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Parallel or Interconnected Pores' Formation through Etchant Selective Silicon Porosification

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Abstract

Effect of oxidizer, present in the etching solution, on the surface morphology and microstructure obtained after porosification of p-type silicon wafer using metal assisted chemical etching has been studied here. The morphologies of Si wafers porosified using two different solutions namely HF/ H₂O₂ and HF/KMnO₄ have been compared to establish how either of the oxidizers (H₂O₂ or KMnO₄) should be chosen depending on the desired application. The comparative study reveals that either parallel pores with wire like structures or interconnected pores with cheese like structures can be obtained when H₂O₂ or KMnO₄ respectively are chosen. Careful analysis of SEM images has been carried out using ImageJ to establish that samples prepared using KMnO₄ are more porous due to aggressive etching. Additionally, experimental and theoretical Raman spectroscopic studies have been utilized to study the presence of low dimensional Si nanostructures of a few nanometers size at the microscopic level in the porosified silicon.

Keywords: Porosity; Silicon nanostructures; Oxidation; Etching; Raman Spectroscopy

1. Introduction

Silicon (Si) and its nanostructures (NSs), including porous silicon (p-Si), is one of the widely used materials for decades, playing important role in the field of electronics, energy conversion & storage, biosensing and so on.¹⁻⁶ Various interesting properties^{7,8} such as large surface area, high density electronic states, size dependent⁹ properties etc. arise due to selective morphology and exhibit superior performance for utilization in many applications¹⁰ in comparison with its bulk counterpart. The possibility to show many applications in one material exponentially grow when the material exists in its nano-form as well as acquires porosity, which implies that 'Porosity' and 'Nanoarchitecture' can be encapsulated together for better performance. Different porous Si vary in terms of their morphology and pores' microstructures and pores may be well aligned, interconnected or mixture of the two. The resultant pore microstructure depends on variety of factors like sample properties and formation method. Optimizing above-mentioned morphological amalgamation would be interesting to study and develop Si NSs for desired application.

Various fabrication methods¹¹, through top-down and bottom-up approaches,¹²⁻¹⁴ used to fabricate Si NSs/p-Si include electron-beam lithography¹⁵, ion implantation, electrochemical etching, laser induced etching¹⁶ etc. Metal assisted chemical etching (MACE), also known as metal induced etching is one of the easier and economic techniques to fabricate various p-Si NSs owing to many advantages^{17,18} such as simplicity, compatibility with existing industrial applications¹⁹. In MACE (a two-step etching process), a thin metal nanoparticles film of noble metal²⁰ (Pt, Pd, Au, Ag) is deposited on the Si surface by mixing an appropriate metal salt in HF in first step which acts as a catalyst to assist etching of Si in etching solution containing HF and an oxidizing agent. Surface of the wafer covered with metal particles gets etched much faster

than the uncovered part, resulting in p-Si containing arrays of wire like structures. The nature of these pores depends upon various factors¹⁸ such as wafer orientation, doping level of Si substrate and oxidizing agent used in etching process²¹. Oxidizing agents perform an important role in the porosification of Si substrate as all the oxidizers have sufficient energy (electrochemical potential) to inject holes into the valance band of Si. The metal²² facilitates charge transfer between the substrate and oxidizer present in the solution to carry out the porosification.

Various oxidizing agents²³ like $K_2Cr_2O_7$, $KMnO_4$ ²⁴ and H_2O_2 are used to carry out MACE but H_2O_2 is the most commonly used oxidizer to oxidize the Si substrate as its electrochemical potential is much more positive than the other oxidizing agents and it can easily inject holes into the valance band. Being a strong oxidizing agent ²⁵ it is difficult to store H_2O_2 without compromising its deterioration. It gets decomposed to oxygen and water at normal conditions and prolonged storage. Thus, an alternate oxidizing agent should be used for etching to avoid uncertainty about the reproducibility of the sample. Furthermore, H_2O_2 based etching yields mainly low porous and unidirectional etching (of course depending on wafer orientation) ²⁶. For various applications like sensing, supercapacitance, solar cell ²⁷ etc. where high surface area is required, samples should be highly porous preferably should be etched in all the dimensions. Hence, alternate oxidizing agent should be explored and a solid one should be preferred so that storage is not a problem. To achieve that, $KMnO_4$ ²⁸ can be a good option to etch Si as it is stable in its powder form hence easy to store. Furthermore, when metal assisted Si substrate is oxidized by $KMnO_4$, then K^+ which are present in the etching solution make K_2SiF_6 and might get deposited inside the pores and due to which a highly poroused Si layer has been formed²⁹.

