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Fabrication and surface modification of micro/nanoporous silicon

J. P. KAR*, S. K. MOHANTA[a], G. BOSE, S. TULI, A. KAMRA[b], V. MATHUR[c]
Centre for Applied Research in Electronics, IIT Delhi, India, 110016
[a]*Department of Physics, IIT Delhi, India, 110016*
[b]*Kurukshetra University, Kurukshetra, India*
[c]*Manipal Institute of Technology, Banglore, India*

We have studied surface and structural properties of micro/nanoporous silicon, synthesized by electrochemical etching of p-type Si (100) with different etching conditions. SEM studies reveal tunable pore sizes from 200 nm to 1.5 μm for etching time 5 to 30 min, and the thickness of pore walls decreases upto 20 nm for 30 min etching. AFM investigations reveal increase in roughness of the porous structure with increase in etching time and saturate around 250 nm at higher etching time. X-ray diffractogram of porous Si surface for etching time 20 min shows the appearance of two peaks at 2θ = 69.13º and 69.33º. For 30 min etching time a broad peak is observed at 2θ = 69.39º. The broadening may due to the size distributions of pore walls, and up ward shifts may due to relaxation of strain in the porous structure. FTIR investigations show the presence of Si-H bending in Si_3-SiH groups at 624 cm^{-1}, Si-O stretching in O-Si-O in between 1056-1160 cm^{-1}. The bands at 2958, 2927, and 2856 cm^{-1} are related to C-H stretching of CH_3, CH_2, and CH groups, which probably come from residual of HF-dimethylformamide.

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1. Introduction

The low-dimensional semiconductors have attracted much attention because of their technologically important electronic and opto-electronic properties, and have become fast growing and exciting area of research [1-4]. In particular, the porous semiconductors are promising because of the ease of synthesis, and reduced size effect leading to modifications in electronic bandgap and optical properties [5, 6]. In addition, the growth of ordered porous structures have become an active area of research due to its possible technological applications such as template for growing nanowires and nanorods, photonic bandgap material, buffer layer for the growth of high crystal quality, strain relaxed heteroepitaxial films [7-11]. Mynbaeva *et al.* reported the evidence of low stress and defect densities GaN film grown on porous GaN than that on the GaN substrate [5]. Kidalov *et al.* have demonstrated the evidence of both single crystalline cubic GaN and hexagonal GaN successfully grown on the porous GaAs (001) substrate [11].

Despite extensive research on the synthesis of porous semiconductors, the development of regular porous structure with high quality and large surface area remains a key issue for the development of future optoelectronic at nanoscale. Though a number of different techniques, such as high dose ion implantation [12,13], reactive ion etching [14,15], reactive beam etching [16], inductively coupled plasma etching [17,18], spark-processing [19,20], electrochemical etching [21,22] have been employed for synthesis of porous semiconductors. The electrochemical etching is attractive in the formation of porous structure due to its important advantages such as low temperature, simplicity and low processing costs. So far a lot of work has been reported on the synthesis and characterization of porous structure. However it is always remain an issue on their crystalline quality and have detail knowledge on the residual elements present after synthesis. In this study, we have synthesized micro/nanoporous Si surface by electrochemical etching and studied their morphological, structural and elemental properties by scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD), and fourier transform infrared spectroscopy (FTIR), respectively.

2. Experimental

The micro/nanoporous Si surfaces were synthesized by electrochemical etching of (100) oriented p-Si (resistivity 9-15 Ω-cm) in HF + DMF solutions by volume 1:5 at current density 10mA/cm^2 with variable etching time 5 to 30 min. After the formation of the porous structures, the samples were rinsed with ethanol and dried in N_2. LBO 435 Vp scanning electron microscope (SEM) was used for morphological investigations of the micro/nanoporous structures. The surface roughnesses of the electrochemically etched micro/nanoporous Si surfaces were studied using Monfrotto-Vicco atomic force microscopy (AFM). The structural properties of the porous layer were studied by Bruker (D-8) X-ray diffractometer. FTIR studies were performed by Perkin-Elmer spectrometer in transmittance mode.

