Enhancement of Porous Silicon Formation by Using laser Irradiation

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ABSTRACT

In this work porous silicon where prepared by chemical etching assisted with laser. The structural and optical properties of porous silicon are investigated using atomic force microscopy (AFM) and FTIR spectroscope. FTIR spectrum exhibit the formation of SiHx (x=1,2) and Si-O bonds. The atomic force microscopy AFM investigation shows the surface roughness (RMS observed was 1.52nm with laser and 1. 86 nm without laser) and pyramid like hillocks surface on entire surface which can be regarded as a condensation point to form small skeleton clusters which plays an important role for the strong visible luminescence.

Keywords: porous silicon, chemical etching, optical properties, structure Properties.

تحسين تشكيل السيليكون المسامي باستخدام أشعة الليزر

الخلاصه

في هذا العمل ، حضر سليكون مسامي بطريقه كيميائيه وبمساعده الليزر . تم دراسه الخصائص البصريه والتركيبه للسيلكون المسامي باستخدام مجهر القوى الذرية ومطياف FTIR. بين طيف FTIR تشكيل SiHx (x = ١،٢) والاصره O-S. يظهر مجهر القوة الذرية AFM خشونة السطح (لوحظ ان RMS ١،٥٢nm مع ليزر و ١. ٨٦ nm بدون الليزر). وهرم مثل سطح التلال على كامل السطح والتي يمكن اعتبارها نقطة تكاثف لتشكيل مجموعات الصغيرة والتي تلعب دورا قويا في الاضاءه المرئيه.

INTRODUCTION

Silicon has been attracted great attention with experimental and theoretical interest in last year's, not only as an interesting material for variety of useful optical and electronic devices [1]. The highly perfect crystalline structure of extremely pure silicon single crystals is considered as the starting point for many metro-logical applications [2]. Research interest in all silicon based light – emitting devices (LED) is stimulated by observation of efficient light emission in structures

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of nanocrystalline silicon [3].Porous silicon can be considered as silicon crystals have a network of voids in it[4]. The nanosized voids in the silicon bulk result in a sponge-like structure of porous and channels surrounded with a skeleton of crystalline silicon nanowires [5]. The physical properties of porous silicon are fundamentally determined by the shape and diameter of pores, thickness, and relative content of silicon, voids and in some cases, the relative content of different silicon compounds in the formed porous layer [6]. Porous silicon is usually prepared by electrochemical etching (p-Si) under an anodic bias or photochemical etching (n-Si) under light illumination [7]. In addition to electrochemical etching the method of stain etching (SE) [8-10] for formation of porous silicon layer has been developed. Along with its simplicity the stain etching method is interesting because it does require special equipment and gives the possibility to prepare very thin (≤ 100 nm) porous silicon layer [11].Fathauer*et al.* carried out stain etching of silicon in HF:HNO_3:H_2O solutions and obtained porous layers similar to those produced by anodic etching [12].The observation of visible room temperature photoluminescence (PL) from porous silicon for understanding the optical properties of silicon .Since the discovery of visible photoluminescence (PL) at room temperature in porous silicon in 1990many nanostructured silicon systems have been fabricated and investigated aiming toobtain applicable silicon-based light emitting devices. Although, it yields high-efficiency red-light emission. Porous silicon has considerable attention for solar cell and sensor applications [13]. Its luminescence properties, large surface area, and compatibility with silicon-based devices are good reasons for used in the sensors and the solar cells. Related to these applications, the ability of adjustment and control of some parameters are more important. The energy band gap and the thermal diffusivity are two important parameters in sensors, solar cells [14, 15], electronic [16] and optoelectronic [17, 18] devices, thermal flow sensors [19], isolators[20] and fuel cells[21, 22]. In this work, study the properties of porous silicon prepared by stain etching with and without laser by using FTIR and AFM microscopy.

EXPERIMENTAL WORK

The silicon wafer that was used is n- type (111) with resistivites about (1.5- 4 Ωcm) and (500 ± 15 μm) thickness. It is rinsed in acetone and ethanol in order to remove dirt and oil, while native oxide layer removed by etching in dilute (1:10) HF: H_2O.

