CHAPTER - IV

STUDIES ON POROUS SILICON (PSi) STRUCTURES PREPARED BY ELECTROCHEMICAL ANODIC ETCHING TECHNIQUE

4.1 INTRODUCTION

Silicon based electronic devices are highly advanced and make the largest sector of all semiconductor devices worldwide. Silicon with p or n-type doping is the most important semiconductor material for the electronic industry because of its availability in large area wafers with excellent quality, large quantity and low cost, when compared to other semiconductors. However, silicon has an indirect-band gap with poor optical emission efficiency, which is not quite suitable for the fabrication of optoelectronic devices [1]. The discovery of visible Photoluminescence (PL) at room temperature from highly porous silicon single crystals has generated lot of interest in this material, which gave rise to new and technologically improved Si-based optoelectronic devices. Over the last few years, there is an ever increasing interest in porous silicon due to its efficient optical emission with respect to the non-emitting bulk silicon. However, the basic problems concerning the origin of the visible PL and the morphology of porous structures in silicon wafers [2] still remain to be completely understood. Porous silicon is normally formed by electrochemical etching of crystalline silicon in aqueous liquid containing hydrofluoric (HF) acid. The dissolution process involves the surface reaction of silicon, which leads to pores of different size in the presence of HF molecules of varying concentrations [3].

Recently, the variation in the PL spectra of the PSi with various oxidation conditions has been examined [4, 5]. PL peaks have been observed in the red light region, but it is not clear how the oxygen-related chemical bonds like silicon oxides are related with the PL features. Specific interest has been concentrated on the oxygen-related phases, nano-structures and defects in PSi. In spite of many investigations of the effects of oxidation process on the PL of the PSi, the exact luminescence mechanism and its relation to nanostructures still remain to be probed needing indepth R&D efforts. Few controversies and unusual behaviors of the visible PL could be solved if one understands the way oxygen gets involved in the PSi structure/matrix and the exact role played by oxygen in the PL emission phenomena of the PSi.

PSi is also claimed to be a promising material for developing various hazardous gas sensing devices. Porous silicon is an efficient, effective and selective material for gas
and humidity sensors, as the specific surface area is large and it is possible to integrate PSi with the already existing technology. PSi is an interesting material to make integrated optical devices because of its easy modifiable refractive index due to its modified reflectance and absorbance. By changing the anodisation current density during its production process, PSi layers could be obtained with different depth and porosities, therefore with different refractive indexes. It is a low-cost semiconductor material, which offers many advantages for integrated photonics technology and accepts new challenges to fabricate silicon based sensor devices and as well as solar cells recently.

Some of the unique properties that make PSi attractive for the above mentioned applications are: highly increased surface area-to-volume, repeatability/reproducibility of fabrication and compatibility with well established silicon (Si) integration technologies. Recently, the porous structure shows the applicability in optoelectronic application such as light-emitting device [6, 7], Optical waveguide [8, 9], filter [10] and photovoltaic devices [11, 12]. In this chapter, the influence of current density on structural, optical and morphological properties of the PSi films prepared by electrochemical anodisation in aqueous solution is discussed in detail and the formation conditions are optimized.

4.2 OPTIMIZATION OF ELECTROCHEMICAL ANODIZATION BY CYCLIC VOLTAMMETRIC (I-V) STUDIES

Single crystalline p-type Si wafers were selected for making PSi in aqueous solution. To fix the current density for PSi formation, cyclic voltammetric studies conducted using Si wafers first and then PSi structures were also studied.

4.2.1 Electrode Formation and Aqueous Bath Composition

Electrodes using p-type, (100) orientation silicon wafers were prepared for electrochemical etching. Aluminium ohmic contact was formed on the back and cutting them into rectangles slightly larger than 1x1 cm². The resistivity is about 10 ohm cm. For electrical contact a teflon-coated, stranded aluminum wire was attached to the back of each sample piece with silver conducting paste. To ensure that etching electrolyte would not contact the ohmic side of the wafer, both sides were covered with insulation electrical tape. Active area was exposed by making 2x2 mm² area hole in the tape at the polished front side of the silicon wafer. The cathode electrode was a square platinum mesh of area 2x2 cm² attached with stranded aluminum wire. The back of the platinum electrode was covered with an insulation tape.
The electrolyte consisted of 48% HF combined with sufficient volume of solvent to give the desired concentrations. The solvent consisted of a 1:2 mixture of deionized (DI) water and anhydrous alcohol (Ethanol). Anhydrous alcohol is mixed with the electrolyte to reduce the amount of bubbles being produced at the electrolyte–silicon interface during the etching process. This is found effective because the bubbles affected the pore formation and impeded the formation of silicon nano pillar formation by oxidizing the silicon surface.

