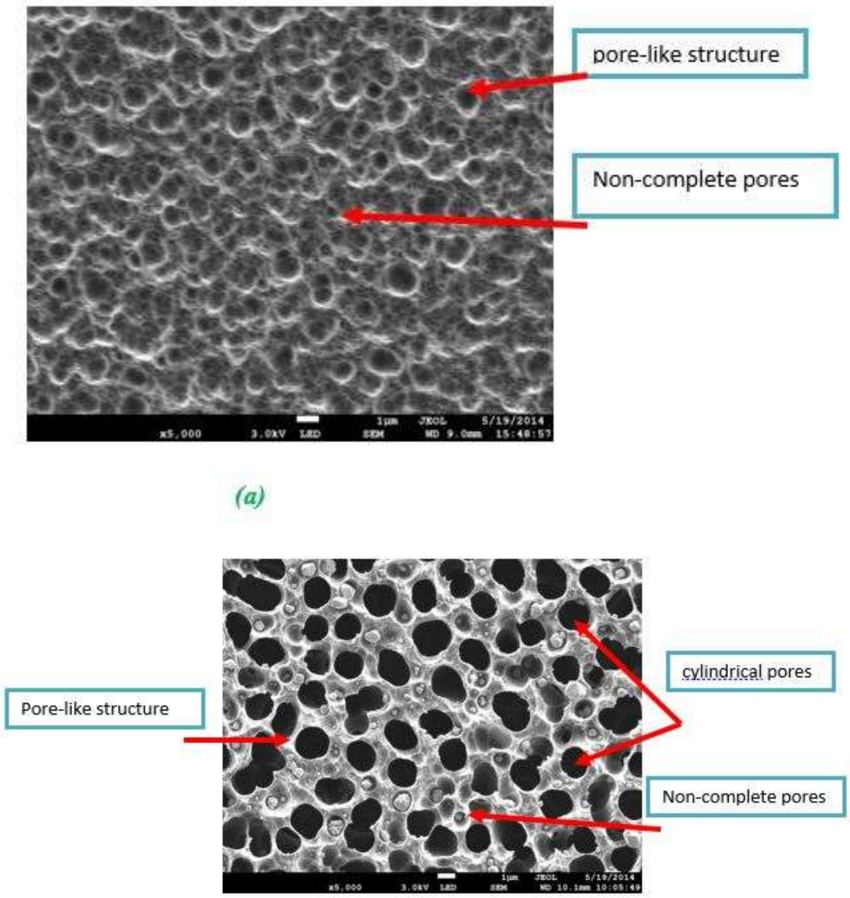

Figure (8): SEM images of (GPSi) porous silicon sample (a) with step-gradient current density and laser intensity of (60mw/cm^2), (b) with step-gradient laser intensity from 20 - 100 mW/cm^2 and etching current density of 16mA/cm^2.

As etching process proceeds in step-gradient current density or step – gradient laser step-gradient laser intensity, extra holes cannot reach sufficiently the surface of silicon; therefore further dissolution of silicon will take place in low rate leading to a new layer as shown in figure (8). In summarized framework, we can deduce several facts from figure (7) and (8).

1- The pore width of single – layer PSi is greater than that of gradient – porosity GPSi layer.

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2- The growth of the imaged pores in figure (7) for single – layer porous silicon is nearly complete, while the opposite is true for pores in figure (8) for gradient – porosity porous layer.

3- In figure (7), when the etching process progresses in steadily state, the photo-generated carriers confined within thin wall leading to an increased etching in these walls and complete removal of PSi layer followed by new growth of pores.

All these results indicate that for single – layer porous silicon samples, the charge carrier gets better opportunity for initiating and growth of pores. On anther hand, the opposite is true for gradient – porosity porous silicon samples.

C) Porosity and porous Layer thickness.