Porous silicon was prepared by chemical etching using an electrolyte containing 40% HF and HNO_3 (1: 3) acids for different etching time (2, 4, 6,8,10 & 12) min with and without laser(10 mW with λ=532 nm), then samples are rinsed in ethanol and dried with a jet of nitrogen gas and stored in a container filled with a methanol to avoid the formation of oxides layer above the porous layer.

chemical stain – etch consisting essentially of HF and nitric acids. The anodic reaction consists mainly of the dissolution of Si, while the cathode reaction is a complicated reduction of HNO_3 which causes holes to be injected into the Si. The proposed anode and cathode reactions as well as the overall reaction are listed below: [23]

Anode $Si + 2H_2O + nh \rightarrow SiO_2 + 4H + (4-n)e$

$SiO_2 + 6HF \rightarrow H_2SiF + 2H_2O$ ….. **(1)**

Cathode $HNO_3 + 3H \rightarrow NO + 2H_2O + 3h^+$ **…….. (2)**

Overall

$3Si + 4HNO_3 + 18HF \rightarrow 3H_2SiF_6 + 4NO + 8H_2O + 3(4-n)h + 3(4-n)e$

…… **(3)**

Where ***n*** is the average number of holes required to dissociate one Si atom. The anode and cathode sites are not necessary fixed during the etching process. HNO_3 is more likely to attack imperfect sites on the crystalline Si surface, such as dislocation, grain boundaries, etc. According to the reactions above, the area where HNO_3 attacks will become local cathode and causes hole injection into the Si. If the injected holes react with Si, the Si atoms will be dissolved and form SiO_2 as shown in equation (1) and thereby turn the original local cathode site into an anode site. The SiO_2 subsequently reacts with HF to form water soluble H_2SiF_6. The residual H^+ at anode site might react with HNO_3 and the cycle repeats.

The surface morphology of stained sample was examined by using optical microscopy (Olymbic), and atomic force microscope AFM (Digital instruments nanoscope). the chemical composition of surface was best probed with Fourier Transform Infrared (FTIR) Spectroscopy (8400S, SHIMADZU),which Scans over range between (400-4000) cm^{-1}.

Porosity and thickness of the samples were calculated by the gravimetric method [17]. The virgin wafer is first weighed before anodization (m_1) then just after anodisation (m_2) and finally after dissolution of the whole porous layer in a molar NaOH aqueous solution (m_3). Uniform and rapid stripping in the NaOH solution is obtained when the PS layer is covered with a small amount of ethanol which improves the infiltration of the aqueous NaOH in the pores. The porosity is given simply by the following equation (18):

$$P(\%) = \frac{m1-m2}{m1-m3} \times 100 \quad \text{….(4)}$$

$$d = \frac{m1-m3}{\rho S} \quad \text{……(5)}$$

Where ρ is the Si density and S is surface area.

RESULTS AND DISCUSSION

The FTIR spectra of p-type porous silicon shown in Figure (1) for etching time (2 & 12) min. The band between "1000 to 1250 cm^{-1}" is the Si-O-Si stretching

vibration. So that Si-O-Si structure with vacancies (υ(Si-O-Si)= 1080 cm^{-1}) called " Not bridge oxygen hole center" (NBOHC), as the surface structure responsible for PL emission . A peak at ~979 cm^{-1} is related to SiH bending vibration, while a peak at ~918 cm^{-1} originates from a bond between Si and F and it is a Si $–F_2$ symmetric stretching mode. Then a peak ~ 902 cm^{-1} is SiH bending vibration. A peak at ~856 cm^{-1} is related to SiH_2 wagging vibration mode ,while a peak at ~840 cm^{-1} is related to Si-O-Si and a peak at~862cm^{-1} is due to SiH_3 symmetric bond, then a peak at ~ 664 cm^{-1} is due to SiH deformation mode and peak at ~ 611cm^{-1} is related to the Si-Si bond vibration. The peak around ~750 cm^{-1} , ~1090 cm^{-1} and ~1438cm^{-1} is related to NO_3 wagging vibration modes, while peaks at ~1460 cm^{-1}, ~846 cm^{-1} and ~ 831 cm^{-1} are corresponding to hydrocarbon vibration mode. While peaks at ~465 cm^{-1} and ~470 cm^{-1} are related to SiO-Si mode. A peak at ~ 856 cm^{-1} is related to SiH_2 wagging vibration mode.

