

# Nanoporous Silicon Prepared by Vapour Phase Strain Etch and Sacrificial Technique

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## ABSTRACT

Porous silicon nanoparticles is a excellent candidates for medical applications as drug delivery devices, for their excellent biocompatibility, biodegradability, and high surface area. In this paper the simple fabrication process of porous silicon by vapour phase strain etch has been observed. The porous silicon nanoparticle has been made by sacrificial technique. This paper also presents the methods of fabrication of porous silicon nanoparticle and measurement of its particle size by dynamic light scattering. Porosity and thickness of porous silicon has been observed by using gravimetric method. Polydispersity index of the dls sample is 0.22.

## Keywords

porous silicon, vapour phase strain etch, sacrificial technique, DLS, polydispersity index, biodegradable and biocompatible property.

## 1. INTRODUCTION

Porous Si has been investigated for applications in microelectronics, optoelectronics, chemical and biological sensors, and biomedical devices. The *in vivo* use of porous Si was first promoted by Leigh Canham, who demonstrated its resorbability and biocompatibility in the mid 1990s. Subsequently, porous Si or porous SiO<sub>2</sub> (prepared from porous Si by oxidation) host matrices have been employed to demonstrate *in-vitro* release of the steroid dexamethasone, ibuprofen, cis-platin, doxorubicin, and many other drugs. The first report of drug delivery from porous Si across a cellular barrier was performed with insulin, delivered across monolayers of Caco-2 cells. An excellent review of the potential for use of porous Si in various drug delivery applications has recently appeared. An emerging theme in porous Si as applied to medicine has been the construction of microparticles (“mother ships”) with sizes on the order of 1–100 μm that can carry a molecular or nano sized payload, typically a drug. With a free volume that can be in excess of 80%, porous Si can carry cargo such as proteins, enzymes, drugs or genes. It can also carry nanoparticles, which can be equipped with additional homing devices, sensors, or cargoes. In addition, the optical properties of nanocrystalline silicon can be recruited to perform various therapeutic or diagnostic tasks—for example, quantum confined silicon nanostructures can act as photosensitizers to produce singlet oxygen as a photodynamic therapy. A long-term goal is to harness the optical, electronic, and chemical properties of porous Si that can allow the particles to home to diseased tissues such as tumors and then perform various tasks *in vivo*. These tasks include detecting, identifying, imaging, and delivering therapies to the tissue of interest.

## 1. LITERATURE STUDY

### 1.1 Review of porous silicon

Porous silicon, a unique “derivative” of silicon, has a

structure of void pores mixed with microcrystalline and/or nanocrystalline silicon. Porous silicon is a versatile material for microelectronics applications. It was first being turned to practical use for device isolation in 1969 by the Nippon Telegraph and Telephone Public Corporation and Sony Corporation. Extremely high chemical reactivity of porous silicon particularly its rapid oxidation is very important property. It is possible to obtain porous silicon through stain-etching with hydrofluoric acid, nitric acid and water. A publication in 1957 revealed that stain films can be grown in dilute solutions of nitric acid in concentrated hydrofluoric acid. Porous silicon formation by stain-etching is particularly attractive because of its simplicity and the presence of readily available corrosive reagents; namely nitric acid (HNO<sub>3</sub>) and hydrogen fluoride (HF). Furthermore, stain-etching is useful if one needs to produce a very thin porous Si films.

### 1.2 Porous silicon nanoparticle

Micro- and nano-based technologies are presently recognized as promising potential tools for drug delivery applications in almost every field of health sciences, aiming to overcome the adverse physicochemical properties of conventional drug molecules, which often lead to poor drug bioavailability. A large amount of the new chemical entities developed by the pharmaceutical industry are poorly water-soluble compounds, which in order to subsist as efficient drugs with improved and controllable *in vivo* behaviour require the aid of more advanced technologies. Porous silicon nanoparticle can be prepared by ultrasonic fracture of porous silicon sample or by sacrificial technique. Here sacrificial technique has been followed for the preparation of the sample. This sample can be used for drug delivery in human body.

### 1.3 Light emission properties and optical properties of porous silicon

Visible light emission in porous silicon is of current interest both scientifically and technologically. Since this system can exhibit a wide variety of structures and particle sizes, however, a large volume of data exists, which at times can be quite contradictory. If uv light falls on porous silicon sample then different colours of light is emitted from ps sample (fig 1). pSi demonstrates optical properties based on porosity and the medium inside the pores. The effective refractive index of pSi is determined by the porosity and refractive index of the medium inside the pores. If the refractive index of the medium inside pores is high, the effective refractive index of pSi will be high as well. This phenomenon causes the spectrum to shift towards longer wavelength.

