Porous Si formation and study of its structural and vibrational properties

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Abstract

In situ current ðIÞ-ðVÞ voltage studies were carried out to get a better understanding of the mechanism of formation of porous silicon (PS). It is observed that on decreasing the anodization current density below a critical value (B75 mA cm⁻²) the size of the PS crystallites increases while for its values above 75 mA cm⁻² electropolishing occurs. Raman spectroscopic studies show that the sizes of the Si crystallites are small and change from 4.7 to 3.8 nm when the current densities are increased from 20 to 50 mA cm⁻². Transmission electron micrographs show preferential propagation of pores whereas transmission electron diffraction (TED) patterns show typical crystalline Si with the cubic structure.

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1. Introduction

Bulk crystalline Si (c-Si) is extremely inefficient in emitting radiation under either optical or electrical excitations. The minimum of the conduction band lies at the Xδß2p=αß1.0,ß p point along the Dδß1.0,ß p direction of the Brillouin zone resulting in an indirect band gap, \( E_g = E_{X1} - E_{G2} \approx 1.17 \) eV, which is responsible for non-radiative recombination of charge carriers. The properties of bulk-Si get modified when Si is prepared such that it acquires low-dimensional structures. Porous silicon(PS) [1-25] is one such low-dimensional structure consisting of a network of randomly spaced pores [6,13,16] in bulk silicon formed by electrochemical etching of a crystalline Si wafer in concentrated hydrofluoric acid (HF). Such porous structures have attracted considerable attention in recent years due to its possible application in optoelectronics [7], sensors [7,8] and solar cells [8]. Although PS is one of the popular materials in Nanotechnology, the origin of the luminescence in it is still not understood. Different models related to quantum confinement (QC) [2],
and the presence of foreign impurities like siloxene [17], and chemisorbed molecules, e.g. SiO$_2$, SiH [9] etc. have been invoked to explain the origin of the interesting and efficient visible luminescence discovered by Canham in 1991 [1]. The presence of foreign impurities has been attributed to arise from the solution during the PS formation. The synthesis of porous Si under anodic bias results in both Si dissolution and the formation of SiH and SiO$_2$ at the interface of PS/HF-electrolyte [10] which in turn is expected to generate surface traps [25-27] of different types within the wide band gap of porous Si. The present work attempts to understand the PS surface morphology, its structure, and the mechanism of the PS formation, through the studies of in situ current $\partial I/\partial V$ voltage characteristics, Rutherford back scattering (RBS) analysis which relates to the estimation of the thickness of the PS layer and the study of vibrational properties by laser Raman scattering.

2. Experimental details

The in situ $I-V$ characteristics measurements were carried out at 3001 K using a three electrode single compartment electrochemical cell comprising of (i) an aluminium back coated p-Si 0 0 0 sample, having resistivity of around 00 1 O cm as an anode having a surface area B 1 cm$^2$; (ii) a saturated calomel electrode (SCE) as reference electrode and (iii) a Pt cathode of area 2 cm$^2$. The electrolyte was a mixture of HF acid (49%) ethanol in equal proportion and the voltage was applied with a Tacusol potentiostat. Porous Si samples were prepared with four different current densities of 20, 30, 40 and 50 mA cm$^{-2}$, respectively, maintained for a constant duration of 30 min each. Transmission electron microscopy (TEM) was performed on the samples using the Philips CM200 Analytical TEM operating at 200 kV and fitted with an EDAX analyser with a super ultra thin window system. For TEM studies, the porous Si layer was peeled off from the sample with a sharp blade and was collected on a carbon-coated Cu grid. Before lifting the grid, the layers were given a dilute HF ($\partial$HF : H$_2$O = 1:3) acid treatment to remove possible SiO$_x$ traces. Raman spectra of the PS samples were recorded at room temperature in the backscattering configuration, using the 488 nm line of the Ar-ion laser and a double monochromator with the standard detection system. Because of the low thermal conductivity of porous Si and the expected temperature dependence of the Raman shifts and line widths, care was taken to avoid laser heating by keeping the laser power low $\partial$E30 mW with beam size of about 10 mm.

3. Results and discussion

The results of various measurements performed on p-Si samples are presented and discussed below. The measurements carried out were the structure and morphology studies using the TEM, the current-voltage ($I-V$) characteristics, the Rutherford back scattering (RBS) studies to determine the size of the silicon nanostructure, and the Raman scattering studies which again provides information on the nanostructure of porous silicon. The results of these measurements were analysed in order to gain a better understanding of the mechanism of pore formation in silicon.

