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Effect of Structural Characterization on Optical Properties of Porous Silicon Fabricated by Metal Assisted Chemical Etching

Karanam Madhavi[1], N.Hanumantharaju[1], Hemalatha K.S[1], Sunanda S[1], Venkateshbabu K R[2]

[1]Department of Physics, Maharani's Science college for women, Palace Road, Bangalore-560001, India

[2]Department of Physics, Nrupathunga University, Bangalore Karnataka-India.

Abstract: Porous silicon is synthesized by two step silver (Ag)assisted chemical etching method. The structural characterization of porous silicon has been carried out by Scanning Electron Microscopy (SEM), X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR). In XRD, two peaks were clearly observed at 69. 19^0 and 69.41^0 for silicon and Ag respectively and the intense peaks with preferred growth direction (400) suggesting the good crystalline quality of porous silicon. The optical properties were carried out by using UV-Visible Spectroscopy which reveals that the optical reflectance of porous silicon is decreased as compared to bulk silicon which is very much efficient for solar cell applications. Photoluminescence (PL)emission has been observed in porous silicon which is in evident with the results of FTIR analysis. These observations concludes that the fabricated structure of porous silicon acts as a potential candidate for improvisation of the solar cell efficiency and in the field of optoelectronic devices.

Keywords: Porous silicon, Photoluminescence, Ag assisted chemical etching, XRD,FTIR

1. INTRODUCTION

Porous silicon (PSi) is s very attractive material in the past decade due to its wide spectrum of applications in the field of Opto -electronics [1], Sensors [2] and Solar cells [3]. The porous silicon (PSi) is one of the silicon nano structures first reported in 1956 by Uhler when he discovered colored deposits on the electrochemically etched silicon. Later, the study on PSi was reported by Watanabe and Sakai in 1971[4]. Porous silicon can be classified as a function of pore size (d_p) according to international union of pure and applied chemistry (IUPAC). PSi nano structures can be classified into three types 1) Microporous (μpSi) dp<2nm 2) Meso porous silicon (mpSi) with 2nm <d_p<50nm 3) Macroporous silicon d_p>50nm.Different methods have come up to fabricate porous silicon, like electrochemical etching, stain etching and metal assisted chemical etching. In Electro-chemical etching the external bias is required thus it is cost ineffective method [5]. In stain etching the external bias is not required but it is very slow and poor control over the pore formation [6]. The drawbacks of ECE method and stain etching were compensated by new method called metal assisted chemical etching (MACE). Metal assisted chemical etching (MACE) is another alternate method to fabricate PSi. MACE is simple and cost competitive method to produce geometrical features of PSi which cannot be produced by other methods. Thus, MACE method is preferred over the above two methods. MACE can be classified as one step MACE (MACE 1) and two step MACE (MACE 2). The details of MACE were reported in our previous work [7]. We adopted two step MACE method to fabricate PSi.In this method, in the first step noble particles such as Ag, Au, Platinum etc.. are deposited on the silicon wafer by various techniques such as sputtering [8], electrochemical [9] or electroless displacement [10] and in the second step, the Si covered with noble metal is etched in the solution containing hydrofluoric acid (HF), oxidizing agent (H_2O_2) and deionized water. The silicon underneath the noble metal etches faster than that of uncovered silicon. As a result, the noble metal sinks and produces pores or pillers depending upon the etching conditions and parameters. Thus, PSi fabrication is influenced by many etchings parameters such as etching time, temperature and concentration of etching solution [11].

The motivation of this work is to improvise the solar cell efficiency.This can be achieved by fabricating the antireflecting coatings.Thus this paper focus on the effect of structural characterization of PSi on the optical properties and necessary conditions for PSi to be used as antireflecting coatings and in optoelectronic devices.

2 MATERIALS AND METHODS:

2.1Materials:

The single crystalline silicon wafers used in this study are 3 inch p-type <100> with resistivity 1-10 Ω-cm. Silver Nitrate ($AgNO_3$), hydrofluoric acid (48%), Nitric acid (HNO_3) hydrogen peroxide (H_2O_2) has been purchased from a commercial

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source. Acetone,ammonia and sulphuric acid (H_2SO_4) are purchased from Aldrich chemical &Co without any purification.