This paper aims to compare the microstructures of porous Si formed by two different oxidizing agents, namely H_2O_2 and $KMnO_4$. For direct comparison, two p-type Si wafer pieces have been

taken and porosified by different oxidizing agents. The morphology of these samples has been investigated using scanning electron microscope (SEM) and analyzed using ImageJ software to quantitatively estimate the resulting porosity. Furthermore Raman spectroscopy^{30–35} has been carried out to study the nature of p-Si at microscopic level by investigating whether low dimensional Si NSs are present inside these pores. Experimentally observed Raman spectrum has been analyzed using the framework of phonon confinement model^{36–39} to estimate the size of the Si NSs.

2. Experimental Details

Commercially available lightly doped p-type Si wafers with resistivity $\sim 11\text{--}25\ \Omega\text{-cm}$ have been used to fabricate the pSi NSs using MACE. Prior to etching, first the wafers were cut into the size $(1\times 1)\text{ cm}^2$ and then cleaned by ultrasonication in iso propyl alcohol, acetone, ethanol and dried. The MACE process was carried out by depositing Ag nanoparticles on the cleaned Si wafers by dipping them into the deposition solution containing 4.8 M HF and 5 mM AgNO_3 for 60 sec at room temperature. The AgNPs deposited wafers, in the previous step, were cleaned with deionized water and kept into the solution for etching. In the next stage, two etching solutions were prepared with two different oxidizing agents namely H_2O_2 and KMnO_4 . The H_2O_2 etching solution contains 0.5 M H_2O_2 whereas the KMnO_4 etching solution contains 3mM KMnO_4 with fixed 4.8 M HF in both the etching solutions. Then, etched wafers were kept into the HNO_3 solution to remove the residual AgNPs present on the etched wafers. A detailed step-by-step recipe has been provided in the Supporting Information (SI). A supra55 Zeiss scanning electron microscope (SEM) has been used to study the surface morphologies of these samples. Raman spectroscopy measurements have been carried out using a Horiba Jobin-Yvon Raman (LABRAM HRTM) spectrometer with a 633 nm excitation laser and CCD detector having a

spectral resolution of $\sim 0.5\text{ cm}^{-1}$. The spot size of laser beam is $\sim 1\mu\text{m}$ focused using 100x objective. Raman data has been collected in backscattering mode.

3. Result and Discussion

As mentioned above, MACE is a two-step porosification technique based on wet etching process carried by a metal catalyst deposited on the surface of the Si and this process employed to form pSi, often with different geometries including fractal, wire-like etc. Above silicon structures including nanopores, nanowires can result depending upon different parameters like doping, orientation of sample surface, temperature and oxidizer used in etching process^{19,40}. The solution-metal-silicon system constitutes a microscopic electrochemical cell that induces anodic silicon etch. The etching rate strongly depends upon the oxidizing agent used, typically H_2O_2 , in the etching solution because of their ability to inject holes into the valance band of silicon, as their electrochemical potential is sufficiently high to directly inject holes in the valance band of silicon. Therefore, it is important to understand the rationale behind choosing any oxidizing ($\text{H}_2\text{O}_2/\text{KMnO}_4$) agent. As mentioned above, H_2O_2 is often used for this purpose because the redox potential is away from the valance band edge of silicon as shown using the schematic representation of relative redox potential/band energies (Figure 1).