### 1.4 Biodegradable and biocompatible properties of porous silicon

Porous Silicon retains the key semiconductor properties of silicon and is machineable at a micro level. Porous Silicon

also demonstrates optical properties that provide the basis for a variety of potential devices for biodegradable and biocompatible diagnostic products. It has created a unique biomaterial that has the potential not only to serve as a biomedical device but also as a novel drug delivery carrier for a wide range of drug entities. During such studies thin layers

of highly porous silicon or poly crystalline silicon of Nano meter size grains could actually dissolve completely away in simulated human plasma.

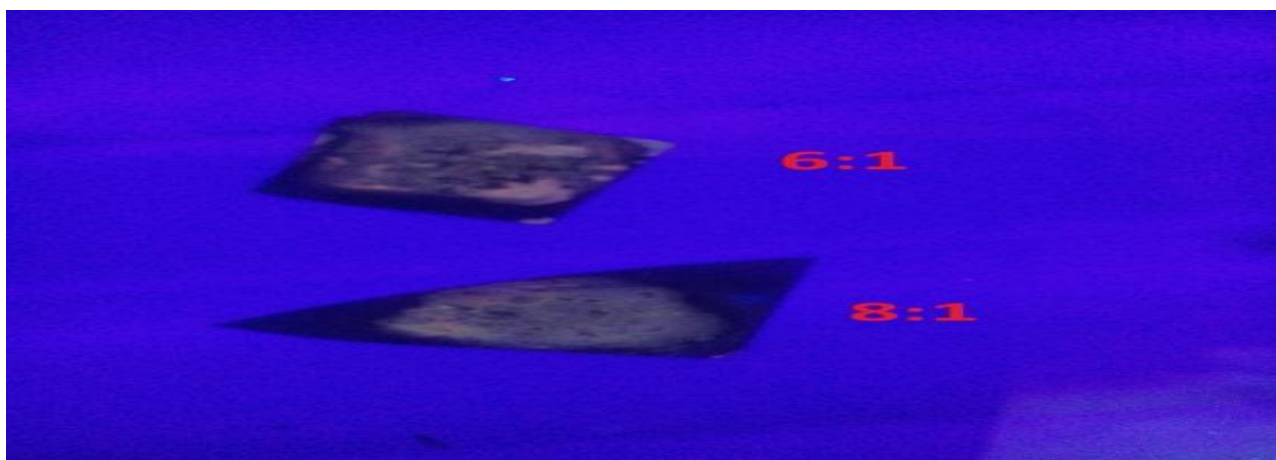


Fig 1: Image of porous silicon in different ratio of HF and HNO<sub>3</sub>.

## 2. EXPERIMENTS

### 2.1 Preparation of porous silicon

Porous silicon samples were prepared from single crystalline p-type<100> Si wafers. These were first cleaned in a solution of 1:1:5 NH<sub>4</sub>OH:H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>O for 10 min at 70-80 °C, then in 1:50 HF:H<sub>2</sub>O for 15 sec and finally in 1:1:6 HCL:H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>O for 10 min at 70-80 °C. Porous silicon has been made by vapour phase strain etch process. The ratio of hydrofluoric acid and nitric acid that have been used in our laboratory is 4:1. Here we used zinc dust as sacrificial metal.

### 2.2 Sacrificial technique for making nanoparticle

Once silicon has been made porous, it can be removed in diluted hydroxide solutions (KOH, NaOH, NH<sub>4</sub>OH, etc) and, because of its high surface area, dissolves very quickly even at room temperature . KOH concentrations as low as 1%, at room temperature have been used to remove porous silicon layers .Care must be taken to keep the etch rate slow enough so that the reaction does not become violent, causing delicate microstructures to be destroyed by bubbles. Porous silicon can also be removed by photoresist remover if this is more compatible with a specific process.

## 3. RESULTS AND DISCUSSION

### 3.1 Dls measurement

Dynamic light scattering is also known as Photon Correlation Spectroscopy. This technique is one of the most popular methods used to determine the size of particles. Shining a monochromatic light beam, such as a laser, onto a solution with spherical particles in Brownian motion causes a Doppler Shift when the light hits the moving particle, changing the wavelength of the incoming light. This change is related to the size of the particle. It is possible to compute the sphere size distribution and give a description of the particle's motion in the medium, measuring the diffusion coefficient of the particle and using the autocorrelation function. In this paper dynamic light scattering measurement of porous silicon nanoparticle have been observed. Here different kinds of

graph have been obtained.

