

Structural and optical properties of *n*-type porous silicon fabricated in dark

M Das & D Sarkar*

Department of Physics, Gauhati University, Guwahati 781 014

*E-mail: sarkardeepali@gmail.com

Received 13 February 2013; accepted 5 August 2013

The *n*-type porous silicon has been fabricated under dark condition. SEM picture shows appreciable porosity with even distribution of pores with pore size ranging from 280 to 570 nm. XRD and FTIR confirm porous silicon (PSi) formation. Photoluminescence gives characteristic yellow orange emission of PSi with peak at 607.5 nm. Raman spectra show red shift of peak at some spots and Raman enhancement of intensity at some other spots along with the characteristic crystalline Si peak.

Keywords: Porous silicon, Luminescence, Quantum confinement, Raman spectra

1 Introduction

Silicon is mostly known for advantage in electronics application while for optoelectronic application mostly III-V semiconductors are thought for. The reason for this is the fact that light emission from Si is almost impractical due to its indirect band gap structure¹. The idea that nano voids, like nano particles can also open up changes in property of bulk materials, promoted people to explore property of porous silicon (PSi). The discovery of visible luminescence^{2,3} from PSi at room temperature nearly two decades ago has raised a great deal of interest on the material. Luminescence of PSi is mostly ascribed to quantum confinement effect of the nano/macro pores, in turn, thus depends on the dimension of the pores. By manipulating the formation parameters, pores of wide range can be produced, which in turn will have decisive role in governing its physical properties⁴. Further, passivation of pores in silicon opens up more dimensions of study. For example passivation of pores in *n*-type silicon by polyaniline^{5,6} known to be a *p*-type material, enhances luminescence efficiency by acting as *p-n* diode. For this purpose, however, one needs to fabricate macroporous silicon so that polymer molecule can get into the pores with ease. In the present paper, we report the fabrication and characterization of *n*-type porous silicon has been reported. Conventionally *n*-type PSi are fabricated under illumination^{7,8} so that holes generated facilitate pore formation. So far, fabrication of *n*-type PSi under dark condition has not been reported, only except under some special technique like Hall effect⁹ type of lateral field

arrangement. In the present paper along with fabrication of *n*-type PSi in dark, its morphological, structural and optical characterization have also been reported.

2 Experimental Details

Materials used for present study are Si-wafer, HF, ethanol and phosphorous doped *n*-type Si-wafers of (100) orientation of (375±25) μm thickness and resistivity of 1-10 Ω cm. Other reagents such as methanol and hydrofluoric acid are obtained from Merck, whereas ethanol is obtained from Changshu Yangyuan Chemical, China and these are used as received. For PSi fabrication, we adopt the conventional anodization method of etching Si-wafer in an electrochemical cell with Pt cathode and Si anode taking HF in 2:1:1 mixture of HF, ethanol and water. Anodization is carried out for current density 17.6 mA/cm² for anodization time of 30 min. The morphology of the sample is studied by FESEM (JSM 6700F), and Bruker D08 Advanced XRD for CuK_α radiation. For optical studies, UV-Visible reflectance spectra are taken by CARY 300 Scan UV-Visible Spectrophotometer, FTIR by Perkin Elmer Spectrum RXI FTIR system, photoluminescence (PL) by F-2500 FL spectrophotometer and Raman spectra by JY Horiba T6400 microraman set-up.

3 Results and Discussion

3.1 Morphological and structural features

The visual observation of the PSi surface after etching shows a golden yellow colour. This is the primary indication of porous structure formation. The

calculated porosity for the sample is 65%. In order to see the microscopic details, the film is characterized by FESEM. In Fig. 1 shows the FESEM image of the sample which is homogeneous distribution of the pores with pore size in the range 280-570 nm. This particular anodization condition of the chosen wafer is suitable for homogeneous pore formation. To look into the structure and crystalline nature, we characterized the wafer by XRD. Figure 2 shows the XRD plot which indicates peak at $2\theta = 33.3^\circ$ with a shoulder towards lower angle and two more at $2\theta = 69.2^\circ$ and 69.5° . The peak at $2\theta = 33.3^\circ$ corresponds¹⁰ to (200) crystalline peak with little