AFM image

Figure (2) shows AFM image for PS prepared at 2 min with (fig.2a) and without laser Figure (2b). These AFM images reveal a roughened surface with roundish microstructures. The root-mean-squares (rms) observed are 11.7 nm (fig.2a) and 6.38 nm Figure (2b). The lateral sizes of the microstructures are also found to be in the range of 50-280 nm Figure (2a) and 80-420 nm Figure (2b).

Porosity and Thickness

Figure (3) shows the variation of thickness Figure (3a) and porosity Figure (3b) with etching time for prepared sample with and without laser. It can be noted that thickness of PSi layers was grows linearly with increasing the etching time , also the porous layer for sample prepared with laser was higher than sample prepared without laser by ~ 4 times. While, The porosity initially increases rapidly with increasing etching time, also the porosity for sample prepared with laser was higher than sample prepared without laser by ~ 1.675%.

Etching rate

Figure (4) show the variation of etching rate with etching time for prepared sample with and without laser. The etching rate was determined by measuring the maximum PSi layer thickness at the spot center. The etching rate could be calculated by the relation [23].

Maximum etching rate = maximum thickness of PSi (μm) / irradiation time (min)

Which found that the etching rate increasing for different etching time as shown in Figure (4). this result related to thickness of porous layer.

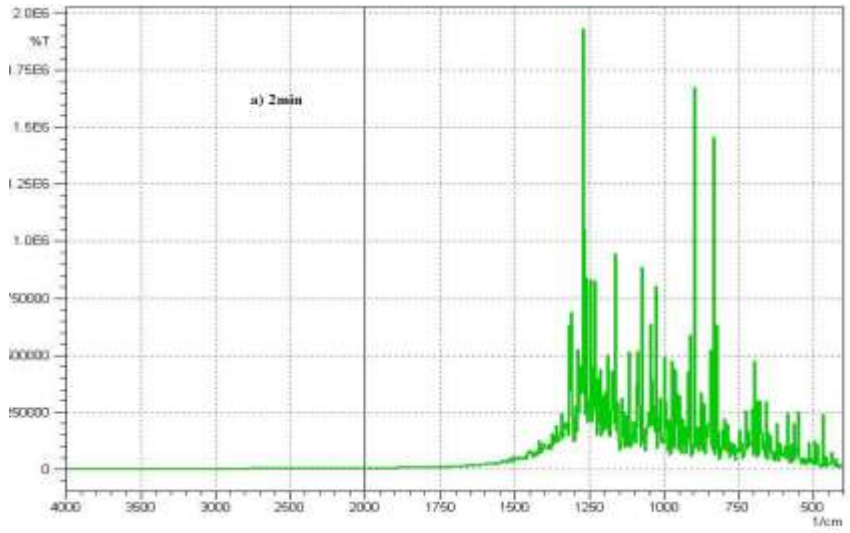
CONCLUSIONS

Porous silicon was prepared by stain etching in HF/HNO_3 with and without laser.. It is obvious that the etching process is being efficient when the surface have be irradiation with laser. Increasing the etching time leads to create surface has fine shapes with large thickness. These shapes have significant effects on the etching rate as well as the porous silicon formation.