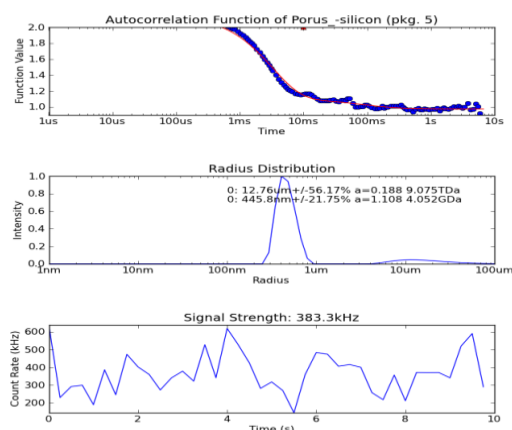


Fig.2: Image DLS of 6:1 etchant (HF:HNO<sub>3</sub>) ratio.

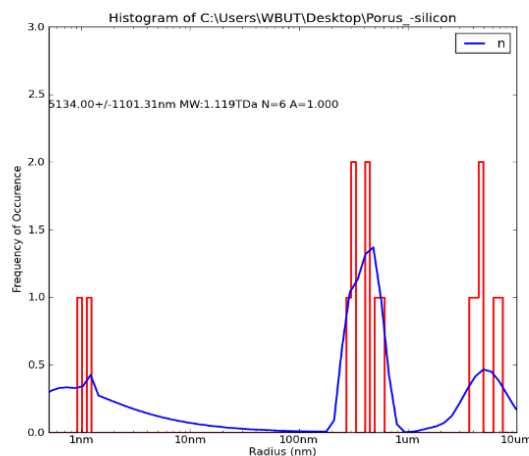


Fig.3: Image DLS of 6:1 etchant (HF: HNO<sub>3</sub>) ratio.

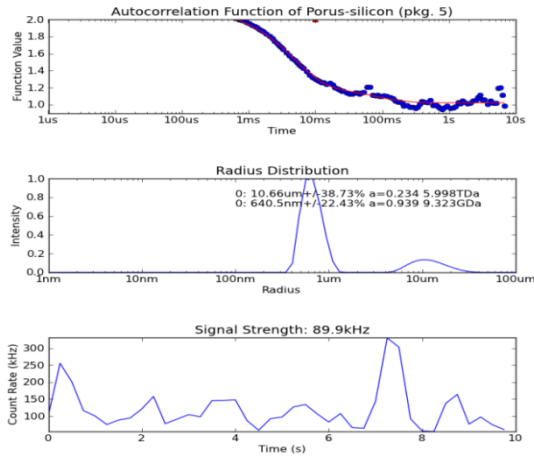


Fig.4: Image DLS of 8:1 etchant (HF:HNO3) ratio.

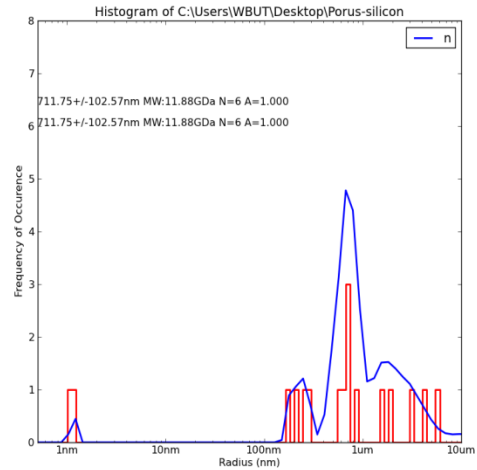


Fig.7: Image DLS of mixing of 6:1 and 8:1 etchant (HF: HNO3) ratio.

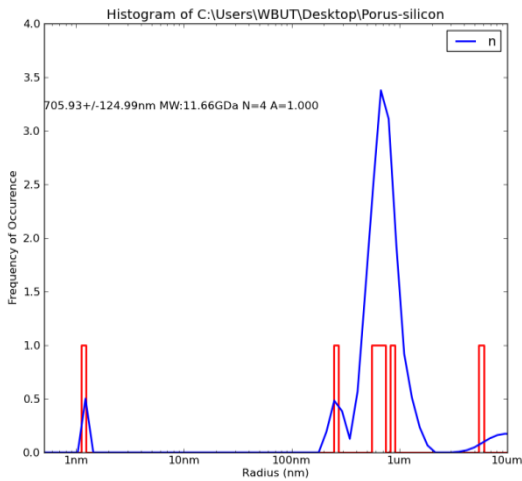


Fig.5: Image DLS of 8:1 etchant (HF:HNO3) ratio.

