Eng.& Tech. Journal ,Vol. 30 , No.4 , 2012

Enhancement of Porous Silicon Formation by Using Ultrasonic Vibrations

Dr. Ali H. Al-Hamdani
Laser and Optoelectronics Engineering Department , University of Technology/ Baghdad
Email: ali_alhamdani 2003@yahoo.com

Received on: 17/5/ 2011 & Accepted on: 5/ 1/ 2012

ABSTRACT

Anodic electrochemical etching enhanced by ultrasonically is developed to fabricate luminescent porous silicon (PS) material. The samples prepared by the new etching method exhibit superior characteristics to those prepared by conventional direct current etching. By applying ultrasonically enhanced etching, PS microcavities with much higher quality factors can be fabricated. The improved quality induced by ultrasonic etching can be ascribed to increased rates of escape of hydrogen bubbles and other etched chemical species from the porous silicon pores surface.

Keywords: Ultrasonic, porous silicon, electrochemical etching, PS enhancement.

تعزيز تكون السليكون المسامي باستخدام الاهتزازات فوق الصوتية

الخلاصة

تم في هذا البحث استخدام تقنية جديدة بسيطة لتطوير عمليات تصنيع السليكون المسامي . أظهرت النتائج ان العينات التي تم اعدادها بطرق الكهروكيمياوية وبوجود الأشعة فوق الصوتية تمتاز بتجانس حيد ومتناسق كما ان حجم الفجوات قد ازداد بزياد التردد المسلط.حفر او نقش بخصائص او أساليب متفوقة على تلك التي تم اعدادها او تحضيرها بالطرق التقليدية الحالية مباشرة.مقارنة بالعينات المحضرة بالطريقة التقلدية. ويمكن أن يعزى التحسن في النوعية الناجمة عن الحفر بالموجات فوق الصوتية هو زيادة معدلات هروب فقاعات الهيدروجين وغيرها من الأنواع الكيميائية المحفورة او المنقوشة من السيليكون التي يسهل اختراقها مسام السطح.

INTRODUCTION

Porous silicon (PS) is a promising material for possible photonic applications in different devices like LED, waveguide, field emitter, optical memory or gas (NO_2, CO, etc.) sensors, etc.[1–2]. Recently, PS has attracted attention due to the property of photoluminescence (PL) in visible light range [3]. The most commonly used method of fabricating PS is direct current (DC) anodic electrochemical etching [1]. During the DC anodic etching process, the reaction product, silicon fluoride [4], tends to deposit at the pore tips. The H2 bubbles are adsorbed at the surface of silicon pillars because of interfacial tension, blocking the silicon pores and leading to a reduction of HF concentration inside the pores [5]. Thus, the etching process will be slowed down. Meanwhile, the dissolved species will increase the resistance of silicon wafer and hence decrease the current density. This factor also slows down the etching rate.

PS material prepared by ultrasound (US) anodic etching has improved qualities in surface morphology, layer interface smoothness and optical characteristics compared with the sample prepared by direct current (DC) electrochemical etching [4,5]. Over

the past decade many different models have been elaborated interpreting the visible light luminescence in PS, several overviews have been published to weigh arguments for/against to understand this phenomenon [6-8]. In this work, an ultrasonically enhanced anodic electrochemical etching is developed to fabricate light-emitting PS material. Taking advantage of the ultrasonic press effect and acoustic cavitations, the diffusion of the dissolved species and H_2 bubbles from silicon pores can be accelerated. Optical microscopy (SEM) and FTIR measurement investigations show that the PS material prepared by ultrasonic anodic etching has improved qualities in surface morphology, layer interface smoothness, etching efficiency and optical characteristic compared with the sample prepared by DC etching.