REFERENCES

[1]. Prabakaran,R. R. Kesavamoorthy, and A. Singtt," Characteristics of Silicon Nanostructures
Produced by High Power Lasers Mate. Sci. 28, 219 (2005).
[2]. Minoli, D. "Nanotechnology Applications to Telecommunications and Netwarking" John Wiley Sons, Inc. New Jersey (2006).
[3]. Timoshenke et al. "Efficient visible luminescence of nanocrystalline silicon prepared from amorphous silicon films by thermal annealing and stain etching" Nanoscale research letters 6:349 (2011).
[4]. Birner,A. R.B. Wehrspohn, U. M. Gosele, and K. Busch," ATwo-Dimensional KTiOPO4 Photonic Crystal Grown Using a Macroporous Silicon Template" Adva. Mate. 13, 377 (2001).
[5]. Edit Pop, A. " investigation of Pristin and oxidized porous silicon " OulunYliobisto, Oulu (2005)
[6]. Uhlir,A. " Electrolytic shaping of germiunum and silicon " the bell system technigalJor. , 35, 333 (1965)
[7]. Shingi, Y. K.Yukinori, and M. Hitoshi " formation of porous silicon by metal particalinhiced chemical etching in hf solution and its application for effecinciy solar cell" electrochemistry communications 5, 632-636 (2003).
[8] D.R. Turner, "On the Mechanism of Chemically Etching Germanium and Silicon" J. Electrochemic. Soc., 107 (1960) 810
[9]. Steckl, A. J. J. Xu, H. C. Mogul and S. Mogren "Doping-induced selective area photoluminescence in porous silicon" Appl. Phys. Lett.62 1982 (1993).
[10]. Fathau,R. W. T. George, A. Ksenzov, T. L. Lin, W. T. Pike, R. P. Vasquez and Z. C. Wu "Fabrication of Luminescent Porous Silicon with Stain Etches and Evidence that Luminescence Originates in Amorphous Layers" Mater. Res. Soc. Symp. Proc., 256. 156. (1992)
[11]. Dimova, D. M. Sendova, N. Tezenov, M. Kamenova "preparation of thin porous silicon layers by stain etching" Thin Solid Films 297. 9-12. (1997).
[12]. Tomioka and S. Adachi, K. "Strong and stable ultraviolet emission from porous silicon prepared by photoetching in aqueous KF solution" Appl.Phys.Lett 87, 251920 (2005).
[13]. Estes,M. J. L. R. Hirsch, S. Wichart, and G. Moddel "Visible photoluminescence from porous a-Si:H and porous a-Si:C:H thin films" J. Appl. Phys. 82**,** 1832 (1997).
[14]. Ozdemir, S. and J.L. Gole, "The potential of porous silicon gas sensors."Current Opinion in Solid State and Materials Science, 11(5-6): p. 92-100, (2007).
[15]. Chen, L.-C., and B.-H. Liu, "Porous Silicon Layer Patterned from Anodic Aluminum Oxide and Application in ZnPcHybird Solar Cell." Electrochemical and Solid State Letters. 13(4): p. H108-H111.

[16]. Marrero, N., et al., "Effect of porous silicon stain etched on large area alkaline textured crystalline silicon solar cells."Thin Solid Films, 2009. 517(8): p.2648-2650.
[17]. Bisi, O., S. Ossicini, and L. Pavesi, "Porous silicon: a quantum sponge structure for silicon based optoelectronics."Surface Science Reports, 2000. 38(1-3): p. 1-126.
[18]. Dubey, R. and D. Gautam, "fabrication and characterization of porous silicon layers for applications in optoelectronics."Optical and Quantum Electronics, 2009. 41(3): p. 189-201.
[19]. Kaltsas, G., A.A. Nassiopoulos, and A.G. Nassiopoulos, "characterization of silicon thermal gas-flow sensor with porous silicon thermal isolation." Sensors Journal, IEEE, 2002. 2(5): p. 463-475.
[20]. Pagonis, D. N., A.G. Nassiopoulos, and G. Kaltsas, "Porous silicon Membranes over Cavity for Efficient Local Thermal Isolation in Si Thermal Sensors."Journal of Electrochemical society, 2004. 151(8): p. H174-H179.
[21]. Chu, K.-L. and et al., "Porous silicon fuel for micro power generation."Journal of Micromechanics and Microengineering, 2007. 17(9): p. S243.
[22]. Pichonat, T. and B. Gauthier-Manuel, "Realization of porous silicon based miniature fuel cells."Journal of Power Sources, 2006. 154(1): p. 198-201.
[23]. Shih Si., Jung K. H., Hesieh T. Y., Sarathy J., Campball J. C and Kowng D.L.," Doping-induced selective area photoluminescence in porous silicon" Appl. Phys. 60, pp. 1863. (1992).
[24]. L Koker, K.W Kolasinski" Applications of a novel method for determining the rate of production of photochemical porous silicon" Mat. Sci. & Eng B69-70 pp 132-135 (2000).