Figure 1 shows that the electrochemical potential of H_2O_2 (1.71 V) is much higher than the valance band of Si thus making it a good choice for making the etching solution because H_2O_2 can easily inject holes into the valance band of Si to initiate the etching process. Similarly, KMnO_4 also can be chosen instead of H_2O_2 due to its favorable energy (1.51 eV) as shown in Figure 1. Thus, a Si substrate subjected to HF/KMnO_4 should be etched, in the same way as that by H_2O_2 , but the etching rate may be comparatively lower due to smaller driving force.

Fig. 1: Relative positions of Si band edge energies and $\text{H}_2\text{O}_2/\text{KMnO}_4$ redox potential on the electrochemical potential scale, indicating that holes are injected into the valance band. E_c and E_v show the electrochemical potential of valance and conduction band edge of Si.

Exploiting this, firstly metal nanoparticles (AgNPs) were deposited on the silicon wafer surface by placing cleaned Si wafer in HF/AgNO_3 solution where the bare Si wafer act as anode onto which the Ag gets deposited and form nanoparticles to be sued in the next step. In the second step, the AgNPs deposited Si wafers are placed in two different etching solutions consisting of $\text{HF}+\text{H}_2\text{O}_2$ and $\text{HF}+\text{KMnO}_4$ to examine the effect of H_2O_2 and KMnO_4 as shown using schematic in Figure 2.

Fig. 2: Schematic showing MACE using two different oxidizers H_2O_2 (grey solution) and KMnO_4 (magenta solution). AgNPs deposited Si wafer is dipped into the solution.

Two different oxidizers H_2O_2 & KMnO_4 have been used, shown in Figure 2, to fabricate the Si NSs samples to understand the nature of etchant oxidizer and its effect on porosification process. It is known that during the etching process, AgNPs (deposition process) present on the silicon surface are oxidized by the oxidizer to create a localized Ag^+ cloud in the close proximity of AgNPs. These Ag^+ ions quickly react with Si and eject electron near Ag/Si interface. In this way, the etching process starts locally around the AgNPs and gets trapped in the nano-pits created by very initial etching of the Si wafer, leading to continued etching in the vertical direction⁴¹. The reaction equation¹⁷ of etching process is described as follows. The oxidizer, H_2O_2 or KMnO_4 present in the etching solution gets reduced at the metal sites and generates a large number of holes (Eq. R1) inside Si

This is accompanied by the oxidation of silicon surface and further gets dissolved in HF solution, causing the formation of SiF_4 followed by further hydrolysis to SiF_6^{-2} (Eq.

When H_2O_2 is used instead of $KMnO_4$, the hole generation step can be written as Eq. R5 below:

In the present study both kind of the etching solutions (H_2O_2/HF and $KMnO_4/HF$) have been used to prepare separate Si NSs samples and their surface morphologies have been studied using SEM. Figure 3 shows the SEM images of Si NSs samples which are subjected to Ag – assisted chemical etching in H_2O_2/HF solution for 60 minutes.

The top view SEM micrographs (Figures 3a, 3b) show porous surface which is expected as a result of continuous removal of Si atoms consequent to repeated etching process taking place in terms of reactions R2 to R4 mentioned above. The SEM images reveal that the etching has taken place, as expected, throughout the surface. It is known that during MACE, the etching proceeds along the depth of the wafer and pores are formed at locations where AgNPs are present whereas the portion not covered by the AgNPs remains unetched. These unetched portion remain on the sample and appear as wire like structures and the length of these wires depend on the etching

time. The long parallel wires have been obtained by etching in $\text{H}_2\text{O}_2/\text{HF}$ solution as can be seen in the cross-sectional SEM image (Figure 3c). Figure 3c also reveals an average pore-depth or

Fig. 3: (a, b) SEM images of the top view of p-Si wafer etched by $\text{H}_2\text{O}_2/\text{HF}$ solution for 60 min at two different magnifications, (c) corresponding cross-sectional view and (d) 3D surface profile extracted from SEM image in (b) using ImageJ.

