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Preparation of Silicon Nano-Structure by Laser-Induced Etching Process

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Abstract:

Silicon nano-structure has been prepared in this work via Laser-induced etching process (LIE) on n-type silicon wafer (3 Ω.cm resistivity) in hydrofluoric acid (HF) (24.5 % concentration) at different etching times (5 – 25 min.). The irradiation has been achieved using laser beam of 2W power and 810 nm wavelength. The morphological and photoluminescence characteristics of these material such as porosity, surface morphology and nanocrystallite size have been investigated using scanning electron microscope (SEM), photoluminescence (PL) measurements, and the gravimetric method.

1. Introduction

During the past years there has been an increased interest in the luminescence properties of silicon nano-structure or porous silicon (P-Si). This material has efficient luminescence in the visible regime even at room temperature [1]. *Canham* was the first who ascribe the visible luminescence to quantum confinement of the excited electron-hole pair inside the small silicon structures, resulting in luminescence energy well above the bulk silicon band gap. It was further argued that the nonradiative recombination is much reduced due to the good surface passivation and the fact that the carriers are confined inside the crystallites and cannot diffuse far away to reach a nonradiative center [2]. Photochemical etching (PE) process or laser-induced etching (LIE) process of silicon is a technique known to create silicon nano-structure material [3,4]. The nature of nanocrystallites and their size distribution depend on the actual experimental conditions during the LIE process which include: nature of the substrate, penetration depth of the used laser, laser power density, laser irradiation time and HF concentration [5,6]. Moreover, illumination of n-type silicon wafers with infrared laser radiation could be used to modify the photoemission characteristics [7,8]. The result behind this study shows that the visible light emission can be obtained from silicon nano-structure at room temperature prepared by laser-induced etching process under defined values of mentioned parameters.

2. Experiment

2.1- preparation of samples

Crystalline wafer of n-type silicon with resistivity of 3 Ω.cm, 508 μm thickness, and (111) orientation was used as starting substrate. The substrate was cut into rectangles with areas of 1 cm^2. The native oxide was cleaned in a mixture of HF and H_2O (1:2). Laser-induced etching process then performed at room temperature in an ethanoic solution of 24.5% HF (1 volume of ethanol and 1 volume (49% wt). Hydrofluoric acid (HF)). The irradiation has been achieved using a commercially available CW diode laser with power (2W) and (810 nm) wavelength (made in Russia).

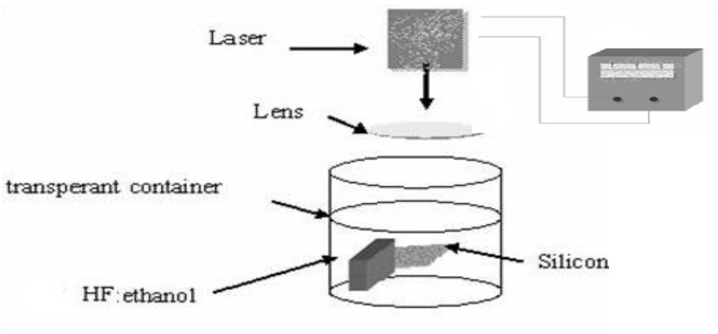

Figure (1): The laser-induced etching set-up.

2.2- Morphological measurements

The morphological properties were measured by scanning electron microscopy (SEM) (Leo-1550). The SEM measurements were carried out in the (Institute for Bio-and Nano-systems (IBN2)-Germany).

The porosity were measured using Gravimetric method and using the following equation [10]:

$$\gamma = \frac{M_1 - M_2}{M_1 - M_3} \quad (1)$$

where M_1 (g) and M_2 (g) are the weights of silicon sample before and after etching process respectively and M_3 (g) is the weight of the sample after removing of layer.

2.3- photoluminescence measurements

The photoluminescence (PL) characteristics have been achieved in University of Technology. The spectroscopic instruments used for this purpose consist of the laser source, the monocrometer and finally the detection system. Figure (2) shows the experimental set-up of the photoluminescence spectra measurements.

2.3.1- Excitation Source

A CW diode laser of 514 nm (made in German) has been used to probe the P-Si layer as an excitation source with photon energy of 2.41 eV which excite a wide range of nanocrystallite sizes. A laser power density of $\approx$ 5 mW/cm^2.

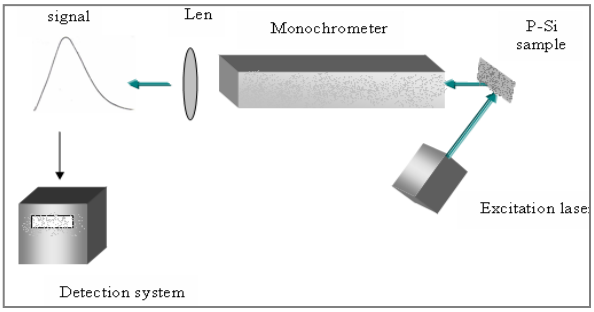

Figure (2): The photoluminescence set up.

2.3.2- The Detection

The analyzed scattered light was collimated by a very small focal length lens and detected by using power-meter (made in Japan) which behaves as a detection device.