2.2 Synthesis and fabrication of porous silicon:

Before the fabrication, the silicon wafers are cleaned by RCA procedure which was developed by Kern and Puotonin in 1970[12]. After cleaning procedure is done, silicon wafers are dipped in piranha solution (H_2SO_4& H_2O_2 in the ratio 3:1) for 10 minute and in HF for 30 seconds to remove the native oxide. The first step of MACE is to deposit the Ag nano particles. The Ag nano particles are deposited on the cleaned silicon wafer by immersing in the aqueous metallization bath consisting of (0.005M) $AgNO_3$ and (4.8 M) HF in the volume ratio 1:1 for 30 sec and then removed and rinsed with deionised water. The second step of MACE is the etching of silicon. The Ag deposited silicon is immersed in the etching solution consisting of 4.8M HF and 0.5M H_2O_2 in the volume ratio 1:1 for a etching time of 60 minutes. The etched silicon is rinsed thoroughly with DI water and then immersed in the 7.2M HNO_3 solution to remove the residual Ag nanoparticles. The oxide layer formed on the etched silicon due to the HNO_3 solution is removed by immersing in the 5% HF. Finally the samples are thoroughly rinsed with DI water and dried by blowing N_2 gas[13].The optical properties such as optical reflectance and PL are measured for silicon and porous silicon.

2.3 Characterization:

All etching steps are performed at ambient temperature. The surface morphology is investigated using scanning electron Microscope(JEOL,JSM-6330F).The crystallographic phase analysis is done by x-ray diffractometer (Rigaku diffractometer). The bond formation on the porous silicon is studied by FTIR instrument in ATR mode. The optical reflectance is measured using CT -25C UV Vis spectrometer(JASCO) and photoluminescence(PL) measurements were carried out using a single monochromator equipped with a charge-coupled device (Princeton Instruments, PIXIS 100) having 325-nm He-Cd laser (Kimmon,IK3302R-E) as the excitation source.

3 RESULTS AND DISCUSSION:

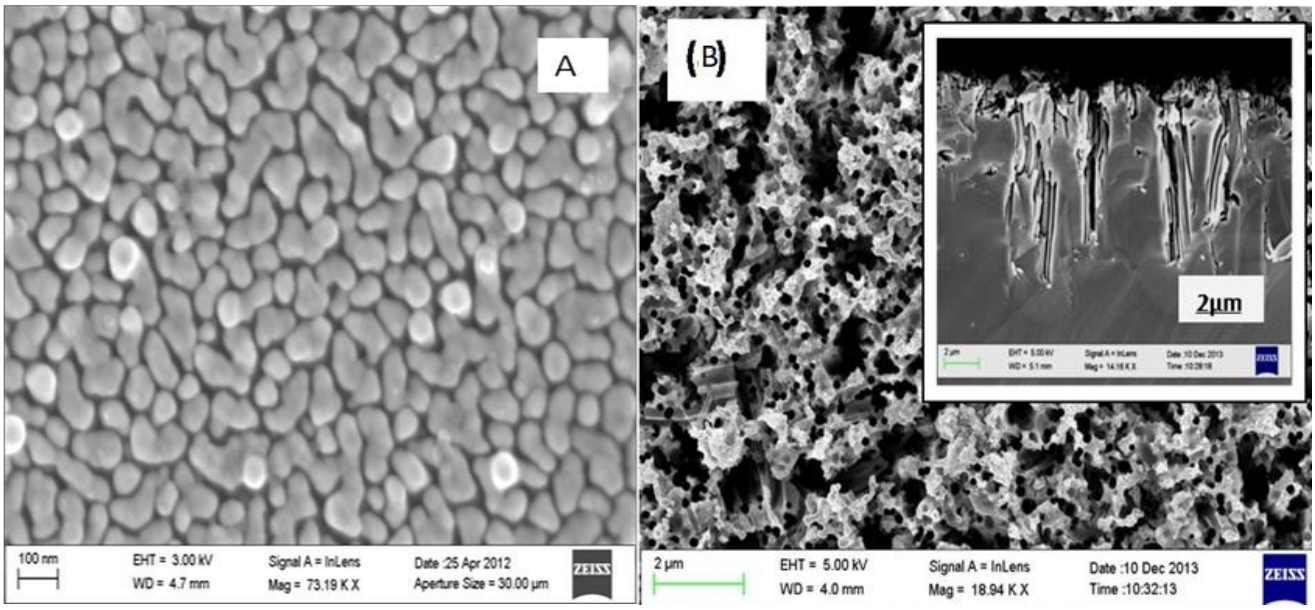

Figure.1. SEM images of A) Morphology of Ag catalyst on silicon substrate for the deposition time of 60 seconds B) Porous Silicon at etching time of 60 minutes etching

Fig 1A. shows the SEM images of morphology of deposition of Ag nano particles for 1 minute on silicon wafer. Figure 1 B shows the plane view and cross section SEM images of PSi after etching time of 60 minutes. We observed that the excessive deposition time for Ag nanoparticle is destructive for porous silicon formation. Thus, the deposition time for Ag nanoparticle is optimized as 60 seconds in our work. However the etching time is also varied and optimized as 60 minutes. The etching of Ag loaded silicon in HF/H_2O_2/DI water solution produces porous silicon [14]. The pores formed after etching is not having uniform diameter which concludes that the deposited Ag nano particles are of different sizes [15]. It is evident from the SEM images that the average diameter of porous silicon and pore depth is of 56 nm &8.56µm respectively after 60 minutes etching .The mechanism of Ag nano particle deposition and fabrication of porous silicon had been reported in our previous work [7].