3.1. TEM study

In order to study the surface pore morphology of porous Si under high-current etching conditions, the sample was synthesized at 50 mA cm$^{-2}$. The porous silicon sample thus prepared was imaged using the transmission electron microscope (TEM). The TEM micrograph which is the bright field (BF) image is shown in Fig. 1(a). The surface shows anisotropy without branching and is relatively smooth and porous. Note that the direction of the current flow during the preparation of sample was from the bottom to the top. We are not able to measure the individual pore diameters due to the overlapping phenomena which is common in less porous material (porosity o70%). However, voids separated by rods running perpendicular to the surface can be seen
clearly. Due to large current density at the pore tips, the voids propagate perpendicular to the surface as seen in Fig. 1(a). The crystallite sizes could not be estimated accurately due again to overlap of adjacent pores normally associated with low porosity samples [24]. The nano-porous Si sample with the above morphology, when excited with the 369 nm wavelength radiation from the Hg-Xe lamp, emits red light in the 600-640 nm range (details will be published elsewhere [28]) which can be seen with the naked eye, which suggests the porosity to be less than 70%. In order to identify the structure and phase of the crystallites, a selected area diffraction (SAD) pattern was taken (Fig. 1(b)) using TEM for the same region of the sample for which the BF image is shown in Fig. 1(a). A single-crystalline pattern typical of the diamond structure is observed. However, streaking of the Bragg spots is also clearly visible, suggesting the possibility of a small amount of disorientation of the crystal planes. The diffraction pattern further suggests that the porous Si is in the cubic phase. It can be seen from Fig. 1(b) that no broad and diffuse rings are present in the diffraction pattern indicating the absence of an amorphous phase. This has been further confirmed by Raman studies to be discussed in a later sub-section.

3.2. Analysis of current $\delta I$-$\delta V$ voltage characteristics

The $I$-$V$ characteristic of the p-Si/electrolyte interface under bias is shown in Fig. 2. Different regions in the figure are labelled as R1, R2, R3 and R4. R1 denotes the reverse bias regime where very low current flows through the samples as shown and no silicon dissolution occurs in this region. In contrast, R2, R3, R4 are the forward bias regimes
where silicon dissolution takes place. Note the two maxima in the current designated as J1 and J2 in the forward bias \( I-V \) characteristic which are clearly seen. The exponentially increasing current density \( \exp(J_{o}J_{1}) \) in regime R2, starting from 0.0 V (SCE) corresponds to the pore formation \([15,16]\) region. The second exponential increase of current density between \( J_{o}J_{1} \) corresponds to the transition regime R3, where pore/oxide formation and electropolishing takes place. The resulting structure in this later region is generally porous in nature and pore diameters are comparatively larger as shown in the idealized model (Fig. 3b), than the pore diameter in the Regime R2 (Fig. 3a). On further increasing the forward potential, the porous structure vanishes with the Si dissolution from all over the surface. This is the electropolishing regime R4, for which one would observe a planar Si surface as shown in Fig. 3c.

From the above arguments, it is clear that in order to achieve large pore diameter vis-à-vis small Si crystallite one should make a judicious choice of the applied potential to control the current flow. On synthesizing PS at low current/potential (Region R3), one would expect the pore diameters to be large and the Si crystallites to be small. Besides, even at lower current density voids are generated in the PS which would penetrate deep into bulk Si. Hence, large diameter pores and small Si crystallites can be achieved with the choice of the anodic etching current density in the range between 20 and 50 mA cm\(^{-2}\) as shown in Fig. 2. Considering the pore tip to be hemispherical with a radius of curvature \( r \), the electric field experienced at the interface (PS/electrolyte) is given by [9]

\[
\mathbf{E} = \frac{\phi_{s}}{r},
\]

where \( \phi_{s} \) is the barrier height of the PS/HF-electrolyte junction. Thus, we can see that there is a considerable field enhancement at regions of high curvature i.e., \( r \). From Eq. (1) it is evident that the electric field at the pore tips can be sufficiently high, to result in a high current flow which would lead to elongation as well as widening of the pores as seen in Fig. 3(b). As a consequence of such an excess current flow there may be a large charge transfer at the interface which is facilitated by the localized trap states present within the PS band gap. The other more likely possibility may be the tunneling of carrier across the small depletion width in the heavily doped \( \delta \times 10^{19} \) cm\(^{-3}\) p-type silicon and the HF-electrolyte system. The schematic pictures of pore propagation for different current densities are shown in Figs. 3(a)-(c). These pictures in Figs. 3(a)-(c) are the depictions of idealized models whereas in actual practice it is expected that there can be pore branching and variation in pore diameter as well as fractal type of pore growth.