Porosity and layer thickness of (GPSi) and (PSi) have attracted a great attention. These two parameters depend on the formation parameters and are governed by the generation rate and recombination of holes (h^+) to the surface [9]. Porosity of the gradient porosity porous silicon and the porous layer thickness were determined from gravimetric measurements [2]. The obtained data is shown in table (1), which reveals higher porosity and the layer thickness of (Psi) layer than that of the (GPSi). The thickness of the porous layer is dependent on the penetration depth of the laser. The absorption depth is defined as the reciprocal of an absorption coefficient (α) at which the photo generated *e-h* pairs are exponentially reduced by factor 1/e [10]. The absorption depth of the 405nm wavelength is about 0.09µm, and therefore a very thin porous can be prepared with the application of this short laser wavelength. The measured porous layer is higher than the theoretical due to the etching current density role in increasing the etching process leading to a thick porous layer.

Based on the reported data in table (1) and from figure (7) and (8) we can deduce several facts.

1- The local photo-generation of minority carriers (h^+) determine the pore shape in the following way:

The photo-generation of carriers in deepest layer promote the pore growth at the tips of pores leading to an increase in the layer thickness, whereas the generation near the surface leads to lateral growth of the pores.

2- The depth of formed pores in the gradient – porosity porous layer was more uniform and non-complete cylindrical-shape) i.e. the pore size is varied across the porous layer thickness, while the contrary is true for pores in the case of single – layer porous silicon.

Table (1); porosity and layer thickness of porous silicon for single – layer and gradient porosity layer

Porous –layer type	Porosity%	Porous layer thickness µm
Single layer	87	5.6
Gradient-porosity *step-gradient current density*	54	0.42
Gradient- porosity ***step-gradient laser illumination intensity***	65	0.39

D) Photoluminescence studies.

The optical properties for both single and gradient porosity have been confirmed by studying the PL emission and their nanocrystallite sizes contributions to its spectrum. It is widely unaccepted that a distribution of crystallites sizes in porous film is responsible for broad emission bands of different peaks.

1) Photo luminescence of single-layer porous silicon

The Photo luminescence emission spectrum of (Psi) sample prepared at illumination intensity of ($80mw/cm^2$) and etching current density of ($16mA/cm^2$) and (8 min) etching time is shown in figure (9). The PL curve has sharp peak intensity at peak wavelength with a Gaussian – like distribution which refers to porous layer with nano-sized silicon distribution. Since the photon energy is larger than the band gap energy of the produced nanocrystallite, an efficient absorption could take place leading to a wide range of crystallites sizes within the single and gradient porous layer. The obtained (PL) spectrum has a peak wavelength of (538) nm and a peak energy gap of porous silicon layer of (2.4) eV. Based on the energy gap of silicon nano-sized in porous layer, the mean silicon nano-size can be calculated according to the following equation:

$$E_g^* = E_g + \frac{88.34}{L^{(1.37)}} \quad \text{.........................(3)}$$

Where L (A°) is the silicon nano size in the layer, Eg* (eV) is the energy band gap of porous silicon, and Eg (eV) is energy band gap of bulk silicon. It was found that the mean size of crystallite is about (2.3 nm).