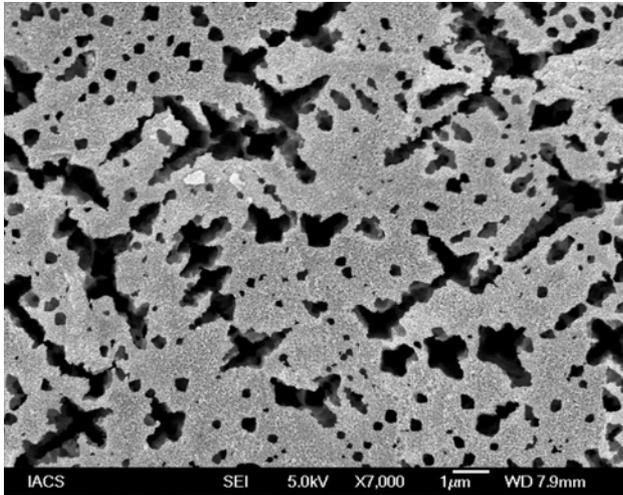


Fig. 1 — SEM image of PSi

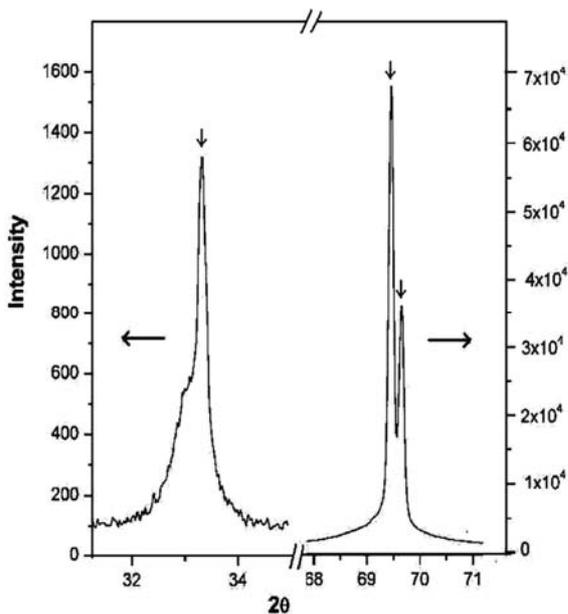


Fig. 2 — XRD pattern of PSi and c-Si

broadening due to nanostructured PSi formation. Sharpness of the peak at $2\theta = 33.3^\circ$ indicates crystalline nature of the silicon pores. The peaks at 69.2° and 69.5° correspond to the bare crystalline silicon (c-Si) substrate remaining amongst the pores.

3.2 Optical features

Optical properties of the sample are studied through UV-Visible reflectance, PL, FTIR and Raman spectra in order to look into optical absorption, emission and vibration analysis. In Fig. 3, the reflectance spectra of the sample with minima at 469.7 nm is shown indicating the absorption in blue-green region of the visible spectra. In Fig. 4, the PL spectra at room temperature is shown for excitation wavelength of