wire-length of $\sim 80\ \mu\text{m}$. Further pore analysis has been done using ImageJ software by obtaining surface profile (Figure 3d) which also shows porous nature with wire like structures in the sample. The surface profile (Figure 3d) has been obtained from the SEM micrograph in Figure 3b and porosity has been estimated which will be discussed later on. It is known that increasing etching time leads to longer Si wires but prolonged etching may lead to the breakage of the formed wires. The wire like structure obtained in Figure 3 can be used in applications where

aligned wires with high aspect ratio are requires like field emission etc^{42,43}. The vertical etching leads to the wire like structures but lack of horizontal etching restricts the increase of overall surface area and porosity thus the $\text{H}_2\text{O}_2/\text{HF}$ etching appears not suitable for the applications where more surface area is required. Therefore, $\text{H}_2\text{O}_2/\text{HF}$ has been replaced by KMnO_4/HF to be used as the etching solution to prepare next set of samples. KMnO_4 can be a good option to replace H_2O_2 because of its advantage in procurement, storage and non-hazardous nature. Hence to know the morphologies' difference by using different oxidizing agent, SEM study has been done as shown in Figure 4. Figure 4 shows the surface morphologies and surface plot profile obtained using ImageJ from the samples which were subjected to Ag – assisted chemical etching in KMnO_4/HF solution for 60 minutes.

Fig. 4: (a, b) Top view SEM images of porosified p-Si wafer etched in KMnO_4/HF solution for 60 min at different magnifications, (b) corresponding cross-sectional view and (d) ImageJ extracted 3D surface profile plots.

The top view SEM images (Figures 4a, 4b) shows porous structures by using KMnO_4 and similar to the one obtained using $\text{H}_2\text{O}_2/\text{HF}$ solution (Figure 3). When etched in KMnO_4 (+HF) oxidizer, the pores are expected as a consequence of etching reactions R1 to R4. From the electrochemical potential scale (Figure 1), the electrochemical potential of KMnO_4 (1.52 V) is smaller than that for H_2O_2 but still more positive with respect to the valance band edge potential of Si which is required to generate holes to initiate the etching process as discussed above. The top view of etched Si wafer (Figure 4a) in KMnO_4 has a cheese-like morphology which means that etching in all the three dimensions of the wafer has taken place leading to highly porous samples. This can be confirmed using the cross-sectional SEM image (Figure 4c) and ImageJ generated 3D surface plot (Figure 4d). Also, it is well-known that bulk Si is indirect band gap semiconductor but at reduced dimensions (i.e., porous Si) it shows direct band gap nature and show visible color emission under UV illumination. The red color emission from etched Si prepared by both oxidizing agents (H_2O_2 & KMnO_4) can be seen in Figure S1 (SI). Apparently, comparison between the surface morphologies of samples porosified using $\text{HF}/\text{H}_2\text{O}_2$ and HF/KMnO_4 reveals that the latter is more porous thus may be appropriate for applications where high surface areas, rather than aspect ratio, are required like sensing etc.

For better quantitative comparison between the samples, porosity analysis⁴⁴ has been done here by using software origin 9.0 which has been shown in Table 1. To calculate porosity, following formula (Eq. 1) has been used:

$$\text{Porosity (\%)} = \frac{\text{Volume of pore } (V_{\text{pore}})}{\text{Volume of solid } (V_{\text{solid}})} \times 100, \quad (1)$$

Table 1: Porosity analysis of top surface of Si wafer etched by KMnO_4 and H_2O_2 done using SEM image in Figure 4a and Figure 3b respectively.