### 3.3. RBS analysis

The small thickness of the PS layer on the Si substrate may interfere with the bulk optical
properties of the PS sample. It is therefore essential to study the thickness of PS layer which is determined using the RBS technique. These RBS measurements were carried out using a He\(^{+}\) ion beam of Energy 3 MeV from the pelletron accelerator at the Institute of Physics in Bhubaneswar. The channel width \((DE)\) of the RBS spectrum is directly related to the thickness of the porous Si layer \((Dt)\) and the energy loss factor \([S]\) by

\[
\Delta t = \frac{DE}{dE} \frac{1}{S} \frac{dE}{St \cos \theta St}
\]

where \(K\) is the kinematic factor:

\[
K = \left(\frac{(m_1 - m_2 \sin^2 \theta + m_1 \cos \theta)}{m_1 + m_2}\right)^2,
\]

\(m_1\) and \(m_2\) are atomic masses of the projectile (He) and target (Si), respectively, and \(\theta\) is the scattering angle. Relations (2) and (3) are taken into account for the thickness measurements within the simulation program itself. Note that in Fig. 4 the RBS yield of PS is much lower than that of bulk Si. The lowering of RBS yield in PS implies Si depletion from bulk Si under anodic etching. Further, the experimental RBS spectrum of both PS and bulk Si agree very well with the simulated spectra with the Si edge remaining the same for both. From the simulated RBS spectrum of PS, the thickness of the PS layer was estimated to be \(B3.2\) mm, which is fairly large. For such a thick PS layer, the optical properties are not expected to interfere with bulk Si as will be discussed in the next sub-section. Fig. 4 also suggest the absence of any other impurity excepting O\(_2\) in PS. Unfortunately, RBS will not be able to detect low Z (atomic number) elements such as Hydrogen which is supposed to be present in PS.

3.4. Raman scattering analysis

The TEM study of the microstructure of porous Si reveals a wire-or dot-like morphology with sizes of these wires (dots) being in the range of a few nanometers and isolated from each other. Because of their low-dimensional character, the motion of the carriers is confined in either one dimension (1D) or zero dimension (0D). Thus, the translational degree of freedom of the quasi-particles and collective excitations of the system is partially lost due to localization. Hence, the \(q = 0\) selection rule for the phonon-Raman scattering corresponding to the phonons in the center of the Brillouin zone for the bulk Si is relaxed, leading to a downward frequency shift, broadening and asymmetry in the first-order Raman peak. It is expected that all the phonons with wave vectors in the range \(0q_o\leq l\) will participate in Raman scattering of PS where \(l\) is the average diameter of spherical Si crystallites in 0D or the diameter of the cylindrical wire in 1D case. A quantitative model [18,19] describing the first-order Raman intensity to estimate the average size (or correlation length) \(l\) of the spherical or cylindrical Si nanocrystals is given by

\[
I_{\omega o\Phi} = \text{const.} \int_0^q \frac{jc_0 q \Phi^2 d^2 q}{\left|c_0 c_0(q)\right|^2 + (T_c)^2}
\]

where \(\omega o\Phi\) is the LO phonon dispersion curve for bulk silicon. The size-dependent parameter \(c_0 q \Phi\) being

\[
|c(0, q)|^2 = \exp\left(-\frac{q^2 l^2}{4a^2}\right),
\]

where \(a\) is the lattice spacing for Si. From Eq. (5) one can see that for \(q a0\) as \(l\) — N; \(c_0 q \Phi\) — 0, indicating that for bulk samples only the \(q = 0\) LO phonon will contribute to the Raman intensity. In the case of a nanomaterial, the contribution of the \(q a0\) phonons to the Raman intensity decreases exponentially with increasing size.

The Raman data of the p-Si samples were analysed by fitting the intensity of the peak using
the spatial correlation function, of Eq. (4). The frequency-dependent background is fitted to a polynomial and subtracted from the raw data. A typical example of the background subtraction along with Raman peak for the Si sample anodically etched at 20 mA cm\(^{-2}\) current flowing for 30 min duration is shown in the inset of Fig. 5(c). In order to numerically simulate the first-order Raman intensity of differently sized nano-crystallites of Si, using the model given by Eqs. (4) and (5), the phonon dispersion around \(q = 0\) is assumed to be \(\omega_0 \delta q \beta = A - Bq^2\) where \(A\) is the near-zone-center LO-mode frequency \(A = 520.5\) cm\(^{-1}\) and the value of the fitting parameter \(B = 120\) cm for Si. This approximation holds near the zone-centre so long as \(lba\). For the zone-centre \(\delta q = 0\) LO phonon of bulk Si we choose \(\omega_0\) and \(G_c\) to be 521.9 and 4.7 cm\(^{-1}\), respectively. The wave vector \(q\) is expressed in units of \(2\pi/a\) where \(\alpha\) is the Si-lattice spacing. The observed Raman shift for \(c\)-Si is 520 cm\(^{-1}\) and it has a symmetric line shape with a width of 7-9 cm\(^{-1}\) (FWHM) [21].