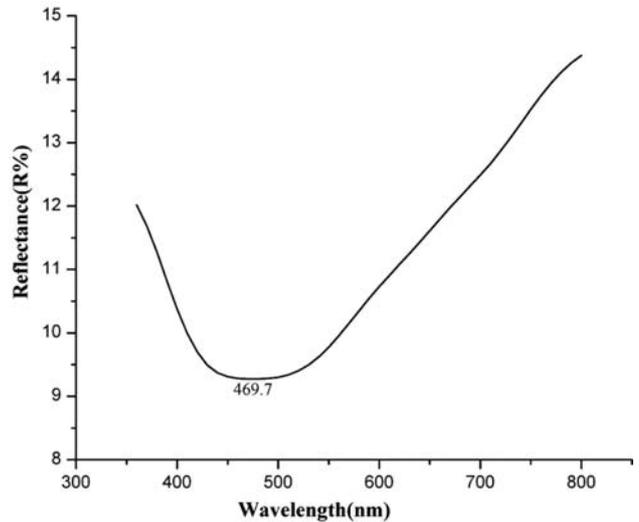


Fig. 3 — Reflectance spectrum of PSi

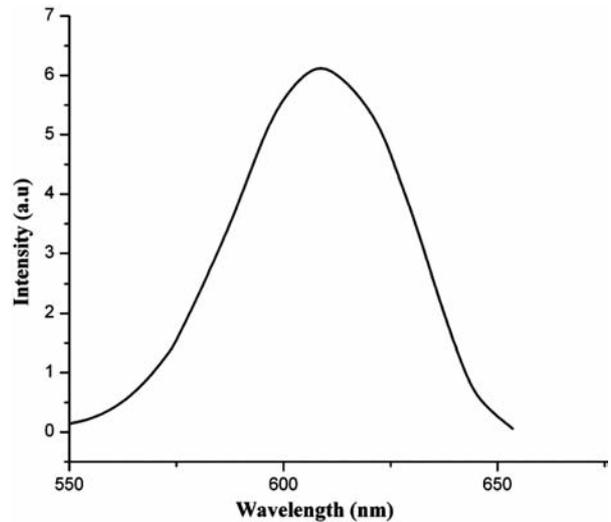


Fig. 4 — PL spectrum of PSi

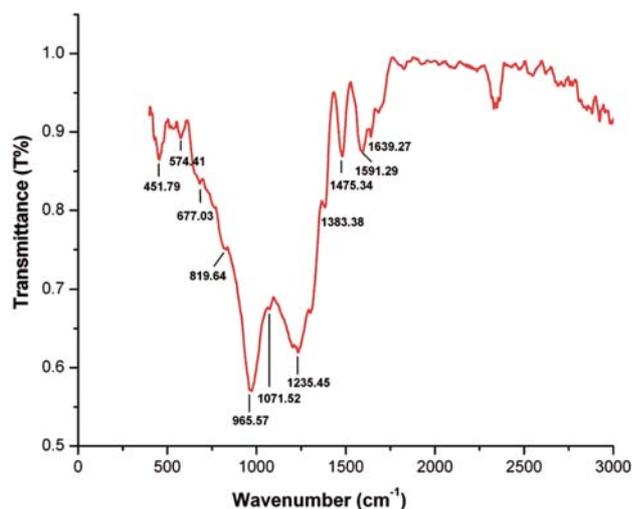


Fig. 5 — FTIR spectrum of PSi

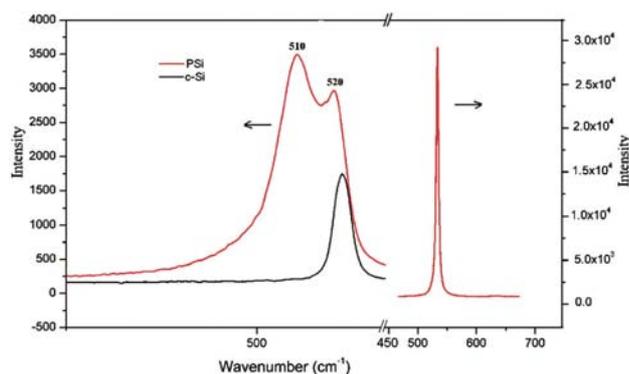


Fig. 6 — Raman spectrum of PSi and c-Si

300 nm. PL spectra cover quite an appreciable range of visible region and show peak at 607.5 nm. This corresponds to the characteristic yellow orange PL of PSi originating from surface states¹¹ facilitated by quantum confinement in Si pores composed of nanometer size crystallites^{12,13}. Figure 5 shows the FTIR spectra in order to assign the types of bonding present. This shows bands at 451.79 cm^{-1} for Si-O-Si rocking or bending, 677.03 cm^{-1} for SiH_2 wag, 819.64 cm^{-1} for mixture of SiH_2 scissor and SiH_2 bend and 1071.52 cm^{-1} for Si-O-Si asymmetric stretch. Co-existence of all these bonds in the sample implies a mixture of the different structural building blocks suggesting PSi formation¹⁴ but does not exclude the presence of some bare small crystallites of c-Si. Therefore, in order to explore more, Raman spectroscopy of the sample has been studied. Figure 6 shows the Raman spectra of the PSi sample where three different types of spectra have been obtained from three types of spots. In one we get normal peak

for c-Si at 520 nm, in the second type, we get the red-shifted (by 10 nm) peak along with the c-Si peak and in the third type, we get Raman enhanced sharp peak at c-Si peak position 520 nm of very less width. The first type is justified as in between the pores there are c-Si regions¹⁵. Type 2 is for quantum confinement i.e. at nanopores¹⁶ and third one is due to some sort of waveguide formation^{17,18} where the setting and size of pores match to cancel out the two photon absorption and may facilitate applicability in cavity for Raman laser which is recently being in progress for application in fabrication of all silicon Raman laser¹⁹. The enhancement is quite appreciable, almost 30 times that of c-Si intensity. The two different types of behaviour from PSi are due to the different types of alignment of the pores.