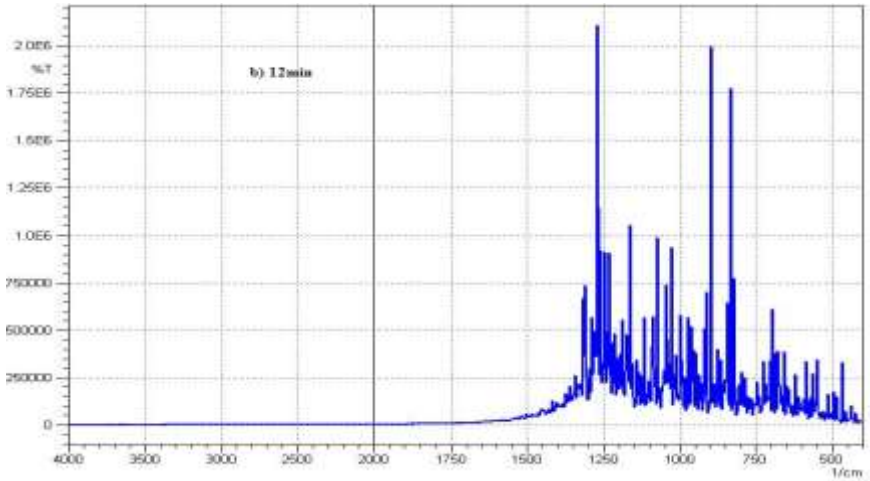
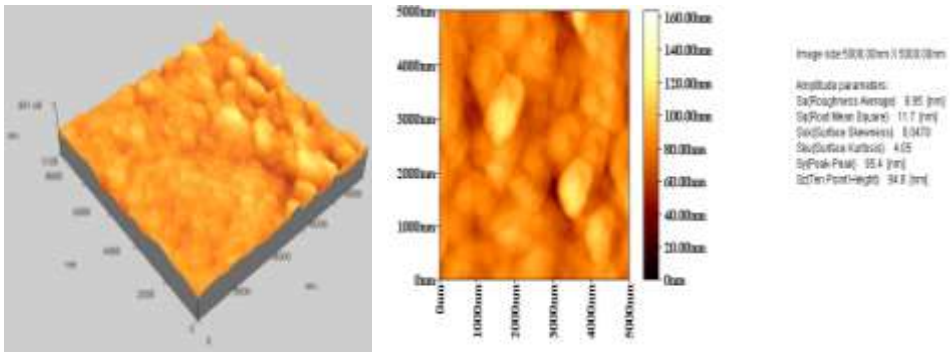
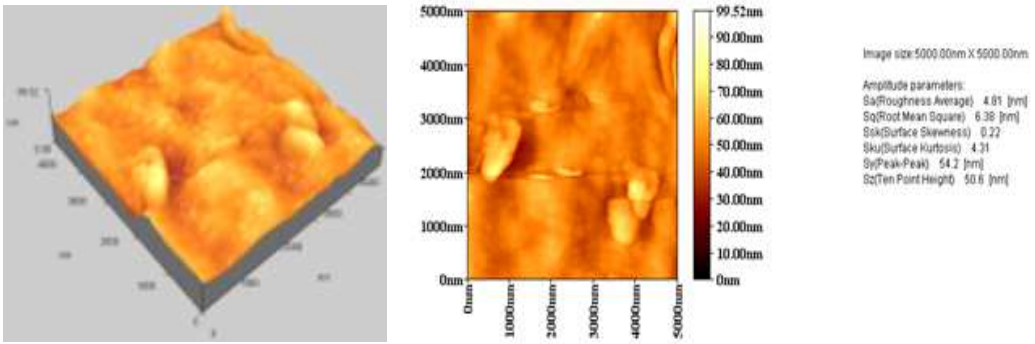


Figure (1) FTIR spectrum of PS/p-Si etching in different time.