EXPERIMENTAL WORK

In this work, ultrasonic treatment during layer formation resulted in the microstructural feature in a p-type (100)-oriented highly doped (0.01)Ω.cm silicon single crystal wafer. It was placed in a Teflon etching cell and etched in the dark with a HF (40%): C_2H_5OH (99%):H_2O 1:1:1 (by volume) electrolyte solution. For comparison, a series of samples were prepared with three different etching conditions. Anodic etching at current density 30 mA/cm^2 for 10 min the ultrasonic wave frequency of the ultrasonic generator were 22 and 35 kHz. In this letter, three samples are presented and referred to as sample A, B and C, respectively. The etching parameters are listed in Table 1. After the etching process, all the samples were immediately rinsed by deionized water and dried. Analysis of surface morphology was carried out using image-j program.

To study the microstructure, optical microscope (model KRUSS, OPTRAT IV Germany) was used to measure the thickness of PS layer. The thickness of the nanostructure layer is calculated by subtracting the maximum depth (which is found by using reflection optical microscopy) from the lower interface. FTIR at room temperature has been used for the subsequent analysis of the samples.

RESULTS AND DISCUSSION

Figure (1) shows the surface optical microscopy image of samples A, B and C; the pores in the PS samples are seen as dark dots. Fig. 1(A) shows the pores of sample A distribute themselves randomly and are irregularly shaped. Most pores have large dimensions that seem to be joined by two or more smaller pores. The result of sample B is shown in Fig. 1(B). One can see from the image that the uniformity of PS pores has been slightly improved. Samples B and C, were fabricated using ultrasonic wave frequency (22 and 35 kHz respectively). The pore diameters are much smaller and the shapes are more circular than in sample A. The more ultrasonic frequency induce the more uniform distributions of homogeneous pores have been appeared (Fig. 1(B,C). The PS layer thickness of samples in optical images (Fig. 1(A)–(C)) increased from 4.5 mμ for sample A, 6 μm for sample B and 7.5 μm for sample C(table 2). In addition, when viewed by naked eye, the fresh prepared samples B and C shine a uniform interference color while for sample A the color varies from the center to the edge. This is indirect evidence that samples B and C have uniform PS layer while sample A does not, which is further confirmed by PL spectra. In the same effective etching time, two obvious conclusions can be obtained: (1) the PS layer thickness of samples prepared by ultrasonic etching (samples B and C) are larger than

that of samples prepared by non-ultrasonic etching (sample A). (2) Morphology studies (table 2) show, layers thickness, number of pore, average size of pore and porosity for the three samples which evaluated by using j- image program.
Morphology studies of the samples indicate that, when fabricated using ultrasonic anodic etching, a sample has a more uniform PS layer with larger silicon pores and the etching efficiency is also higher than those prepared without ultrasonic anodic method. The reason is believed to be that when employing simply the EC etching method, the chemical reaction products will deposit at silicon pores, mostly at pore tips, and prevent the dissolution of silicon wafer, consequently enlarging the lateral etching. A lot of micro-bubbles will appear in the electrolyte solution when the ultrasonic wave acts on it. These bubbles will shrink and expand repeatedly with the variety of sound pressure and result in desorbing of the chemical products from silicon pillars. If the bubble is broken, an extreme high pressure will be produced. This pressure will bring the dissolved species out of the silicon pores. In addition, the other ultrasonic effects, such as vibration, will also speed up the diffusion of chemical products. All these reasons cause the chemical reaction to concentrate on the pore tips, thereby reducing the lateral etching and improving the uniformity and etching efficiency.

The chemical composition of the surface of the porous layer was investigated by means of the transmission spectra in the FTIR spectroscopy. The FTIR transmission spectrum on freshly prepared PS layer which prepared by EC at different wavelength from 400 to 4000 cm^{-1} is shown in figure (3). Different vibration modes could be seen from this figure. The freshly prepared PS layer showed well defined, Si-H absorption bands at 2087-2400 cm^{-1}. These modes are related to groups adsorbed at the extended PS surface. It is already well known that $Si–H_x$ content is necessary for the passivation quality, as hydrogen may easily diffuse at the PS/Si interface as well as inside the Si wafer itself.