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3.1 Structural properties:

3.1.1 X-ray diffraction Analysis:

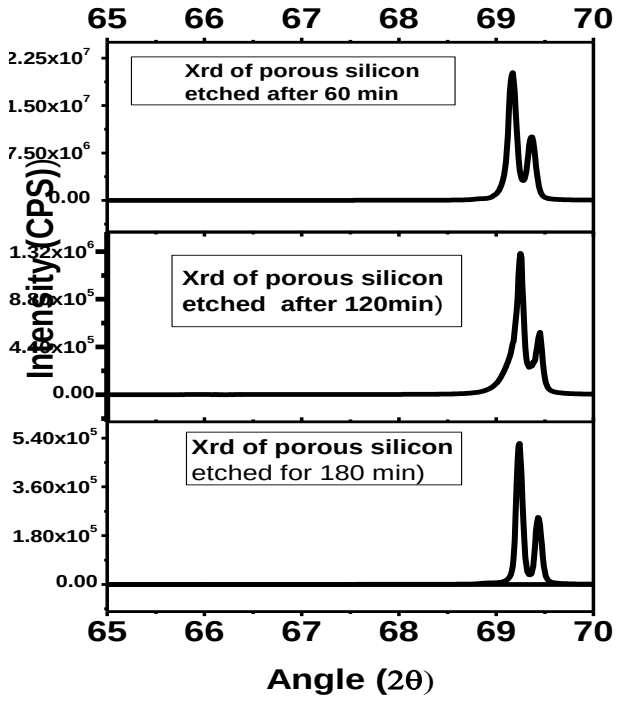

Figure.2. .Xrd patterns of porous silicon fabricated from different etching time

After the fabrication of porous silicon, the XRD analysis has been carried out to know the structural information. The X raydiffraction of PSi was done by X-ray diffractometer (Rigaku diffractometer).Figure 2 depicts the variation of intensity with the angle 2θ with different etching times. XRD of PSi clearly shows the existence of two peaks at the positions of 69. 19^0 and 69.41^0 for silicon and Ag respectively [16]. It is observed that the peak intensity of silicon is higher than Ag which is in good agreement with previous studies [16]. It is clearly shows that the peak intensity of Ag is decreased with the increase of etching time. This can be attributed that as the etching time increases the dissolution of Ag increases which in turn increases the pore size and pore depth which is supported by SEM analysis. The XRD pattern of porous silicon indicating the preferred direction (100) suggests the good crystalline quality of the porous silicon [17].

From the obtained XRD data, by measuring full width half maxima (FWHM) values for respective diffraction peaks,the average grain size d can be calculated by using Scherrer's formula[18]

$$d=\frac{0.9\lambda}{\beta\cos\theta}\ \text{nm}$$

Where d is the crystalline size in nm, λ is the wavelength of X-rays in nm, β is FWHM in radians and θ is the Bragg's angle in radians.

Table.1 shows the XRD data of porous silicon at different etching times.

Table.1

Etching time	2θ (Degree)	FWHM(β) (Degrees)	Grain size(nm)
60 min	69.25	0.078	104.53
120 min	69.24	0.1120	72.79
180 min	69.25	0.2732	29.84

From the above data it is shown that crystalline size d is decreased with etching time which in good agreement with SEM analysis.

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3.1.2 FTIR Analysis:

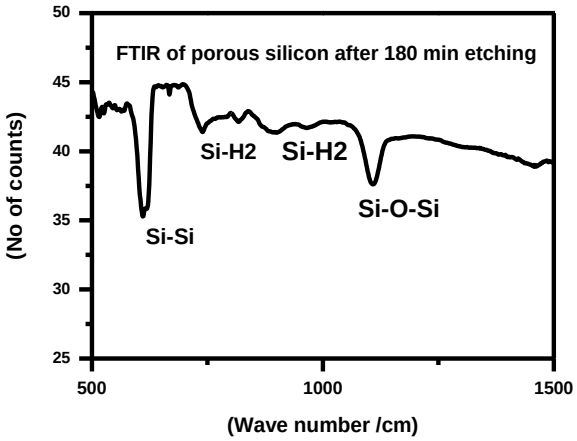

Figure.3. FTIR Spectra of porous silicon etched for 180minutes'

Figure.3. shows the FTIR spectra of porous silicon using p-type silicon after etching for 180 minutes. It is seen that the FTIR spectra consists of absorption bands in the range of 600-2400 cm^{-1} .The strong absorption bands at 1100 cm^{-1} and at 626 cm^{-1} corresponds to Si-O-Si, Si-H bonds & weak bonds at 817cm^{-1} at 908 cm^{-1} corresponds to Si-H_2 wagging and Si-H_2 scissors respectively[19].The strong Absorption peak at 626 cm^{-1} was due to Si-H bonds which are surface bonds[20].Thus, Porous silicon surface consists of hydrogen complexes. The presence of hydrogen bonds on the surface of the porous silicon will not only passivates the dangling Si bonds and also widens the optical energy gap which can be attributed as the reason of PL emission in porous silicon [21].The band assignments and vibrational modes are given in Table 2 [22].