3. Results and discussion

Fig. 1 shows the SEM images of micro/nanoporous Si surfaces synthesized by electrochemical etching of p-type Si under different etching conditions. For current density 10mA/cm^2 and etching time 5 min small pores of size 200 nm to 500 nm with non-uniformly distribution are observed on the sample surfaces. With increase in etching time to 10 min, the pore sizes increase up to 700 nm with minimum size 200 nm, and the uniformity of the pore increases. With further increase in etching time to 20 min, more uniform pores are observed with pore size increases to maximum of 900 nm to minimum 350 nm. At 30 min etching time regular and uniformly distributed pores with size 1.5 μm are observed on the sample surfaces. Thus, as it is observed the etching time has significant affect on obtaining regular and uniformly distributed pores within the porous structures. The basic mechanism for the formation of porous structure is due to the charge carrier generation at semiconductor electrolyte interface by external biasing. When etching time increases, more and more numbers of carriers which take part in etching process come into the semiconductor electrolyte interface, leading to increase in the pore size. Furthermore, the increase in pore size leads to decrease in sizes of pore wall, and pore wall size of minimum value less than 20 nm is observed for etching time 30 min. It is also observed from color contrast of SEM images that, the depth of the pore increases with increase in etching time, and is further confirmed by AFM investigations shown in Fig. 2. As shown in Fig. 3, the roughness of the porous structure increases with increase in etching time and saturates around 250 nm at higher etching time. AFM images also show that the uniformity of the porous structure increases with increase in etching time, and regular and more uniform micro-pores are observed for etching time 30 min.

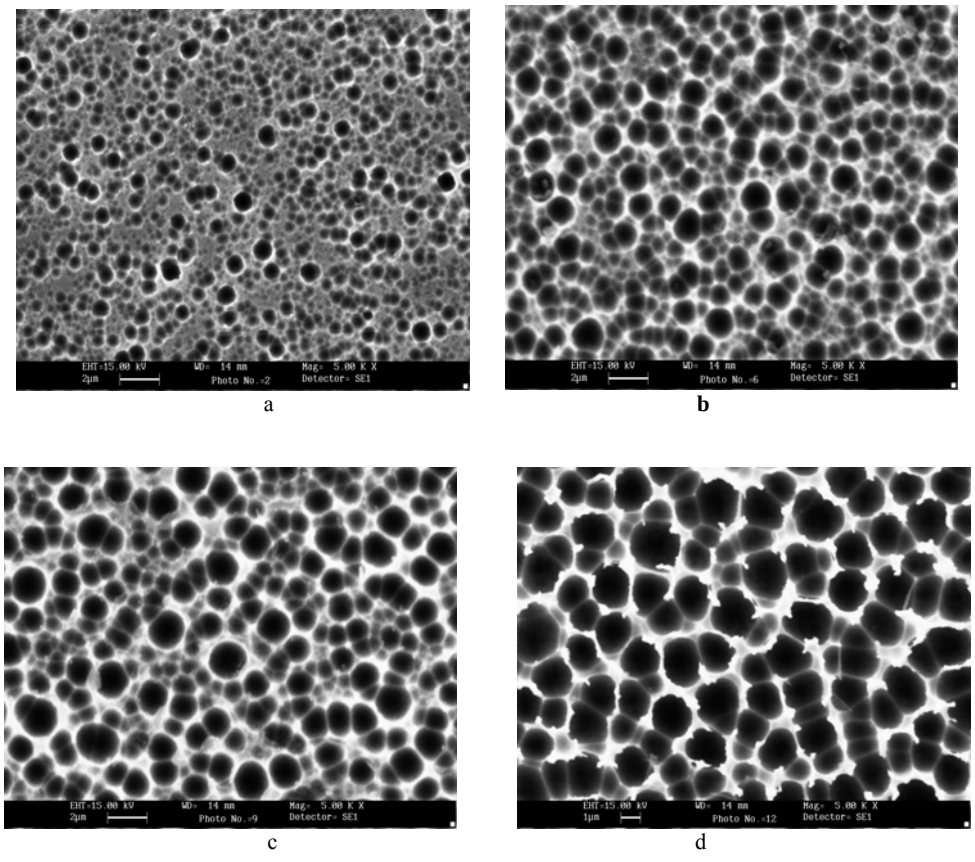

Fig. 1. SEM images of micro/nanoporous Si surfaces synthesized by electrochemical etching of (100) oriented p-type silicon in HF + DMF solutions at constant current density 10 mA/cm^2 for different etching time; (a) 5 min, (b) 10 min, (c) 20 min, and (d) 30 min, respectively.