The PS samples show Si-O-Si peaks 1070, 1112 cm^{-1} corresponds to the stretching modes of the Si-O-Si bridges in SiO_x. As this peak dose not undergoes important changes when the samples are processed, it can be argued then this mode is related to the Si substrate. Otherwise, the mode at 1070 and 1112 cm^{-1} appear only is PS layer with some oxidation degree, the frequency can be related to the highly stressed SiO_2-Si interface of defective Si oxide at the PS surface. These modes are the symmetrical and antisymmetrical vibrational modes of the Si-O-Si bridges. The peak at 464 cm^{-1} is from the mode of vibration between tetrahedral Si-O-Si. Therefore, it can be concluded that the enhanced PL intensity is not related to Si-H or Si-O-Si surface bonds.

US cavitation has been considered as a useful tool for cleaning and etching applications in microelectronics processing. In this work, we have shown that it can be used to induce useful microstructural changes in the porous layers. The ultrasonic treatment during layer formation resulted in the following microstructural features in p-type (1 0 0) Si (30mA/cm^2 and 10 min of electrochemical etching): i) Change in bonding configuration, ii) decrease in oxidation and hydrogenation, and iii) Si H band narrowing (Fig. 3). The decrease in Si-H and Si-O band intensities indicates probably that there is some etching activity induced by US cavitation. The reason for the Si H band narrowing is attributable to the fact that US cavitation enables us to prepare structurally homogenous samples. As shown in Fig. 3, there is a significant shift

toward low energies at the stretching mode peak position at around 2200 cm^{-1}. This result indicates that the US cavitation favors the formation of monohydrides to the detriment of multihydride formation. The relative increase of hydrogenation compared to oxygen is also confirmed by the Si-H. The ratio of Si H to Si-O Si is much stronger in US cavitated sample as estimated from the relative band intensities. Figure 3 (A) and (B) shows the spectra of Si-H and Si-O-Si stretching modes, respectively. As evidenced from the FTIR spectra, the 30 kHz frequency leads to a considerable increase in the amount of hydrogenation and oxidation. We attribute this effect to an increase in the concentration of free hole carriers, which are necessary elements for porous layer formation.

CONCLUSIONS

We have presented an ultrasonic anodic etching method for fabricating light-emitting PS material. Surface morphology investigations reveal that when other etching parameters are constant, the ultrasonic etching creates a thicker and more uniform PS layer, with smaller silicon pores than EC etching. Surface of etching layer observations further confirm the improved structural properties, which can be explained by the PS formation mechanics, especially by ultrasonic cavitation. The US cavitation leads to porous layers with decreased oxidation and hydrogenation and to an affective etching when combined with EC etching only.

REFERENCES

[1] Canham,L.T. " Silicon quantum wire array fabrication by electrochemical and chemical dissolution of wafers", Appl. Phys. Lett. 57, 1046 (1990):1046-1048.

[2] Lehmann, V. and U. Gosele, "Porous Silicon Formation: a Quantum Wire Effect. Appl. Phys. Lett., 1991. 58(8): p. 856-858.

[3] Andersen, O. K. and E. Veje, "Experimental study of the energy-band structure of porous silicon," Physical Review B,vol. 53, no. 23, pp. 15643–15652, 1996.

[4] Abramof, P. G. A. F. Beloto, A. Y. Ueta, and N. G. Ferreira, "X-ray investigation of nanostructured stain-etched porous silicon," Journal of Applied Physics, vol. 99, no. 2, Article ID 024304, 5 pages, 2006.

[5] Wallacher, D. N. K¨unzner, D. Kovalev, N. Knorr, and K. Knorr, "Capillary condensatioen in linear mesopores of different shape," Physical Review Letters, vol. 92, no. 19, Article ID 195704, 4 pages, 2004.

[6] Kalem, S. O. Yavuzcetin and C. Atineller, "Effect of Light Exposure and Ultrasound on the Formation of Porous Silicon", Journal of Porous Materials 7, 381–383 (2000).