After giving electrical connections to the reaction cell, it was covered with a cabin to prevent light exposure during etching. Cyclic voltammetric studies were conducted using Autolab Instrument. The etching was programmed for a timed application of the desired current density. Figure 4.1 a shows the silicon electrode and the above mentioned experimental set-up (Fig. 4.1 b) with the electrochemical cell. Constant current etching was carried out in the dark for 30 min with current densities of 5, 10, 30, 45 and 60 mA/cm². The weight of the silicon wafer before and after etching was measured using a Mettler semi micro balance to find the amount of etched silicon material from the starting Si wafer.

4.2.1 Cyclic Voltammetric Studies on Fresh Si surface

In order to produce PSi structure, the current density at the Si side of the Si/electrolyte interface must be optimized, which is carried by holes that are injected from the bulk towards the interface. Hence, fresh Si wafer (area 0.04 cm²) were biased anodically. Imposing positive voltage at some rate will induce a precise electrochemical reaction, which is forming porous structure by the dissolution of process effected on the silicon surface.

4.3 PSi STRUCTURE FORMATION STEPS IN HF + ETHANOL + H₂O AQUEOUS SOLUTION

The general shape of the voltammograms reported in the present work consists of a plateau after reaching a current maximum. Pore formation occurs only in the initial rising part of the I-V curve for a potential value below the potential of the peak [13]. At low current densities, the electro-oxidation ultimately results in the reaction of Si with HF + water to produce significant amount of surface hydroxyl groups. This reaction leads to the formation of silicon hydride and siliconhydroxide bonds across with the silicon surface atoms (Fig. 4.2). Subsequent to this reaction of a water molecule at a silicon atom, formation of oxides with the release of hydrogen or the insertion of oxygen into a
silicon-silicon surface bond [14] takes place. At relatively low voltages less than 2.0 V, the rate of silicon dissolution as SiO₂ or Si(OH)₄ is very slow. As the current density increases, formation of water-based oxidation intermediates Si=O, Si-O-Si and SiOH at the surface increases. At potentials higher than 2.0 V, a transition zone exists where pore formation and electropolishing compete for control over the surface morphology [15]. The resulting structure within this region is generally porous in nature and the diameters increase rapidly as the current density is varied keeping the potential nearly constant in this voltage region. From the current-voltage (I-V) curves of Si wafer (0.04 cm² area), the potential zone observed in 2.1 – 2.6 V. The associated current density is about 25 – 45 mA/cm², which may be assigned as the optimum (Iₜₐ₉) current density zone for the formation of PSi under the present electrochemical etching condition. Above this Iₜₐ₉, the rate of further oxidation of the surface intermediates increases and the rate of dissolution as SiO₂ or Si(OH)₄ increases proportionately and silicon surface gets electropolishes [13].

Fig. 4.2 outlines the cycle of the suggested conversion steps in an aqueous electrolyte etching process that provides the dissolution of silicon through the ultimate formation of a SiF₄ leaching group from the surface of the Si wafer.

The starting situation (A) represents a kink site of a (100) surface in which the Si atom has two bonds to the silicon lattice and the two remaining bonds are saturated by H ligands.

Taking into consideration the suggested mechanism for the steady-state oxidation of the hydrogen–coated silicon surface in an aqueous electrolyte (Fig. 4.2), the hydrolysis of silicon (B, C) can compete favorably with fluorination, as oxide bonds are readily formed during silicon anodization [16, 17]. The hydrolysis of the silicon radical (B) represents an important alternate oxidation route as water can lead to the formation of an Si-OH bond, which is a form of oxyhydride, with an incomplete hydride formed silicon surface considering the possible formation of the other bonding units like Si=O or Si-O-Si bond through a water molecule reaction with silicon surface. This can be explained that the combination of water reactions produce an [Si(O)(OH)] or [Si(O)-(OSiH₃)] oxyhydride fluorophor. The formation of the hydroxide bond controls and reduces the reactivity of the remaining Si-H bond (C), which is now less prone to electron injection or nucleophilic attack. The lower induced polarization of the hydroxide group also weakens the Si-Si bonds to a lesser extent, signaling an increased stability for the hydroxy intermediates indicated in C and E. Presence of water in the electrolyte can lead
to the formation of silicon oxide and hydroxide bonds in comparison with silicon fluoride bond. This results in the creation of silicon oxyhydroxide surface entities, leading to stable surface product. It seems that, in aqueous etching solution, the competitive branching between hydroxide and fluoride formation is in large part responsible for the formation of photoluminescent emitters in direct competition with dissolution and SiO$_2$ formation [18].