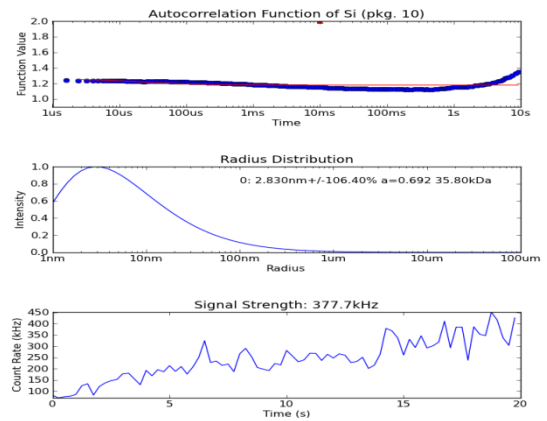


Fig 8: Image DLS of mixing of 4:1, 6:1 and 8:1 etchant (HF: HNO3) ratio.

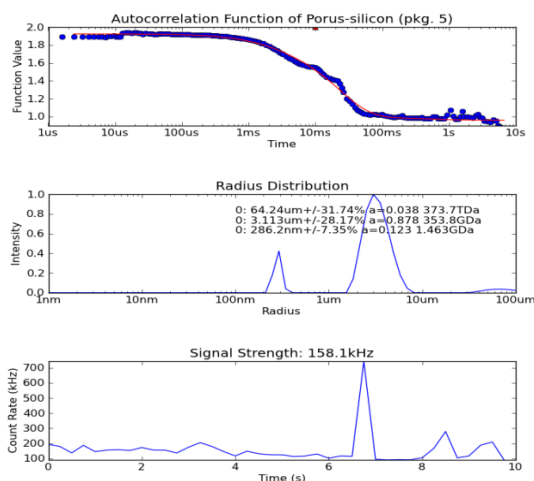


Fig.6: Image DLS of mixing of 6:1 and 8:1 etchant (HF: HNO3) ratio.

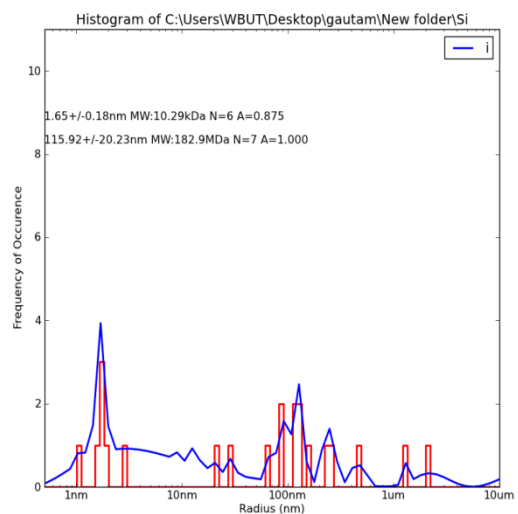


Fig 9: Image DLS of mixing of 4:1, 6:1 and 8:1 etchant (HF: HNO3) ratio.

### 3.2 Porosity of RIVPSE PS sample using gravimetric method

The porosity of PS substrate, which is etched in the solution of HF: HNO<sub>3</sub> (4:1) for 4 minute is 78%. The porosity of PS substrate, which is etched for 4 minute in HF: HNO<sub>3</sub> (6:1) solution for is 58%. And the porosity of PS substrate, which is etched for 4 minute in HF: HNO<sub>3</sub> (8:1) solution for 44%.

### 3.3 Thickness measurement of RIVPSE PS sample

The thickness of PS substrate, which is etched in the solution of HF: HNO<sub>3</sub> (4:1) for 4 minute is 19.22 micro meter. The thickness of PS substrate, which is etched for 4 minute in HF: HNO<sub>3</sub> (6:1) solution for is 21.52 micro meter. And the porosity of PS substrate, which is etched for 4 minute in HF: HNO<sub>3</sub> (8:1) solution for 17.99 micro meter.

### 3.4 Polydispersity index

The term polydispersity (or more recently dispersity without the poly, as per IUPAC recommendation) is used to describe the degree of “non- uniformity” of a distribution. In the field of molecular/ nanoparticulate characterization there are in principle two different definition of polydispersity, depending on the under laying property of interest. For a uniform sample  $D = 0.0$ . Polydispersity index from DLS = (the square of standard deviation) / (the square of mean diameter). Polydispersity index calculated from fig. 3 is 0.22. so the distribution is moderate in nature.