[7] Liua, Y. Z.H. Xionga, Y. Liua, S.H. Xua, X.B. Liua, X.M. Dinga, X.Y. Houa,, "A novel method of fabricating porous silicon material: ultrasonically enhanced anodic electrochemical etching", Solid State Communications 127 (2003) 583–588.

[8] El-Bahar, A. S. Stolyarova,A. Chack,R. Weil,R. Beserman, and Y. Nemirovsky," Ultrasound treatment for porous silicon photoluminescence enhancement", physica status solidi (a),Volume 197, Issue 2, pages 340–344, May 2003.

Table (1):The parameters of different etching methods for fabricating PS

Sample	Etching method	Current density (mA/cm^2)	Time (min)
A	EC etching	30	5
B	EC etching+US(22kHz)	30	5
C	EC etching+US(35 kHz)	30	5

Table (2): the properties of samples (A, B &C) determined by image j program.

	Layer thickness (µm)	No. of pore	Average size of pore (µm^2)	Porosity %
Sample A	4.5	133	2	30
Sample B	6	160	2.47	39.8
Sample C	7.5	196	4.3	85

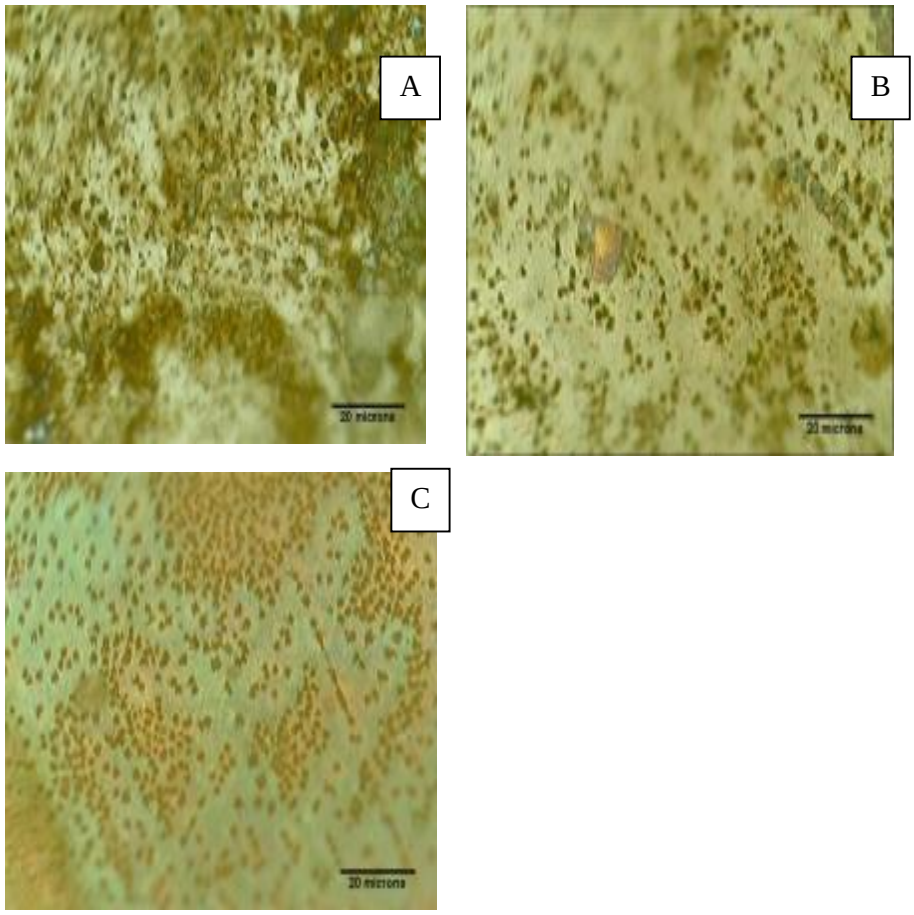

Figure (1): surface morphology of porous silicon samples fabricated by different condition A) EC etching B) EC etching and ultrasonic effect (22 kHz) and C) EC etching and ultrasonic effect (35 kHz).