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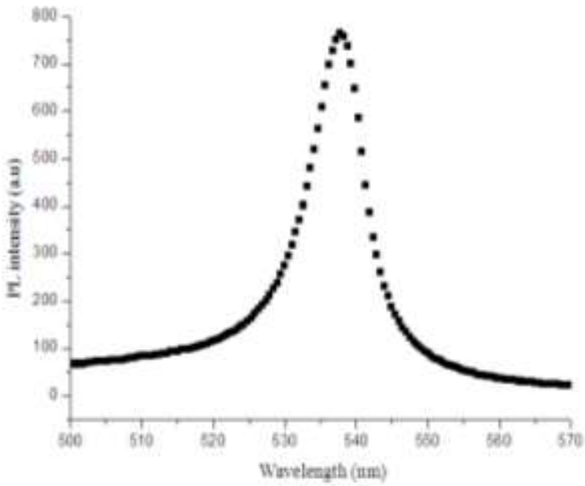
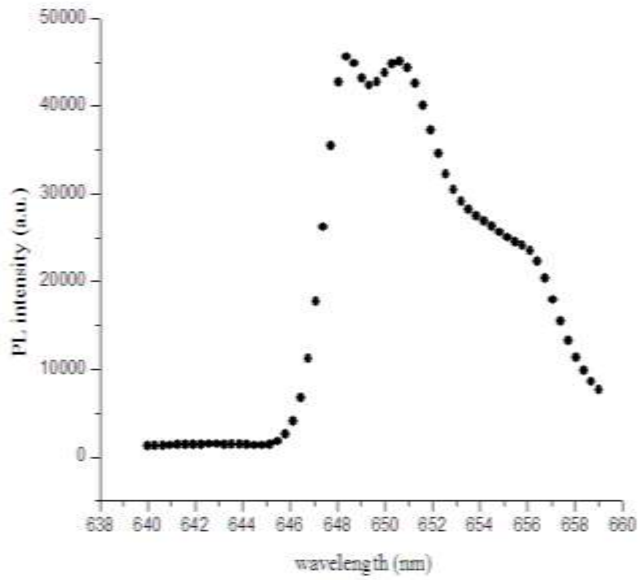
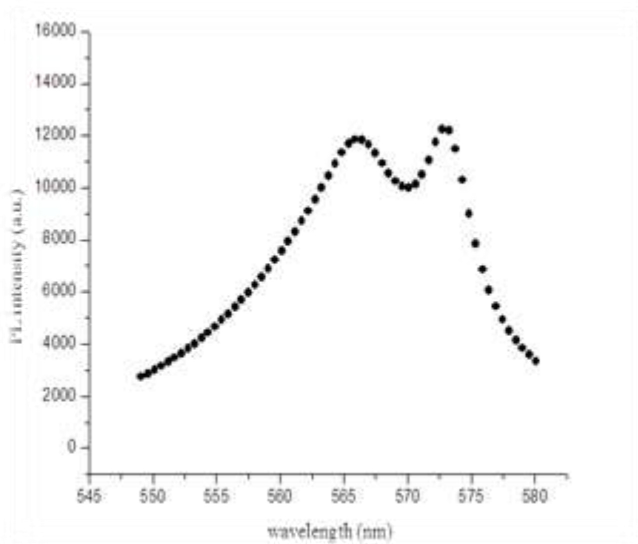


Figure (9): Photo luminescence emission spectrum of (Psi) prepared by laser-assisted etching at laser illumination intensity of (80mw/cm^2) with etching conditions (16mA/cm^2) and (8 min).

2) Photo luminescence of gradient-porosity porous silicon

The variation of etching laser intensity and etching current density in step –gradient form can modify the emitted PL spectra to form a multi – peak (PL) spectra instead of individual peak. This could be attributed to the formation of multi- porous silicon layer at different sizes. The PL spectra of gradient porosity – porous silicon layer is shown in figure (10). The obtained (PL) spectrum of figure (10-a) shows two peaks at (562) nm and (572) nm corresponding to energy gap of porous silicon layer peak of (2.2) eV and (2.1) eV respectively. The silicon nano-size has two different values: (2.4) nm and (2.6) nm respectively. Figure (10-b) also shows two-peak (PL) spectrum at wavelengths (**?**) nm and (**?**) indicating energy gap of porous silicon layer peak of (**?**) eV and (**?**) eV respectively.





(a) (b)

Figure (10): Photo luminescence emission spectrum of (GPSi) porous silicon sample (a) with step-gradient current density and laser illumination intensity of (60mw/cm^2), (b) with step-gradient laser illumination intensity from 20 - 100 mW/cm^2 and etching current density of 16mA/cm^2.

The (PL) peak intensity of (GPsi) shows maximum value of 45000 a.u whereas the (PL) peak intensity is about (800 a.u) for **(Psi)**. This enhancement at PL intensity of (GPsi) is generally attributed to quantum size effects in nano structures. The variation in laser illumination intensity or etching current density leads

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to the transformation of some silicon nano-wires to more energetic quantum dots [11]. The increase of PL intensity may be also attributed to the increase of silicon nanocrystallite density in the (PSi) layer and also to the increasing porosity of the porous layer [11].

Conclusion

Efficient and thin layers of gradient- porosity porous (GPSi) have been fabricated by laser - assisted etching by two techniques, a step- gradient etching current and a step- laser intensity with the illumination of short laser wavelength of 405nm. In the prepared (GPSi) layers by these two techniques, the decreased reflectivity is superior for broad band AR applications, such as solar energy collection. The photoluminescence spectra (PL) of (GPSi) showed multi - peak photoluminescence emissions with higher value of (PL) peak intensity as compared with that of (Psi)

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