## 4. CONCLUSION

Today the porous carriers have a major role to play in the pharmaceutical industry. Nanoparticle mediated drug delivery approaches provide potential opportunities for targeting and killing of intracellular bacteria. Calcium insufficiency has long been related to the occurrence of various diseases. The aim of this work is to produce porous silicon nanoparticles and measurement of particle size by dls measurement. Here result shown that the particle size of less than 1 micrometer which can be used in medical application. In case of 6:1 and 8:1 etchant ratio only one kind of highest peak have been observed but mixing this two ratio two main peak have been observed. In case of mixing of 4:1, 6:1 and 8:1 etchant ratio the result shown that radius distribution in all over the range. Porosity of 44% has been achieved by gravimetric method. From dynamic light scattering the polydispersity index, a parameter calculated from a cumulants analysis of the DLS-measured intensity autocorrelation function. By fitting the correlation curve to an exponential function, the diffusion coefficient(D) can be calculated (D is proportional to the lifetime of the exponential decay). With the diffusion coefficient (D) now known, the hydrodynamic diameter can be calculated by using a variation of the Stokes-Einstein equation.

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## 7. REFERENCES

- [1] R. Guo, L. Li, W. H. Zhao, Y. X. Chen, X. Z. Wang, C. J. Fang, W. Feng, T. L. Zhang, X. Ma, M. Lu, S. Q. Peng, and C. H. Yan, *Nanoscale*, 4 (2012) 3577-3583.
- [2] F. Gao, L. Li, T. Liu, N. Hao, H. Liu, L. Tan, H. Li, X. Huang, B. Peng, C. Yan, L. Yang, X. Wu, D. Chen, and F. Tang, *Nanoscale*, 4 (2012) 3365-3372.
- [3] O. Tabasi, C. Falamaki, and Z. Khalaj, *Colloids Surf. B*, 98 (2012) 18-25.
- [4] S.D. Alvarez, A.M. Derfus, M.P. Schwartz, S.N. Bhatia, and M.J. Sailor, *Biomaterials*, 30 (2009) 26-34.
- [5] A.V. Pavlikov, A.V. Lartsev, I.A. Gayduchenko, and V. Yu Timoshenko, *Microelectron. Eng.*, 90 (2012) 96-98.
- [6] S. Lopera, C. Guzmán, C. Cataño, and C. Gallardo, *Vitae*, 16 (2009) 55-65
- [7] H. Wang, L. Zheng, C. Peng, M. Shen, X. Shi, and G. Zhang, *Biomaterials*, 34 (2013) 470-480.
- [8] J.B. Condon, *Surface Area and Porosity Determinations by Physisorption*, Elsevier 2006.
- [9] E.J. Anglin, L. Cheng, W.R. Freeman, and M.J. Sailor, *Adv. Drug Delivery Rev.*, 60 (2008) 1266- 1277.
- [10] Conibeer G, Green M, Corkish R, Cho Y, Cho E C, Jiang C W, Fang-suwannarak T, Pink E, Huang Y D, Puzzer T, Trupke T, Richards B, Shalav A and Lin K L 2006 *Thin Solid Films* 511 65.
- [11] Lin, V. S.-Y.; Motesharei, K.; Dancil, K. P. S.; Sailor, M. J.; Ghadiri, M. R. A porous silicon-based optical interferometric biosensor. *Science* 1997, 278, 840-843.
- [12] IUPAC. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (Recommendations 1984). *Pure Appl. Chem.* **1985**, 57, 603-619.
- [13] Langford, J.I.; Wilson, A.J.C. Scherrer after Sixty Years: A Survey and Some New Results in the Determination of Crystallite Size. *J. Appl. Cryst.* **1978**, 11, 102-113.
- [14] Anglin, E.J.; Cheng, L.; Freeman, W.R.; Sailor, M.J. Porous silicon in drug delivery devices and materials. *Adv. Drug Deliv. Rev.* **2008**, 60, 1266-1277.
- [15] Plescia, P.; Gizzi, D.; Benedetti, S.; Camilucci, L.; Canizza, C.; De Simone, P.; Paglietti, F. Mechanochemical treatment to recycling asbestos-containing waste. *Waste Manage.* **2003**, 23, 209-218.
- [16] Boldyrev, V.V. Mechanochemical modification and synthesis of drugs. *J. Mater. Sci.* **2004**, 39, 5117-5120.
- [17] Park, J.H.; Gu, L.; von Maltzahn, G.; Ruoslahti, E.; Bhatia, S.N.; Sailor, M.J. Biodegradable luminescent porous silicon nanoparticles for *in vivo* applications. *Nat. Mater.* **2009**, 8, 331-336.