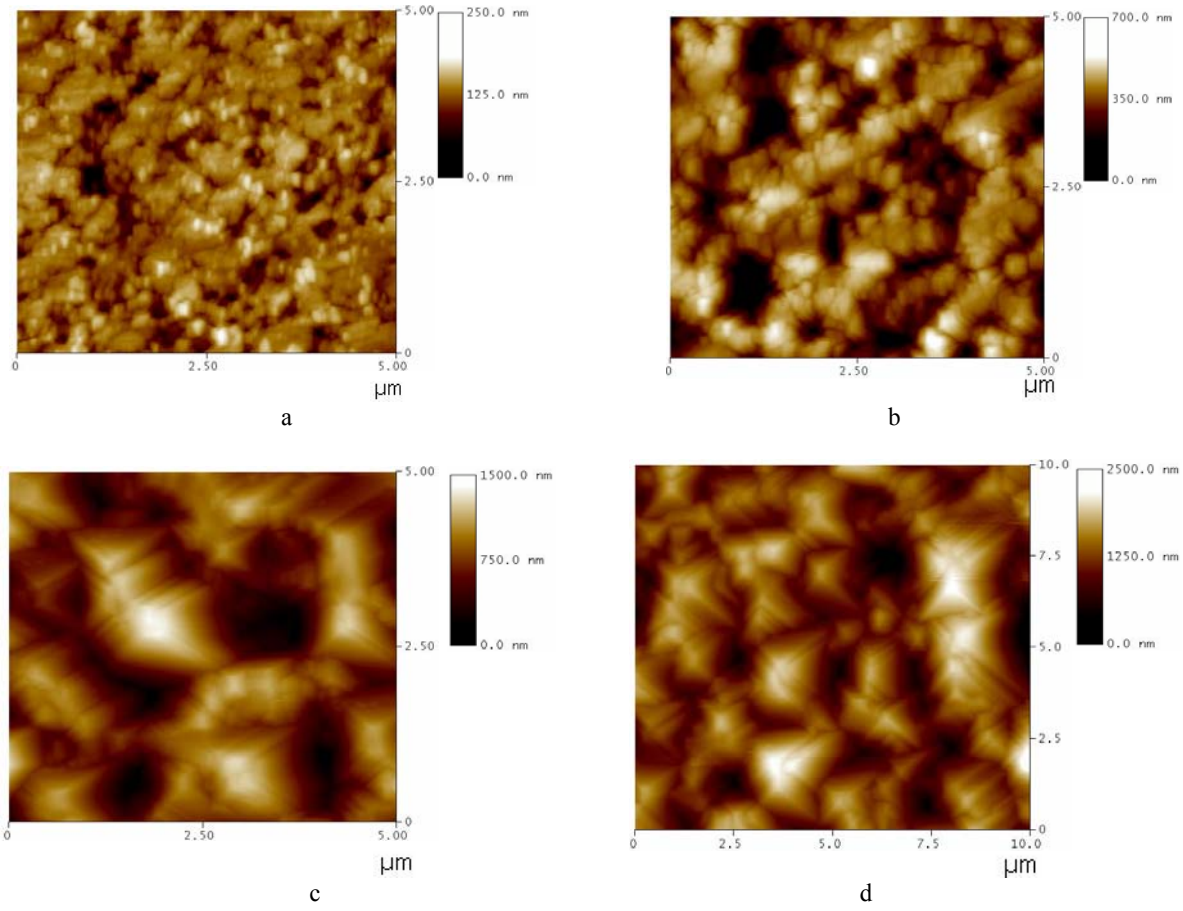

Fig. 2. AFM images of micro/nanoporous Si surfaces synthesized by electrochemical etching of (100) oriented p-type silicon in HF + DMF solutions at constant current density 10 mA/cm^2 for different etching time; (a) 5 min, (b) 10 min, (c) 20 min, and (d) 30 min, respectively.

