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Influence of HF concentration and current density on characteristic morphological features of mesoporous silicon

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ABSTRACT

This report explores the variations in morphological features of electrochemically fabricated mesoporous silicon as a function of two important fabrication parameters, HF concentration and current density. Four set of samples corresponding to four different HF concentrations (15%, 25%, 35% and 45% HF) were prepared with systematically varied current density (10, 20, 30, 60 and 100 mA/cm^2). The effect of these parameters on many significant features like mean pore diameter, mean neighbor distance, pore count per unit area, surface roughness, surface area etc. of resulting mesoporous structure have been determined by very sophisticated UHV SPM (Omicron VT AFM XA) in contact mode. The analysis has been performed using Scanning Probe Image Processor (SPIP Version 6.0.9). The AFM analysis is supported by the results of FESEM JSM 7600F and DXR Raman Microscope. The comparative study shows that some features are more sensitive to HF concentration while others seem to depend more on current density. Pore diameter varies mainly with HF concentration while pore depth varies largely with current density. Exceptionally high pore count (450pores/100 nm^2) is found at 45% HF while samples have higher average roughness (3.5 nm) at 15% HF. Sponge like layer is formed at lower current density while well aligned very straight channels are formed at higher current density. Some very interesting regimes found at high current density conditions, recorded by FESEM have also been discussed to develop more understanding of porous silicon formation mechanism.

1. Introduction

Discovered by Ulhir in 1956, porous silicon (PS) caught the attention of scientific community in 1990 when Canham reported red photoluminescence from it [1,2]. Since then PS has always been a material of interest for many researchers and has emerged as one of the most versatile nanomaterial investigated till now. The remarkably advantageous properties of PS like photo- and electroluminescence, high specific surface area, chemical and bioactivity, biocompatibility, biodegradability. etc. have attracted scientists from optoelectronics [3–5], microelectronics [6–8], photonics [9–12], medicine [13–16], chemical sensing [17–20], biosensing [21–24], drug delivery [25–29], bioengineering [30–32] and other areas of research. The very fact that these properties distinctly depend upon the morphology of porous silicon, is a big advantage as, in case of electrochemical synthesis of PS, morphology can be desirably tuned by choosing a correct combination of fabrication parameters. Depending upon pore diameter IUPAC definition categorizes porous structure as macro (≥50), meso (2–50 nm) and microporous (≤2 nm). In the light of current advances in PS research, the possibilities for potential applications of microporous silicon [33,34] and mesoporous silicon [35–38] is easy to find.

A lot of literature is available on the formation parameters of PS synthesized by electrochemical method [39,40]. Effect of all the parameters like i) type of electrolyte [41–43], ii) concentration of electrolyte [44–50], iii) current density [51–54] iv) etching time [55–57], v) illumination [58–60], vi) resistivity [61] and vii) substrate doping [62] etc., on electrochemically produced PS structure have been discussed in various reports.

But reports containing rich experimental data covering a whole range of electrochemical fabrication conditions and resulting morphological features of mesoporous silicon can rarely be found in the literature. This report comprised of comprehensive fabrication and structural relationship in terms of current density and HF concentration. In addition to commonly reported features like pore

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diameter and pore depth many other important morphological feature like pore count per 100 nm^2, mean neighboring distance, material and void volume, surface roughness etc. have been determined by SPM study. These features are of paramount importance from application point of view but have not been sufficiently investigated so far particularly for the case of mesoporous silicon.

This report presents the effects of systematically varied current density (10, 20, 30, 60 and 100 mA/cm^2), with 15, 25, 35 and 45% HF concentrations on the resulting porous structure of electrochemically fabricated PS. Etching duration of 20 min was chosen to observe the consistency of etching process. A very detailed pore, volume and roughness analysis have been performed by very sophisticated Ultra High Vacuum SPM (Omicron VT AFM XA) in a contact mode, supported by FESEM and Raman characterization. At a particular current density of 60 mA/cm^2 a decrease in mean pore diameter (21, 11, 7 and 5 nm) and increase in porous layer thickens (38, 46, 50 and 54 μm) are found for 15, 25, 35 and 45% HF concentration respectively. These results are in total harmony with published literature [63,64]. Pore count per 100 nm^2 has also been calculated which is found to be exceptionally high for 45% HF concentration. However the roughness of the samples is very high in case of 15% HF concentration. These parameters can be of great help in choosing a particular condition for drug loading, sensing and other important application of mesoporous silicon. Some special results, found repeatedly on repeating the same high current density condition, has also been discussed in the last section which can give some insight into the formation mechanism of PS if they are quantitatively investigated in detail.