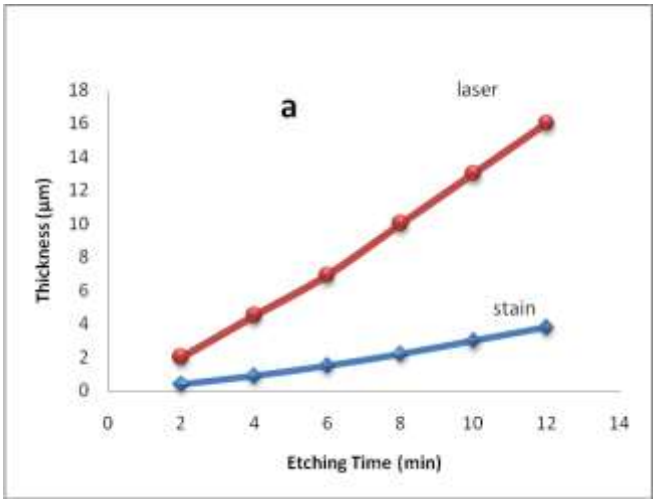


a) With lsaer



b) Without laser

Figure (2) AFM image for stained samples a) with and b) without laser illumination for etching time 2 min.



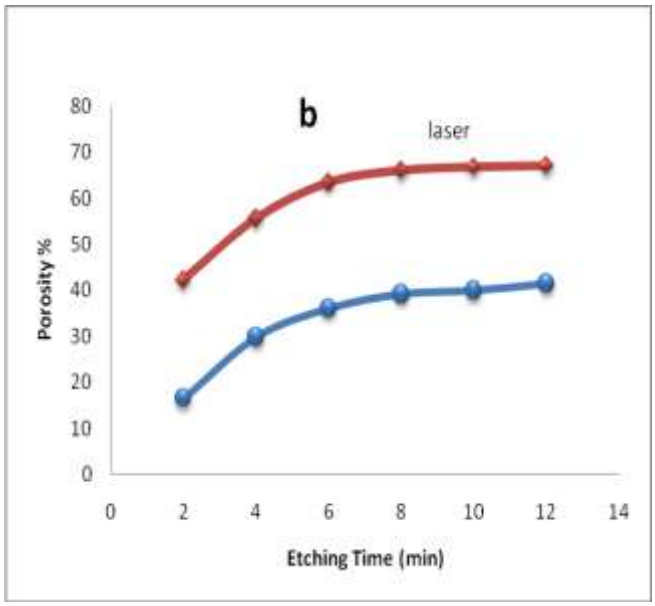


Figure (3) the relation between etching time with a) thickness andb) Porosity for prepared sample.

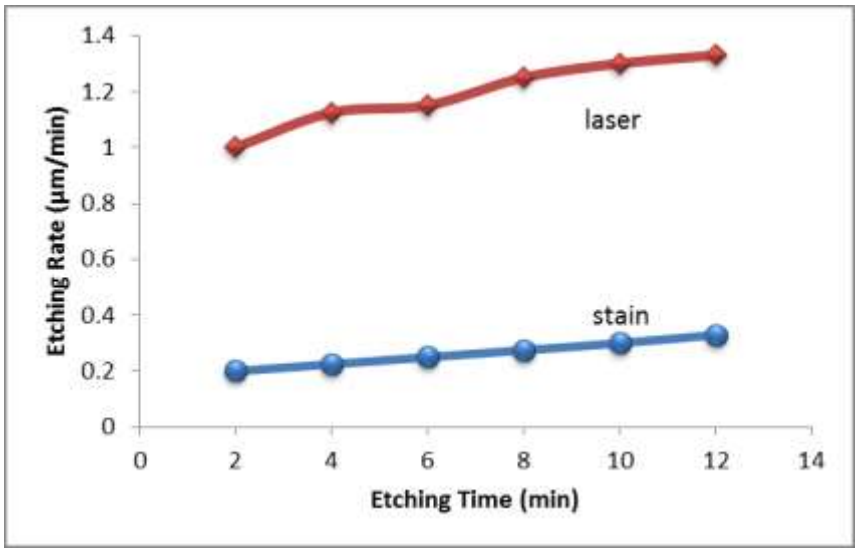


Figure (4) the variation of etching rate with etching time for prepared sample.