4 Conclusions

Porous silicon has been successfully fabricated under dark condition with homogeneous pore distribution and appreciable porosity. XRD shows characteristic peak for PSi formation with the peak at $2\theta = 33.3^\circ$. IR spectra confirm PSi formation through characteristic Si-O-Si and SiH_2 bonds. PL peak at 607.5 nm suggests possible application potential of the material for optoelectronic devices. Raman spectra of the sample gives red shift of 10 nm for quantum confinement effect from some pores as well as Raman enhancement from others, which may have application probability in cavity formation for fabrication of Raman laser.

Acknowledgement

Authors are thankful to Department of Science and Technology (DST) for its financial support through the project DST/TSG/PT/2009/96 and to the Department of Chemistry, Gauhati University, Guwahati for PL and FTIR measurements and Indian Association for the Cultivation of Science, Kolkata for FESEM and XRD measurements.

References

- 1 Canham L T, *Appl Phys Lett*, 57 (1990) 1046.
- 2 Halimaoui A, Oules C, Bomchil G, Bsiesy A, Gaspard F, Herino R, Ligeon M & Muller F, *Appl Phys Lett*, 59 (1991) 304.
- 3 Lehmann V & Gosele U, *Appl Phys Lett*, 58 (1991) 856.
- 4 Dian J, Macek A, Nizansky D, Nemele I, Vrkoš V, Chvojka T & Jelinek I, *Appl Surf Sci*, 238 (2004) 169.
- 5 Halliday D P, Holl & E R, Eggleston J M, Adams P N, Cox S E & Monkman A P, *Thin Solid Films*, 276 (1996) 299.
- 6 Harraz F A, *Phys Status Solidi C*, 8 7 (2011) 1883.
- 7 Lim J C, Chen W L & Tsai W C, *Optics Express*, 97 (2006) 64.

- 8 Sailor M J, *Porous Silicon in Practice, Preparation, Characterization, & Application* (Wiley-VCH Verlag GmbH & Co KGaA) Chapter I (2012) .
- 9 Lim J C, Lee P W & Tsai W C, *Appl Phys Lett*, 89 (2006) 119.
- 10 Jayachandran M, Paramasivam M, Murali K R, Trivedi D C & Raghavan M, *Matter Phys Mech*, 4 (2001) 147.
- 11 Cullis A G, Canham L T & Calcott P D, *J Phys* 82 (1997) 909.
- 12 Bessais B H, Ezzaouia, Boujmil M F, Ben O Youes, Elhouichet H & Chihi A, *Journal of Porous Mater*, 7 (2000) 311.
- 13 Prabakaran R, Kesavamoorthy R & Alok Singh, *Bull Mater Sci*, 28(3) (2005) 219.
- 14 Brandt M S, Fuchs H D, Stutzmann M, Weber J & Cardona M, *Solid State Commun*, 81 (1992) 307.
- 15 Deb S K, Mathur Neelu, Roy A P, Banerjee & Sardesai A, *Bull Mater Sci*, 17 5 (1994) 505.
- 16 Abidi D, Jusserand B & Fave J L, *Phys Rev B*, 82 075210 (2010) 1.
- 17 Mamichev D A, Gonchar K A, Timoshenko V Yu, Mussabek G K, Nikulin V E & Taurdaev T I, *J Raman Spect*, 42 (2011) 1392.
- 18 Sirleto L, Ferrari M A, Jalali B & Rendina I, *J Opt A*, 8 (2006) S 574.
- 19 Rong H, Liu A, Jones R, Cohen O, Hak D, Nicolaescu R, Faaj A & Pariccia M, *Nature*, 433 (2005) 292.