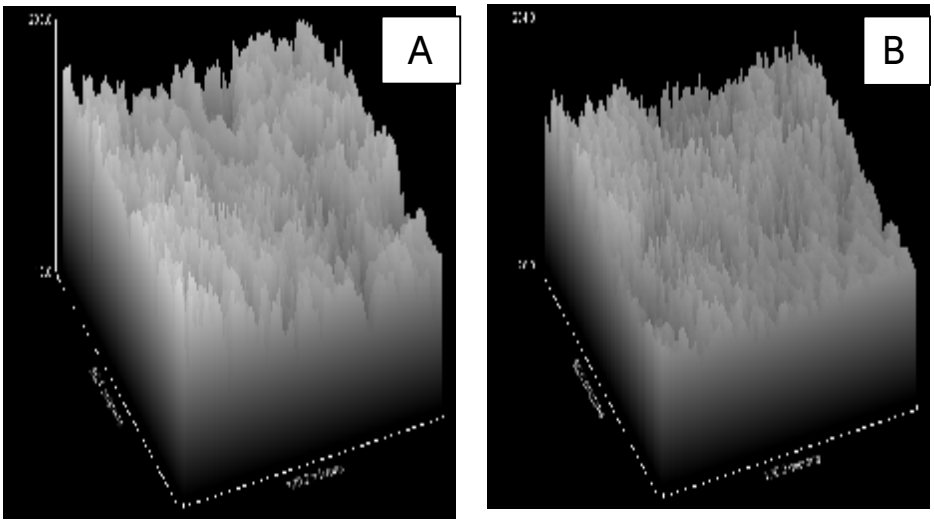

Figure (2): Image of sample B and sample C with frequencies 22 and 35 kHz respectively.

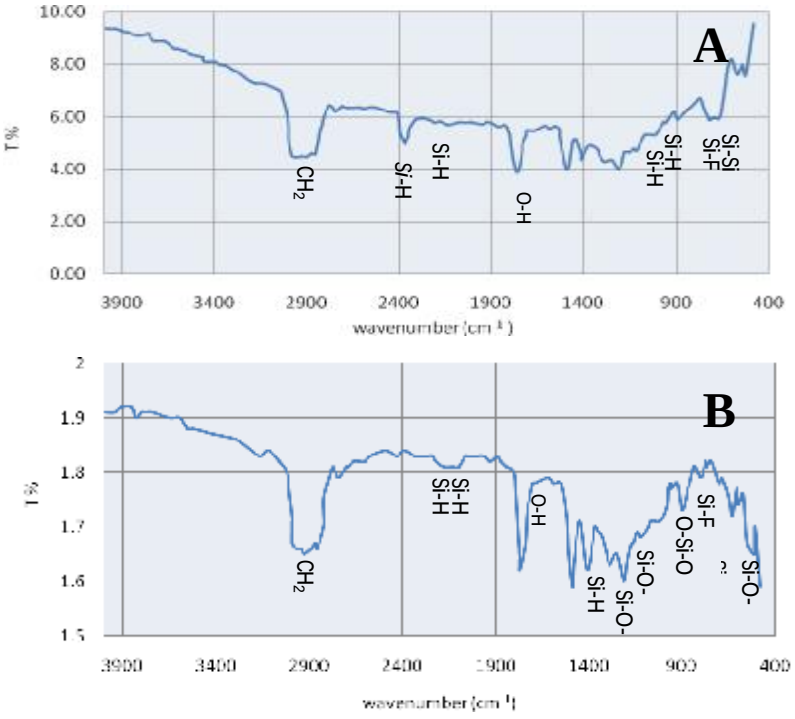

Figure (3): FTIR spectra showing the effect of ultrasonic treatment. A) 22 kHz andB) 35 kHz.