2.3.3- The Monocrometer

A single pass monocrometer (Jobin-Yvon Co.) were used to analyze the scattered light from the sample. The sample was mounted on a sample holder and placed in front of the monocrometer entrance slit which was about 200 μm while the exit slit was around 300 μm, where the optical system which consist of a set of different mirrors and a grating which was blazed for 6000 A° has a total length of 50 cm.

3. Results and Discussion

3.1. Surface morphology

Figure (3) represents scanning electron microscopy (SEM) images (top-view) of P-Si layers which prepared at different etching times.

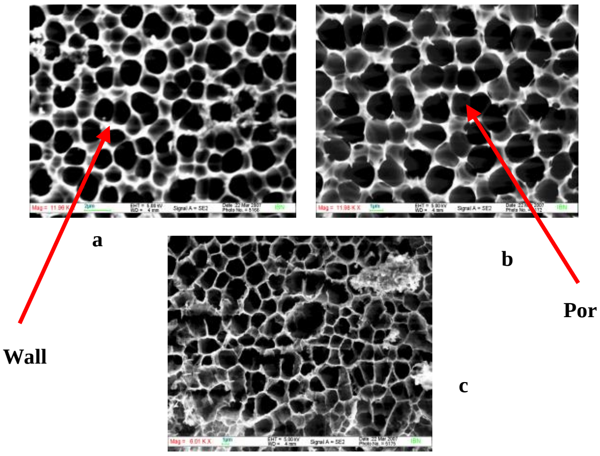

Figure (3): SEM images (top-view) of P-Si layers (a) 5 min., (b) 10 min., (c) 15 min.

Figure (3), proved growth of P-Si layers on the surface of silicon, and growth process of these P-Si layers can be illustrated according to Lehmann model as follows [1]: If photo-generated charge carriers (hole (h^+)) reach the surface, nucleophilic attack on Si-H bonds by fluoride ions (F^-) can occur and a Si-F bond is established. Due to the polarizing influence of the bonded F, another F^- ion can attack and bond under generation of an H_2 molecule and injection of one electron into the bulk silicon. Because of the polarization induced by the Si-F groups, the electron density of the Si-Si back bonds is lowered and these weakened-bonds will now be attacked by HF or H_2O in a way that the silicon surface atoms remain bonded to hydrogen, when a silicon atom becomes removed from an atomically flat surface by this reaction, an atomic size dip remains. This change in surface geometry will change the inert electric field distribution in such a way that holes transfer occurs at this location preferentially. Therefore pores of about 1 μm will establish in a few minutes on polished n-type silicon surface by this process [9,11].

Figure (3) shows that the pore width increases with increasing of etching time. This largeness in pore width may be attributed to increasing of holes number on surface of silicon electrode with etching time which leads to preferential dissolution between nearest-neighbor pores, thereby promoting the pore-pore overlap.

However, the etching rates may be different and then leads to nonuniformity in values of the pores width as summarized in table (1). This due to the nonuniform of the power density distribution of illumination, which leads to nonuniform photocurrent densities consequently, resulting in different pore width. The nonuniform of the power density distribution of illumination is attributed to fact that the laser beam intensity will decrease gradually from its center to its periphery (Gaussian-laser beam). Figure (3,a) shows the P-Si

layer possesses pores with cylindrical shape, while the P-Si layer in figure (3,b) has nearly structure with cylindrical shape.
From figure (3,c) we can observe P-Si layer possessing approximate construction composed of pores with starful and rectangular shapes.

Table (1); Wall thickness, pore width and pore shape of prepared P-Si layers under different etching times (5-15 min.).

3.2.

Etching time (min)	Pore width (μm)	Pore shape	Wall thickness (μm)
5	0.37 – 2	Cylindrical	0.14 – 0.98
10	0.42 – 2.56	Cylindrical	0.089 – 0.78
15	1.45 – 7.11	Starful & Rectangular	0.067 – 0.56

Porosity

Figure (4) shows the relationship between porosity of P-Si layers prepared under different etching times (5-25 min.) and etching time.

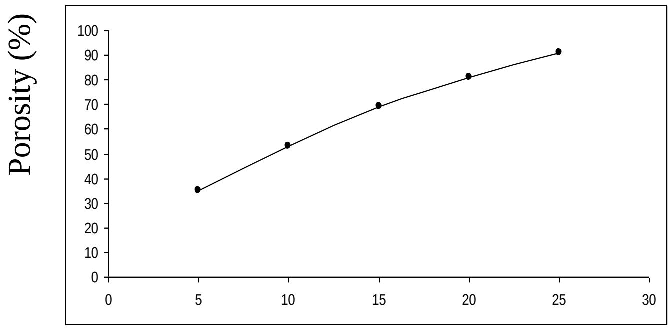

Figure (4); Porosity of P-Si layers as a function of etching time.

From previous figure, we can see the values of porosity are increasing with increasing of etching time. These results are ascribed to increasing the number and width of the pores with increasing of etching time. These consequences are consistent with SEM images, where the roughness of surface is a function of etching time and porosity as shown in figure (3). Our results agree other studies of [12,13].