Similarly, the presence of C$_2$H$_5$OH in the etchant can alter the etching cycle through direct reaction or possibly through production of constituencies such as C$_2$H$_5$F i.e.,

$$HF + C_2H_5OH \rightarrow H_2O + C_2H_5F$$

which can rapidly react with the silicon surface [19].

### 4.3.1 I-V Studies on Fresh Si Surface

In order to fix the anodic etching current density region, current (I) and voltage (V), characteristics of the electrochemical cell were recorded and are shown in Fig. 4.3. The anodic current increases when positive voltage range imposed to the silicon wafer is increased. It can be seen from the I-V curves performed with a slow scan rate of 5 mV/sec. Anodic and potential range was varied from +1.0 V to + 4.0 V. Uniform hydrogen evolution is observed up to the scanned potential range of 2.1 – 2.6 V. The current density is found increasing with enhanced potential range. The current density values observed at the peak changed from about 6.0 mA/cm$^2$ to about 70 mA/cm$^2$. Porous structures are formed in this potential region, which is in accordance with the mechanism proposed by Lehmann and Gosele [20]. Above this potential region, the curves behave in a different way indicating some competing reaction at the silicon surface. This leads to the observation that dissolution of the formed porous surface happens and polishing is effected. Further, these I-V characteristics of the p-type Si/HF$+H_2O$ junctions behaves like a Schottky diode as proposed by Zhang et al [15] for porous silicon formation during anodic etching.

The observed hydrogen release during the I-V studies is due to the fact that during pore formation only two of the four available electrons from Si atom participate in the interfacial charge transfer. The remaining two undergo a corrosive hydrogen liberation [21].

Based on these observations of anodic current variation, it is observed that the etching at current densities less than about 70 mA/cm$^2$ may produce PSi with desirable
uniformity. Hence, the etching current density was varied up to a maximum of 60 mA/cm² and further structural, optical and materials characterization were done.

4.3.2 I-V Studies on PSi Surface

I-V studies were conducted on PSi structure formed over a planar area of 0.2x0.2 cm². Fig. 4.4 shows the I-V curves of PSi electrodes at different anodic end potential range, from +1.0 V to +4.0 V. The scan rate was fixed at 5 mV/Sec. The associated current densities are found to vary from about 40 mA/cm² to 240 mA/cm². It shows that the PSi structure has about ten times more area than the planar Si electrode, which confirmed porous structure formation also.

4.4 STRUCTURAL ANALYSIS BY XRD

The porous silicon formed on p-type silicon wafers were characterized by X-ray diffraction (XRD) studies. The crystallinity of the porous silicon is one of the interesting phenomena qualifying the properties of device structure made on its surface. XRD pattern was used to evaluate the degree of crystallinity or grain size of anodized samples. Non-anodized silicon wafer showed a very sharp and high intense peak at \( \theta = 69.2^\circ \) demonstrating its single crystalline (c-Si) nature (Fig. 4.5 a). A PSi sample showed broader XRD peak depending on its porosity. Diffraction peak broadening not only can be produced by reduced crystallite size, but also by the developed stress in crystallites [22] as well as due to size distribution of crystallites. Fig. 4.5 (b-f) shows the XRD pattern of PSi formed at different current densities keeping the anodization in constant at 30 min. A single peak at \( \theta = 69.2^\circ \) is observed corresponding to the (400) orientation of the p-type silicon. As the current density of electrochemical etching increased, the intensity of the parent silicon peak at \( \theta = 69.2^\circ \) decreased and for 60 mA/cm² of electrochemical etching, the peak intensity reached a minimum value. When the current density increased, the peak width, Full Width at Half Maximum (FWHM) was also found increasing. This is an expected and interesting observation since higher current density produces PSi structures with higher porosity, leading to the formation of smaller crystallites [23].

A detailed PSi formation steps at different current densities can be explained as follows. At very low current densities less than 10 mA/cm², the etching current is very small which is not sufficient enough to perturb the whole Si surface but just cleans the surface and etching is initiated at the pure Si surface. At 10 mA/cm², etching current is just more than sufficient to start pore formation and the entire surface shows sponge like
structure. It is seen clearly from the broad peak at 69.2° revealing an amorphous like nature but at the same location, where the peak due to single crystal Si is observed. These features are observed in the SEM picture in which very finely etched surface fragments are seen all over the surface. At 30 mA/cm², there are well defined porous structures uniformly distributed over the entire Si surface. This is due to the fact that the depth and diameter of the pores increase with current density.

