Study of the Properties of the Porous Silicon Synthesized by Ag Assisted Electrolysis Etching

Madhavi Karanam^{1,a}, Mohan Rao G.^{2,*b}, Habibuddin Shaik^{3,c}
and Padmasuvarna R.^{1,d}

¹Department of Physics, Jawaharlal Nehru Technological University, Anantapur, India 560001

²Department of Applied Physics & Instrumentation, Indian Institute of Science,
Bangalore, India 560012

³Department of Physics, Nitte Meenakshi Institute of Technology, Bangalore, India 515002

^akaranamadhavi@yahoo.com, ^bgmrao@isu.iisc.ernet.in, ^cskhabibuddin@gmail.com,
^dpadmantua@gmail.com

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Abstract. Porous Silicon (PSi) is synthesized by Ag assisted electroless etching and characterized by Scanning electron microscopy (SEM). The effect of etching time on the optical reflectivity, optical absorbance of PSi is investigated. Reflectivity measurements showed gradual decrease in the reflectivity with respect to etching time. 45% reflectivity of bare silicon drops to 10% for 2 hours etching and to 6% for 3 hours etching. The decrease in the reflectivity shows that the PSi can be employed as an anti reflecting substrate in optoelectronic devices. The absorbance measurements revealed that the average absorbance of PSi is 0.60 in the wavelength range 300-800 nm after 2 hours etching. From the photoluminescence spectra it was found that PL intensity of PSi is high compared to bare silicon wafer. Static water contact angle measurements were performed to examine the hydrophobic properties of the PSi prepared under different conditions. The porous silicon surface after etching has been demonstrated to be suitable for self cleaning applications.

1. Introduction

Porous silicon (PSi) has been under special investigation in the past decade due to wide spectrum of applications in Optoelectronics [1-3] and in Chemical and Bio chemical sensors [4-7]. PSi is normally prepared by anodic etching [2], electrochemical etching (ECE) and stain etching. The ECE method is cost inefficient in wafer scale [8] where as stain etching is slow and it is useful in preparing the pores of few nano meters only [9]. The drawbacks of the above methods are compensated by new method called metal assisted chemical etching (MACE). MACE is purely solution based method used to produce uniform porous silicon layer very rapidly without any external biasing. The method we adopted is two step MACE in which in the first step noble metal layers (Ag, Au, Pt, etc.) are deposited on the Si wafer by various techniques such as sputtering [10], electrochemical [11] or electroless displacement [12] and in the second step noble particles covered silicon (Si) is etched in the solution containing Hydrofluoric Acid (HF) and an oxidizing agent. The Silicon below the noble metal is etched faster than without noble metal [13]. Due to this, PSi layer is formed within few seconds and can be controlled by the morphology of the deposited noble metal. Also PSi fabrication is influenced by many MACE parameters like etching time, temperature, concentration of etching solution etc. [14].

The motivation for this work is towards developing self cleaning surfaces. This could be achieved by making a superhydrophobic surface. In this paper, a detailed report is given on the fabrication of PSi using two step MACE known as Ag assisted chemical etching with silver (Ag) as the noble particle and hydrogen peroxide (H₂O₂) as an oxidizing agent as a function of etching time. We then provide an analysis on the optical and wettability properties of PSi indicating necessary conditions for PSi to be used as antireflecting coatings and also as non-wetting surfaces.

2. Materials and Methods

2.1 Material

One side polished p-type (100) oriented silicon (Si) wafer with a resistivity of 1-10 Ωcm , Silver nitrate AgNO_3 (0.02M), Nitric acid (HNO_3), and Hydrofluoric acid (48%) has been purchased from a commercial source. Sulphuric acid (H_2SO_4), Acetone and Ammonia (Sigma Aldrich Chemicals) are purchased from Aldrich Chemical & Co without further purification. The silicon wafer is immersed in hydrofluoric acid (HF) (1% electronic grade) aqueous solution for 30 s. The wafer is then washed in an ultrasonic bath with deionized water for 5 min and dried under nitrogen gas flow before use.

2.2 Synthesis and Fabrication of Porous Silicon

Si wafers are cleaned by standard RCA cleaning procedure. After cleaning, Si wafer is dipped in the piranha solution (H_2SO_4 & H_2O_2 in the ratio 3:1) for 10 min and in 5% HF for 30 sec to remove the native oxide and finally rinsed with DI water thoroughly. Ag particles are deposited on the cleaned Si surface by immersing in the aqueous metallization bath consisting of AgNO_3 (0.005M) and HF (4.8M) in the volume ratio of 1:1 for 30sec. Si wafer covered with Ag nano particles is etched in the solution containing 4.8M HF and 0.5M H_2O_2 for different etching times. Then the samples are immersed in HNO_3 solution to remove the residual Ag particles and then in HF to remove the oxide formed due to HNO_3 . Finally, the etched Si wafers are rinsed thoroughly with DI water and dried by blowing N_2 [15]. All the chemicals used are purchased from sigma Aldrich and used without purification. The Optical properties such as reflectance and absorbance of PSi are studied as a function of etching time and wettability of PSi is tested by measuring the contact angle.