The fitted Raman spectra of PS samples synthesized by impressing anodic currents of 20, 30 and 40 mA cm\(^{-2}\) are shown in Fig. 5(a)-(c). Using Eqs. (4) and (5) and the spherical phonon dispersion curve, the crystallite sizes of the different PS samples have been estimated and found to be 4.7, 4.1 and 3.9 nm, corresponding to the current densities 20, 30 and 40 mA cm\(^{-2}\), respectively. Along with the observed red shift of the Raman frequencies with increasing current/decreasing crystallite size, the phonon line width changes from 7.0 (bulk) to 14, 18.6 and 20 cm\(^{-1}\) for samples prepared with current densities of 20, 30 and 40 mA cm\(^{-2}\), respectively. Note that a clear demonstration of Raman shift towards low frequency has been consistently observed for increasing anodic etching current densities. This also suggests that the Raman contribution is exclusively from the thick PS layer and not from bulk Si. A shift of 514 cm\(^{-1}\) compared to the bulk-phonon frequency of 520 cm\(^{-1}\) has been observed in case of the 40 mA cm\(^{-2}\) anodically etched PS sample whereas the observed shift is 516 cm\(^{-1}\) for 20 mA cm\(^{-2}\) anodically etched sample. This amounts to a maximum change in frequency of 6 cm\(^{-1}\) from the bulk-phonon mode observed in the present experiment. One can raise the question whether the phonon mode observed at 514 cm\(^{-1}\) is not a consequence of the other contaminants in PS such as the presence of siloxene. If it were so, one would expect the same 514 cm\(^{-1}\) mode to show up for all the anodically etched PS samples. On the contrary, the observation of a consistent red shift of the phonon mode in samples prepared with increasing anodic current suggests that the 514 cm\(^{-1}\) peak is not due to the presence of siloxene or other contaminants. Furthermore, it should be noted that a broad and weak phonon mode at 480 cm\(^{-1}\) supposed to arise due to the presence of an amorphous component in the structure is not observed in our Raman spectra implying thereby that the PS still retains its crystallinity as confirmed from the earlier TEM results [2,24].
The PS samples exhibit a structure which predominantly consists of Si wires as depicted by the TEM micrograph. The dimension of these wires decreases with increasing anodic current, leading to a decrease in crystallite size. If the size is comparable to Bohr’s exciton radius, \( a_B \) (\( a_B = 5 \) nm for bulk Si [1]) one would expect the quantum confinement effect (QCE) which would lead to band-gap widening. In the present work, the size of the crystallites in the PS samples linearly decreases with increasing current density as shown in Fig. 6(a) and falls in the range of 4.7-3.8 nm. Hence, it is expected that these samples should show the QCE. Along with the QCE with decreasing size there is an increase in the asymmetry in the low-frequency part of the Raman spectra. As can be further noted from Fig. 5 the Raman intensity increases with decreasing crystallite size and the asymmetry also increases. Furthermore, no splitting in the Raman peak corresponding to the longitudinal optic (LO) and transverse optic (TO) modes has been observed in the present study in contrast to the report by other workers [23]. Fig. 6(b) shows the size dependence of the Raman half-width \( \Delta \Phi \) and shift \( \Delta \Phi_d \) with respect to that of bulk Si. The solid lines are results of the calculation of the quantities for spherical crystallites using different weight factors such as (i) exponential, (ii) sine and (iii) Gaussian functions. The data points marked s1, s2, s3, s4 and s5 correspond to the spherical Si crystallites of sizes of 3.8, 4.1, 4.4, 4.7 and 4.8 nm, respectively. The experimental curves for the Raman widths and peak shifts agree well with the theoretical curve obtained with the Gaussian weight function.

4. Conclusion

The in situ \( I-V \) studies identify the pore/oxide formation and electropolishing regimes for the p-Si/HF acid-electrolyte system. TEM studies indicate that the porous Si retains its crystallinity and the pores propagate perpendicular to the Si surface. Raman-scattering studies show a red shift of the Raman frequencies with decreasing crystallite size.

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