2. Experimental

2.1. Synthesis

Preparation of PS samples were done by anodisation of p -type boron doped silicon wafer (⟨100⟩, 0.01–0.02 Ω cm) in ethonic solution of 15% HF, 25% HF, 35% HF and 45% HF respectively. The concentration of HF solution in the anodizing solution should be treated with care. This concentration, in percent, is a mixture of the weight and volume. In each series a set of five samples was prepared by applying different current densities 10, 20, 30, 60 and 100 mA/cm^2 respectively for 20 min. The process of pore growth were accomplished in a teflon made etching cell keeping silicon sample for anode and platinum mesh for cathode. A circular wafer surface area of 0.79 cm^2 (1 cm diameter) was exposed to electrolyte while the constant currents were applied by SP 200 Bio Logic electrochemical system using galvanostat mode. The fabrication parameters and the respective sample names are given in Table 1.

2.2. Characterization

Surface morphology, shape of the channels and thickness of the porous layer were studied using Scanning Probe Microscope (UHV Omicron VT AFM XA) and Field Emission Scanning Electron Microscope (FESEM-JSM 7600F). The topography images were recorded in contact mode. High sensitivity silicon probes of having force constant 0.27 N/m were used for imaging (Nano World). Other specifications of the probe are - Resonance Frequency 15 kHz, Force Constant 0.27 N/m Length 452 μm, Mean Width 55 μm, Thickness 2.2 μm. A deviation up to 10% from these values may be expected as per the manufacturers claim. The Raman spectra of the samples were recorded with DXR Raman Microscope (Thermo Scientific) using 532 nm Filter, Laser Power 10 mW, Estimated resolution11.7–17.7 cm^{-1}, Estimated spot size 0.7 μm, Allowed range 50–3500 cm^{-1}.

Table 1
Fabrication parameters of PS with sample names.

Name of series	Time (min)	HF concentration (%)	Current density (mA/cm^2)	Sample id
S1	20	15	10	S1S1
			20	S1S2
			30	S1S3
			60	S1S4
			100	S1S5
S2		25	10	S2S1
			20	S2S2
			30	S2S3
			60	S2S4
			100	S2S5
S3		35	10	S3S1
			20	S3S2
			30	S3S3
			60	S3S4
			100	S3S5
S4		45	10	S4S1
			20	S4S2
			30	S4S3
			60	S4S4
			100	S4S5

3. Results and discussion

The morphological features of mesoporous silicon play a very critical role in its sensing and drug delivery applications. For example, the surface roughness and shape of the channels can directly affect the response and recovery time of a PS sensor, while spacial distribution of pores and surface area can be a deciding factor for the sensitivity, which is determined by the adsorbed quantity of analytes per unit time [65]. Roughness is also an important factor in controlling the dimension, alignment and density of metal oxide nanorods grown on porous substrate [66]. Similarly in drug delivery application number of pore counts per unit area, pore volume and particle size etc. can be optimized for the best performance [67].

3.1. AFM analysis

For series S1, 250000 nm^2 area was imaged since the pore size is larger compared to the other series. For the remaining 3 series 62500 nm^2 area was imaged. Images were recorded with 400 lines having 400 raster points with a raster time 2500 μS giving a scan speed around 416 nm/S for Series 1 and 250 nm/S for remaining series. Set point force was between 0.5 and 0.9 nN. Scanning conditions were kept similar to the possible extend for getting comparable results.

Further analysis was done by Scanning Probe Image Processor (SPIP Version 6.0.9). Images were de-spiked and plane corrected before analyzing which is the most crucial step before roughness and histogram analysis. Global leveling using a second order polynomial fit followed by a line wise leveling was done. The most frequent z-value is set to zero using Zero back ground leveling. Above procedure was enough to level and de-spike all the images since the best images with less spikes and artifacts were selected for final analysis. Pore size analysis and roughness analysis were done on the corrected images and the results were tabulated and plotted for comparative study.

In order to keep the comparative study easily observable the topography and 3d images of only first and fourth sample of each series, which corresponds to the current density of 10 mA/cm^2 & 60 mA/cm^2, are given in Figs. 1 and 2. Due to the peeling of the 5th sample of series S2 and S4, we have kept the comparative study upto the 4th sample of each series. However some very interesting