3.3. Photoluminescence Characteristics and Nanocrystallite Size

A quantum confinement model has been used by *Canham* [2] and modified by Yorikawa *et al* [14] to study the nanocrystallite size distributions in P-Si layer from their PL spectra.
According to this model, each nanocrystallite in a P-Si sample contributes a characteristic sharp PL spectrum so that the total PL intensity S(E) from an assembly of crystallites including size distribution is given by [15]:

$$S(E) = c\alpha\,(E_{exc} - E)\,D(R_E)\,\frac{1}{n}\,\frac{R_E}{E - E_g{}^0} \quad ..... (2)$$

where E_g° is the energy gap of bulk silicon and R_E is the crystallite radius defined by $R_E = \{\delta / E - E_g^{\circ}\}^{1/n}$, $\alpha = 14.8$ (eV. $A^{\circ n}$) and n=1.25.

PL spectra of three P-Si samples prepared under different etching times (5, 10, 15 min.) as shown in figure (5), left column represents the experimental and the theoretical calculation obtained by the equation (2). For the sample prepared with a 5 minutes etching time, it is found that the crystallite size was 32 A° and the standard deviation was 0.09 A° as shown in figure (5a). With increasing the time up to 10 minutes, as shown in figure (5b), the obtained nanocrystallite size decreases to 31 A° with a standard deviation of 0.18 A°. While the nanocrystallite size decreases to 30.3 A° for 15 minutes, as shown in figure (5c), the standard deviation was found to increase up to 0.23 A°.

When the silicon wafer is illuminated with the 810 nm wavelength where the photon energy is 1.53 eV, the energy gaps of the produced crystallites are smaller than the excited energy leading to generate electron-hole pairs within the illuminated area to form the P-Si layer.

Therefore, larger irradiation time duration leads to further etching and size reduction. However, as the etching proceeds, the small crystallites in the porous layer increase the band gap and the porous layer becomes transparent to the laser light. At that time, an optical absorption would take place at the P-Si /bulk Si interface and leads to increase the P-Si layer thickness.

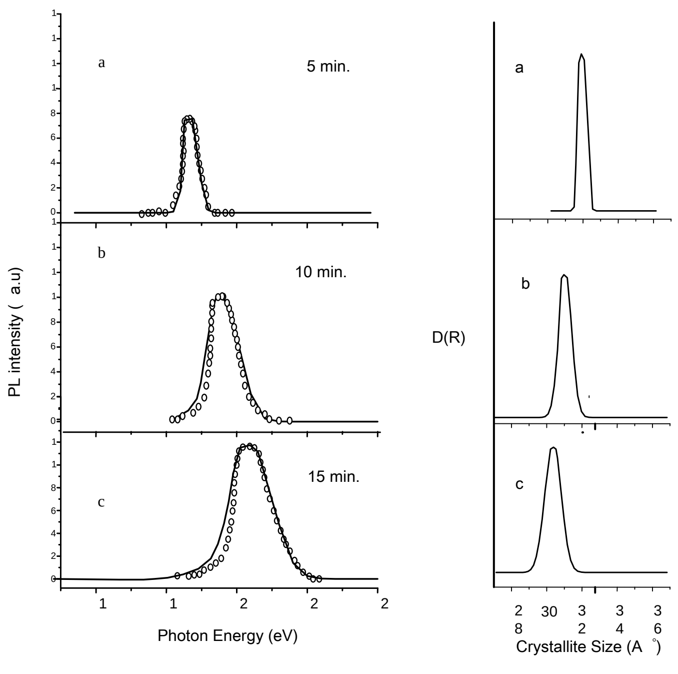

Figure (5): The left column represents the experimental data (discrete plot) fitted on the quantum confinement model. While the right column represents the Gaussian distribution of crystallites sizes contribute the PL emission.

4. Conclusion

We can conclude from previous results and facts that the laser-induced etching with 810 nm wavelength of the silicon can be produce a luminescent silicon nano-structure. The photoluminescence characteristics of etched silicon are attributed to possess this material to crystals with nano-size.

5. Acknowledgement

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تحضير السيلكون النانوي التركيب باستخدام عملية القشط المحتثة بالليزر

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الخلاصة

تم في هذا البحث تحضير مادة السليكون النانوي التراكيب بواسطة عملية القشط المحتث بالليزر لشرائح سليكون من نوع -n ذي مقاوميه كهربائية نوعية مقدارها (3 Ω.cm) باستخدام حامض الهايدروفلوريك (HF) (بتركيز % 24.5) عند أزمنة قشط (5−25 دقيقة) التشعيع أنجز باستخدام شعاع ليزر ذو قدرة 2 W و طول موجي 810 nm. تم دراسة الخصائص الطوبوغرافية وكذلك التلألؤية لطبقات السليكون المسامي المحضرة مثل المسامية, طوبوغرافية السطح وحجم البلورات النانوية باستخدام قياسات المجهر الالكتروني الماسح والتلألؤية وكذلك الطريقة الوزنية.