2.3 Characterization

All etching steps are performed at ambient temperature. The surface morphology is investigated using a scanning electron microscope (JEOL, JSM-6330F). The Optical absorption measurements are carried out using a CT-25C spectrometer (JASCO), a 50-W halogen lamp and a liquid-nitrogen-cooled Ge photodiode (Hamamatsu, B6175-05). PL measurements are performed 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. The wettability of the samples is measured using a commercial contact-angle measurement apparatus (Kyowa Interface Science).

3. Results and discussion

3.1 Study of deposition of Ag on Si

When Si wafer is dipped in the AgNO_3 and HF, a galvanic displacement reaction takes place which consists of two simultaneous processes [16]. Initially, Ag^+ ions attract electrons from Si wafer and convert to Ag nuclei. These Ag nuclei act as catalyst for the reduction of Ag^+ ions and Ag nuclei approaching the Si wafer attracts more electrons from Si because of its high electronegativity value [16]. This mechanism enables conversion of Ag nuclei to Ag particles. Fig. 1 shows the morphology of the Ag particle loaded Si wafer as a function of deposition time. We can see from the Fig1.a that for a deposition time of 40sec, the deposited Ag nano particles are spherical with a well proportionate different diameters, high density and also low interstitial size between the particles. In order to optimize the Ag particle deposition, a systematic study has been carried out with respect to the deposition time. As the deposition time is increased to 1 min, the Ag nano particles agglomerate to form clusters as shown in Fig1.b. It is evident that as the deposition time increases, the Ag nano particle size also increases and shows the linear relationship between the particle size and time [16]. SEM images in fig.1 clearly shows that the coverage area of Ag increased with time which is very important in tuning the morphology of porous silicon [17].

Fig. 1. SEM images of Morphology of Ag catalyst on silicon substrate for etching time: (a) after 40sec (b) after 1minute.

3.2 Study of PSi formation with etching time

In order to synthesize porous silicon, the Ag loaded Si wafer is rinsed with DI water and subsequently dipped in the etching bath consisting of HF and H₂O₂. The reduction of H₂O₂ occurs on the surface of the Ag particles which act as catalyst. This can be understood from the following equation [17]

As a result Ag nano particle gets oxidized to Ag⁺ ion. These Ag⁺ ions again convert to Ag particle by extracting the electrons from silicon. In other words, oxidative dissolution of Si occurs in the fluoride solution leading to PSi layer. This could be represented by the following equation [17].

After etching, the colour of the normal crystalline silicon (gray colour) converts to black or brown depending on the etching time. To study the optimization of PSi, we varied the etching time by keeping AgNO₃ concentration fixed. Fig.2 shows the plan-view and cross section SEM images of PSi at 60 min, 120 min, 180 min and 240min respectively. It is clear from the SEM images that the average pore diameter has increased from 56 nm to 200nm and also it is very clearly understood that the Ag catalyzed etching is in one direction (100) increased from 8.56 μm to 23μm. Thus the pore depth increased with etching time as shown in the Fig 3. which is in good agreement with previous studies [18]. This is consistent with proposed mechanism that higher etching time results in deeper holes and thus longer pore depth [16].

Fig. 2. SEM images of Porous Silicon at different etching times: a) 60 min etching b) 120 min c) 180min d) 240 min (insets show the cross section images).

Fig. 3. Variation of Etch depth with Etching time.

3.3 Optical studies

3.3.1 Reflectance behavior

Fig.4 shows the reflectance spectra of porous silicon in the wavelength of range 300nm-800nm. It is observed that the PSi shows lower reflectance compared to bare silicon. The maximum reduction in light reflectance occurs within the range of 300nm to 600nm and later it showed slight increase in the reflectance. It is clear from the Fig.4 that the average reflectance of PSi is 40% less than reflectance of unetched Si and the increase at higher wavelengths is probably due to the random distribution of the pores and increased roughness. The overall attenuation in the optical

reflectance of PSi was caused by light transmission at the porous and bulk interface[19]. Thus the maximum attenuation in the reflectance around 5% is observed after 120 min etching, which can be used as antireflecting surface. The morphology of etched surface in Fig.2 has a direct relation with decrease of optical reflectance, indicating that the nano porous structure creates the refractive index gradient between air and silicon wafer and the optical reflectance is suppressed to lower values [20]. This antireflective behavior of the porous silicon is observed from the colour of etched silicon(black).