Parameter	KMnO_4 (Figure 4b)	H_2O_2 (Figure 3b)
V_{solid}	4.59×10^{10}	4.59×10^{10}
$V_{\text{integrate}}$	10.52×10^9	8.36×10^9
V_{pore}	3.23×10^{10}	2.57×10^{10}
Porosity	0.7037	0.5599
Porosity (%)	70.37%	55.68%

From table 1, it is clear that the porosity of KMnO_4 etched wafer is more than the porosity of H_2O_2 etched wafer and the morphology of sample prepared using KMnO_4 looks cheese-like structure whereas that prepared using H_2O_2 looks wire like. The difference in above mentioned microstructure can be understood as follows.

It is clear from the above discussion that different morphologies (cheese like v/s wire like) result when different etching oxidizer is used even though the etching time is kept same (60 min in the present case). It means that the etching is limited when H_2O_2 is used whereas with KMnO_4 makes etching rapid and apparently etch from more sites on the wafer. This happens due to the K^+ ions present in the etching solution which might sit on the pits of the wafer and form K_2SiF_6 . Then, K_2SiF_6 layers were deposited via heterogeneous nucleation and growth of SiNw in three dimensions takes place which can be seen in cross sectional SEM image in Figure 4c. Comparing Eq. R1 and R5, one can see that each molecule of H_2O_2 generates two holes in Si wafer whereas

one KMnO_4 generates five holes. Since the etching is essentially initiated by holes, the surplus holes in the latter case will provide more sites to attract fluorine attack. Since Si atoms get dissolved in the etching as a result of removal from the Si wafer in the form of H_2SiF_6 (Eq. R3) therefore more sites are attacked randomly by F^- ion. This increases the etching rate and initiates a rather less controlled etching process to yield more porous morphology when KMnO_4 is used as oxidizer in the etching solution. Due to the high concentration of KMnO_4 and multi-dimensional etching, the porosity of Si wafer is high in comparison with the wafer etched by H_2O_2 . Above results are consistent with the results shown by Douani et al²⁶, who have also shown that oxidant plays an important role in the formation of porous Si. Thus, choosing an appropriate oxidizer during the MACE process can increase the versatility of the process which can enable one to use this method to prepare samples for variety of applications. As for the various applications like sensing, supercapacitor etc. highly reactive surface is required, so the KMnO_4 etched wafer can be a good option because of its multi-dimensional etching. This can be understood as follows. Mainly two things govern the porosification of Si wafer by MACE⁴⁵. Firstly, the oxidation potential of the oxidizer with respect to the wafer and secondly, the nature of band bending at the metal nanoparticle/silicon contact⁴⁶. The latter has been studied by Yogi et al, which summarizes that if an ohmic contact is formed between the metal/silicon junction, a typical tent-shaped morphologies are obtained. In other words, for obtaining a tent-shaped morphology of porous Si metal work function and wafer type (p- or n- type) can be appropriately chosen so that an ohmic contact is formed. On the other hand, a random fractal porous morphology is obtained if schottky junction between the metal/Si is formed. The nature of junction (ohmic or schottky) play a role because the movement of holes and its flux is associated with the nature of band bending in a given metal/Si junction⁴⁶. In the present study, two different

oxidizer has been used by keeping the nature of metal/Si junction same. It means that the change in surface morphology (Figs. 3 & 4) observed in the present study is due to the effect of relative oxidation potential as discussed above.

Generally, porosified Si wafers prepared using $\text{H}_2\text{O}_2/\text{HF}$ solution shows fractal nature^{47,48} which consists of Si NSs at microscopic level present in the wire like structures. These Si NSs often are small enough ($\sim$ a few nanometers) to show quantum confinement effects. To investigate whether such Si NSs are present in porous samples prepared using KMnO_4 also, Raman spectroscopy has been used as it is one of the most sensitive tools to probe such subtle effects like confinement^{34,49–54}. It is also one of the most widely used techniques for phase and size identification of the material. To know whether samples porosified using KMnO_4 also contains low dimensional microstructures, Raman analysis has been done.

Fig. 5: Raman spectrum from porous Si sample etched using KMnO_4/HF etchant. Discrete points represent the experimentally observed data whereas solid red line is theoretically generated Raman line shape using phonon confinement model. Inset shows observed Raman spectral parameters.