Table 2:

Peak position(cm^{-1})	Attribution
626	Si-H wagging
817	Si-H_2 wagging
908	Si-H_2 Scissors
1100	Si-O-Si bending

3.2 UV - Visible Spectroscopy:

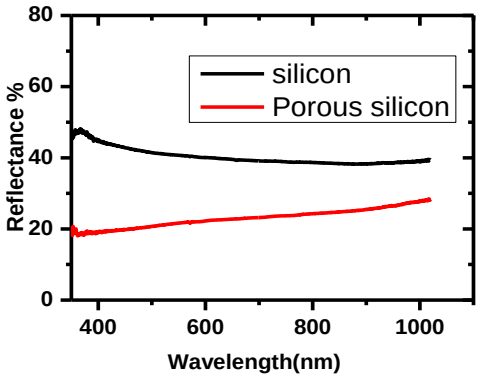

Figure.4. UV-Vis reflectance spectra of porous silicon and silicon

Fabricated nanostructure form like PSi modifies the optical properties of bulk silicon [23]. The optical characterization of PSi is performed with in the range of 300nm -1200 nm. Figure 4 shows the optical reflectance spectra of porous silicon together with that of polished silicon wafer for comparison. It is observed from the figure that the optical reflectance of

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bare silicon is found to be 40% whereas the reflectance of porous silicon was supressed to 20%in the wavelength range of 400-700 nm. The attenuation in the reflectance of porous silicon can be attributed due to the porous structure of silicon which contains the preferential formation of sharp peaks at the pore tips which creates the refractive index gradient between air and silicon [24] which is confirmed through SEM analysis. Therefore, possibility of using the porous silicon as an anti-reflecting surface.

3.3 Photoluminescence spectral studies:

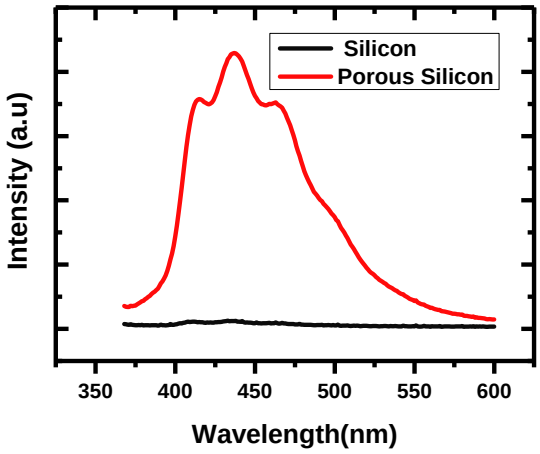

Figure.5. PL spectra of porous silicon

Figure.5. shows the PL spectra of PSi etched for 180 minutes because no PL emission was observed at lower etching times. The photoluminescence in porous silicon has been observed at 439nm wavelength which corresponds to the energy of 1.82 eV. The spectrum shows the two lower intensity peaks on either side of the maximum intensity peak at 410nm and at 466 nm [25]. The three emitted wavelengths by porous silicon at 439nm, 410nm and 466 nm allow us to suppose three different sized nanoparticles which is in agreement with SEM analysis. The density of pores emitting the light of wavelength 439nm dominates compared to the other sized particles emitting the light with the wavelength of 410nm and 466 nm. This is an interesting observation which can be explained only through quantum confinement theory [26]. The porous silicon etched for 180 minutes emitted the PL in the blue wavelength region. It is confirmed from FTIR analysis that the porous silicon surface is fully covered with Si-H_n bonds which are responsible for PL emission [27].

4. CONCLUSIONS:

This work demonstrates the Ag assisted chemical etching which is low cost and effective method to synthesize porous silicon.XRD analysis had been carried out for porous silicon for different etching time and concludes that porous silicon has single crystalline quality and crystalline grain size decreased with increases of etching time. FTIR analysis of porous silicon concluded that porous silicon surface is a mixture of Si-H_n bonds, Besides, the optical reflectance is found to be supressed compared to bulk silicon which is essential for the preparation of antireflecting coatings. It is observed that the PL produced by porous silicon is in the blue wavelength region. The FTIR shows that the Si–Hn peaks are observed at the surface of the PS layer and these chemical species also give rise the PL in porous silicon.

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