Fig. 4. UV-Vis reflectance spectra of porous silicon at different etching times.

3.3.2 Absorbance studies

The absorption curves in Fig.5 shows that the absorbance of PSi is very high compared to unetched Si and also the higher absorbance value is within the wavelength range of 300 nm to 600 nm. The high absorbance of PSi is due to the multiple scattering of light internally between two successive pores which enhances the absorbance of light [20]. As the etching time is increased, pore density increases and hence absorption, which is revealed in the absorbance spectra in Fig.5.

Fig. 5. UV-Vis absorbance spectra of porous silicon at different etching times.

3.3.3 Photo Luminescence

Fig.6 shows the Photo Luminescence(PL) spectra of PSi etched for 180 min and 240 min only because at lower etching times no PL spectrum could be obtained. It is clearly shown that the PL peak intensity increased for 180min etching time and it is decreased for 240 min. This can be attributed to the fact that as the etching time increases, the microporosity increases which in turn reduces the amount of light emitting nano crystallites and hence the PL peak intensity [21]. The PL emitted spectra showed one high intensity peak at 439 nm with two lower intensity peaks on either sides at 410nm and 466nm respectively. This is an interesting observation which can be explained only through quantum confinement theory[22] according to which the emitted wavelength and PL peak intensity are correlated with nanostructure size(pore) and also density of pores respectively. In the Fig.6 three emitted wavelengths 439 nm, 410nm and 466nm allow us to suppose three different

sizes of the pores which is supported by the SEM images of the Ag particles deposition shown in fig.1. And also the density of pores emitting the wavelength of 439nm with higher peak intensity dominates compared to two lower peak intensity peaks at 410nm and 466nm. This is an interesting result and could be useful in the fabrication of blue emitting laser.

Fig. 6. PL spectra of PSi for different etching times.

3.4 Wettability studies

We tested the wettability of PSi by measuring contact angle. The wettability of PSi surface is examined by measuring the contact angle between water and PSi surface. The contact angle was also measured for unetched Si for reference. When the water is dropped on the Si surface it is spread with 85° contact angle which shows hydrophilic nature, whereas on the PSi surface the water did not spread. It stayed almost like a water drop on the lotus leaf. When the etching time is increased from 60 min to 240 min, the contact angle also increased from 110° to 133° showing hydrophobic behavior as shown in the Fig.7. The variation of wettability or contact angle on the unetched Si surface to PSi surface can be interpreted by changing from wenzel state (wetting surface) to Cassie-Baxter state (non-wetting surface) respectively [23]. According to Cassier equation,

$$\cos\Theta^{cb} = f \cos\Theta + f - 1 \quad (3)$$

Θ^{cb} is the measured contact angle on the rough surface, f is the area fraction when the liquid, solid are in contact and Θ is the intrinsic contact angle on the flat surface. The surface wettability depends on the value of f . The surface can achieve the hydrophobic or superhydrophobic as the value of f decreases. The value of f can be decreased by creating the porous structure which can decrease the wettability [24].

The Optical profilometer image shown in Fig.8 confirms that the porous silicon is combination of sharp peaks which enhanced the surface roughness which in turn decreased the wettability.

Fig. 7. Contact angle Measurements of P Si at different etching times a) unetched silicon b) 60min etching c) 120min d) 180min e) 240 min f) Variation of contact angle with etching time.

Fig. 8. The Optical profilometer Image of Porous Silicon (After 1 hour etching).

4. Conclusions

This study clearly demonstrated the fabrication of PSi by Ag assisted chemical etching. The deposition of Ag nano particle size on silicon is controlled by deposition time. With the obtained Ag deposited system, fabrication of PSi, as a function of etching time is studied in detail and concluded that the pore depth has been increased with etching time. PSi optical and wettability properties are studied as a function of etching time. The optical reflectance of Porous Silicon is totally suppressed almost to 10% which is very effective for enhancement of optical absorption and in the preparation of antireflecting coatings. It is observed that the PL produced by porous silicon is in the blue wavelength region. The static contact angle measurements of PSi with etching time shows that an increase in the etching time results in increase of contact angle which is effective result in achieving superhydrophobicity and self cleaning property without any external surface modification. Thus PSi fabricated by Ag assisted chemical etching showed low reflectance which offers significant advantage for the high efficiency solar cells with self cleaning properties. The superhydrophobic characteristics of porous silicon demonstrate that this material could be used as a self cleaning surface.

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