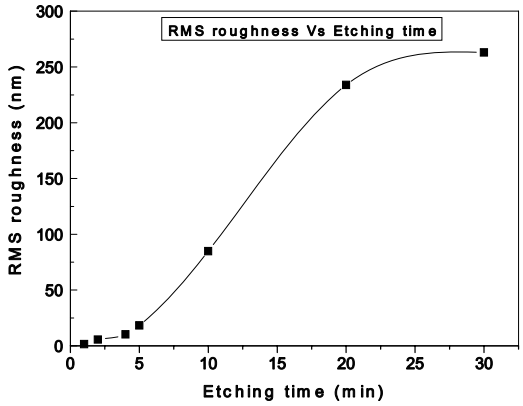

Fig. 3. The estimated RMS roughness of the porous Si structures as a function of etching time.

The (004) X-ray diffraction curves of micro/nanoporous p-type Si surfaces, synthesized by electrochemical etching in HF + DMF solutions at current density 10mA/cm^2 for different etching time from 5 to 30 min, are shown in Fig. 4. For etching time 5 min and 10 min, it is observed that only one peak at 2θ = 69.33º, which corresponds to the (004) plane of bulk Si. However, for etching time 20 min XRD curve shows two peaks at 2θ = 69.13º and 69.33º. The additional peak at the lower angle at 2θ = 69.13º may be attributed to a lattice expansion of the porous layers, whereas the main XRD peak at 69.33º is from Si substrate. The increase in lattice constant than that of the substrate has also been observed in porous silicon by Young *et al.*, and suggested that the increase in lattice constant arises from stress induced by growth of a native oxide on the surface on the pore structures [23]. It is also observed that the separation between the two peaks remains constant upon changing the X-ray azimuthal angle, suggesting same crystallographic orientation of porous layer as that of substrate. Hao *et al.* demonstrate that the separation between the two peaks is due to the strain in the porous layer [24]. The most interesting feature is observed in the X-ray diffractogram from porous Si surface synthesized by etching time 30 min. For 30 min etching a broad peak is observed at 2θ = 69.39º. The broadening in the XRD spectrum may due to the size distributions of pore walls, and up ward shifts is due to relaxation of strain in the porous structure.

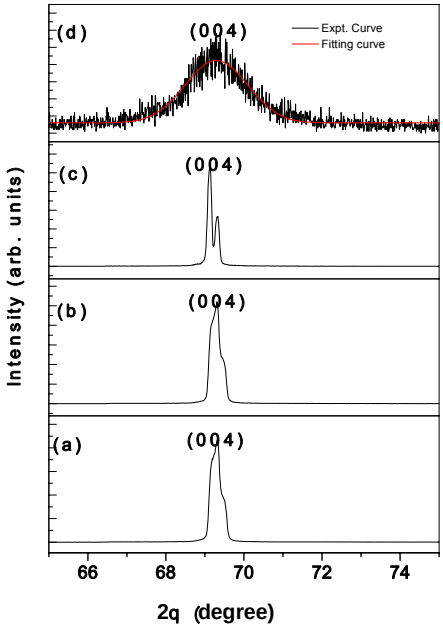

Fig.4. XRD spectra of micro/nanoporous Si surfaces synthesized by electrochemical etching of (100) oriented p-type silicon in HF + DMF solutions at constant current density 10 mA/cm^2 for different etching time; (a) 5 min, (b) 10 min, (c) 20 min, and (d) 30 min, respectively.

According to Debye-Scherrer formula:

$$\Delta(2\theta) = \frac{0.9\lambda}{D\cos\theta} \qquad (1)$$

where Δ is the FWHM of the XRD peak, λ=1.5406 Å and D is the crystallite diameter.