The observed Raman spectrum from sample porosified using KMnO_4 shows (discrete points, Figure 5) red shifted an asymmetrically broadened spectral line-shape as compared to that observed for crystalline Si (c-Si). It is well known that the peak of Raman spectrum of c-Si is observed at $\sim 520 \text{ cm}^{-1}$ having a width of 4 cm^{-1} due to the momentum selection rule where only zone center ($k = 0$) phonons participate in Raman scattering^{38,39,55–57}. On the other hand, this peak gets red-shifted and show asymmetric broadening when the crystallite size decreases upto a few nanometers. This happens due to the relaxation in the above-mentioned momentum selection rule. Thus, by analyzing the observed Raman line shape, one can estimate the crystallite size. Raman spectrum in Figure 5 is positioned at 518.5 cm^{-1} and 9 cm^{-1} broad (inset, Figure 5) which is typically observed from Si NSs as reported earlier^{58,59} for fractal porous Si prepared using etching in $\text{H}_2\text{O}_2/\text{HF}$ solution. To calculate the size of SiNSs present in the KMnO_4/HF etched wafer, experimentally observed Raman spectrum was fitted by the theoretically generated Raman

line shape using phonon confinement model (PCM). The red solid line in Figure 5 represents the theoretical curve corresponding to the best fit which was obtained by choosing nanocrystallite size of 8 nm. Presence of 8 nm sized Si NSs in the porous sample means that low dimensional Si is present which are capable of weak confinement effect. It can be said that Si NSs of size ~ 8 nm are present at the microscopic level in porous Si prepared using KMnO_4 which are found to be more porous as compared to those prepared using H_2O_2 . In other words, porous Si of desired nature, wire like or cheese like, can be prepared by appropriately choosing the etchant oxidizer. Due to more exposed area in the porous sample prepared using KMnO_4 it can be used for appropriate application in many fields like solar cell, supercapacitor, sensing etc. which requires high surface to volume ratio or high surface area for the high reactivity. On the other hand, H_2O_2 seems more appropriate for applications where aligned wire like microstructure are desired like field emission.

4. Conclusion

A surface morphology and Raman spectroscopic study of porous Si prepared by MACE technique using two different oxidizing agents namely H_2O_2 and KMnO_4 reveals that choice of oxidizing agent can affect the resultant morphology obtained as a result of porosification process. When H_2O_2 is used (with HF) as the etching solution typical controlled aligned Si wires like structures are formed whereas more porous and cheese like structures result when KMnO_4 is used in the etching solution. Increased porosity in the samples prepared using KMnO_4 , as validated using SEM and ImageJ analysis, likely originates due to its ability to generate more holes in Si wafer as compared to H_2O_2 making more sites available for etching to progress. The porous Si sample also contains nanostructures of Si at microscopic level as revealed using Raman spectroscopic study. An experimentally observed asymmetrically broadened and red

shifted Raman spectrum was analyzed within the framework of phonon confinement model and it was found that nanocrystals of $\sim 8\text{nm}$ size are present in the porous Si. One can conclude that either of the oxidizer, H_2O_2 and KMnO_4 , should be chosen to prepare porous silicon of desired nature, wire like or cheese like. For etching, H_2O_2 should be chosen where wire like structures are desired (e.g, applications in field emission) whereas KMnO_4 should be chosen for application where higher surface areas are required (e.g, Supercapacitors, sensors etc.).

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Data availability statement: All data that supports the conclusions are provided in the manuscript and/or Supporting information.

Supporting information available: Step-by-step MACE recipe; Images showing luminescence

Author contribution: Conceiving, overall supervision and PI (R.K.); Experimental work, data analysis and manuscript- first draft (C.R.); Data validation and part analysis (M.T., T.G., D.K.P., S.K.); Experiment Design & Planning, manuscript preparation & finalization (M.Y.M & R.K.)

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