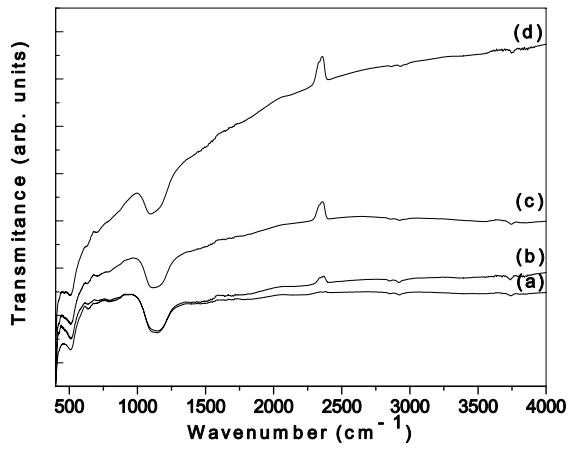

Fig. 5. FTIR spectra of micro/nanoporous Si surfaces synthesized by electrochemical etching of (100) oriented p-type silicon in HF + DMF solutions at constant current density 10 mA/cm^2 for different etching time; (a) 5 min, (b) 10 min, (c) 20 min, and (d) 30 min, respectively.

The average crystallite size calculated from the full width at half maximum (FWHM, 1.6º for 30 min) of the XRD spectrum of micro/nanoporous Si surface etched with current density 10 mA/cm^2 and etching time 30 min is 2.5 nm.

Fig. 5 shows the FTIR spectra of micro/nanoporous Si surfaces etched with current density 10 mA/cm^2 for different etching time; (a) 5 min, (b) 10 min, (c) 20 min, and (d) 30 min, respectively. It measures the absorption of infrared energy by the molecules that are present in a given sample. The FTIR spectra show peaks between 1056-1160 cm^{-1}, which are corresponding to Si-O stretching in O-Si-O. The bands at 2958, 2927, and 2856 cm^{-1} can be related to C-H stretching in CH_3, CH_2, and CH groups. These organic groups probably come from residual HF-dimethylformamide solution on the samples. Since carbon is located in the same column of the periodic table as silicon, it can easily replace a silicon atom, leading to the presence of carbon in the porous structure. The well-resolved and sharp features below 1000 cm^{-1} are mainly associated to Si-H bond bending modes. All the free-standing PS samples present a broad absorption band in the region 3200 to 3800 cm^{-1}, which corresponds to stretching mode of O-H bonds [25, 26].

4. Conclusions

We have synthesized micro/nanoporous Si surface by electrochemical etching of (100) oriented silicon (p-type, 9-15 Ω-cm) in HF + DMF solutions by volume 1:5 at constant current density of 10mA/cm^2 with variable etching time 5 to 30 min. SEM studies reveal micro/nanoporous Si surface of tunable pore sizes from 200 nm to 1.5 μm for etching time 5 to 30 min. The thickness of pore walls decreases upto 20 nm with 30 min etching. AFM investigations reveal increase in the roughness of the porous structure with increase in etching time, and saturate around 250 nm at higher etching time. X-ray diffractogram of porous Si surface for etching time 20 min shows the appearance of two peaks at 2θ = 69.13º and 69.33º, corresponding to the (004) plane of Si. The peak at the lower angle (2θ = 69.13º) may be attributed to a lattice expansion of the porous layers, whereas the main XRD peak at 69.33º may be of silicon substrate. For 30 min etching time a broad peak is observed at 2θ = 69.39º, the broadening may due to the size distributions of pore walls, and up ward shifts may due to relaxation of strain in the porous structure. FTIR investigations show the presence of Si-H bending in Si_3-SiH groups at 624 cm^{-1}, Si-O stretching in O-Si-O in between 1056-1160 cm^{-1}. The bands at 2958, 2927, and 2856 cm^{-1} are related to C-H stretching of CH_3, CH_2, and CH groups, which probably come from residual of HF-dimethylformamide. The studies of micro/nanoporous Si surfaces on large scale are triggered for their application in light emitting devices, and as buffer layer in hetero-epitaxial films.

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*Corresponding author: karjp@rediffmail.com