When the current density is increased to 45 mA/cm², the top portion of PSi structure is getting dissolved and the bottom of the silicon pores and silicon pillars near to the parent silicon substrate is exposed. Here, the silicon pillar dimensions will be slightly larger in size. This is evident from the increased intensity and reduced width (FWHM) of the (400) peak. At relatively high current densities (60 mA/cm²), dissolution of the top porous surface takes place and the inner silicon surface with large number of pits exhibiting larger silicon grains are exposed. This is confirmed by the appearance of the broad feature at (400) plane associated with a small peak.

The presence of the (400) peak confirms that the cubic structure of the starting single crystal silicon is retained even in all porous structures [24]. This is similar to the results of XRD rocking curves obtained by Buttard et al [25] where two sharp peaks pertaining to Si substrate and PSi layer are present.

The XRD peak was used to estimate the grain size, lattice parameter, strain and dislocation density and they are given in Table 4.1. From the table, it is observed that the lattice parameter values are in the range 5.4271 to 5.4309 Å. The value of the lattice strain is observed to change from 3.50 x 10⁻⁴ to 18.02 x 10⁻⁴ with increase of electrochemical etching current. It is observed that the dislocation density changes from 5.198 x 10¹³ to 1.011 x 10¹³ lines cm⁻², as the electrochemical etching increased from 10 to 60 mA/cm².
Table 4.1
Microstructural parameters of porous silicon electrochemically etched for different current densities at constant time 30 min

<table>
<thead>
<tr>
<th>Etching Current density</th>
<th>(hkl)</th>
<th>Lattice Parameter (a) Å</th>
<th>Grain Size (D) nm</th>
<th>Strain (ε) (10^-4)</th>
<th>Dislocation density (δ) (10^13 line/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 mA/cm²</td>
<td>(400)</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>10 mA/cm²</td>
<td>(400)</td>
<td>5.4309</td>
<td>13.87</td>
<td>18.02</td>
<td>5.198</td>
</tr>
<tr>
<td>30 mA/cm²</td>
<td>(400)</td>
<td>5.4300</td>
<td>22.21</td>
<td>7.02</td>
<td>2.027</td>
</tr>
<tr>
<td>45 mA/cm²</td>
<td>(400)</td>
<td>5.4271</td>
<td>23.59</td>
<td>6.23</td>
<td>1.797</td>
</tr>
<tr>
<td>60 mA/cm²</td>
<td>(400)</td>
<td>5.4281</td>
<td>99.45</td>
<td>3.50</td>
<td>1.011</td>
</tr>
</tbody>
</table>

4.5 OPTICAL STUDIES OF PSi STRUCTURE

Fig. 4.6 (a-e) shows the reflectance spectra of the porous silicon samples etched at different current densities 5, 10, 30, 45 and 60 mA/cm² for 30 min. Intensity of the reflectance significantly lowered with porous layer formation from 10 mA/cm² to 60 mA/cm². The formation of the porous layer will lead to a reduction of the refractive index to a value intermediate between the indexes of silicon and air depending on the porosity. Because, the porous structure contains a mixed phase of silicon solid pillars or dots and air trapped inside the pores. Reflectivity is found minimum for the PSi structures found at 30 mA/cm². On further increase in current density, the Si surface is having larger grains and reflectivity once again increases as seen in Fig. 4.6 d and e.

4.6 SURFACE MORPHOLOGICAL STUDIES

The overall surface morphology has been studied by scanning electron microscope (SEM) studies. Close details of the silicon pillars are observed by atomic force microscope (AFM) and the results are presented here.

4.6.1 SEM Analysis

Figure 4.7 a, b, c, d and e show SEM surface morphology of PSi surfaces formed at different current densities keeping the etching time constant at 30 min. The surfaces are rather well packed structures of nearly circular pores separated by thin column of walls. The dimension of pores range from about 5 to 20 μm. There may be columnar structures of silicon inside the pits and also between the pits which are not observed in
these SEM pictures. Figure 4.7 a shows the surface etched at 5 mA/cm² exhibiting the initiation of etch pits all over the Si surface. At 10 mA/cm², the pore formation starts (Fig. 4.7 b) which makes uniform pores at 30 mA/cm² with thin silicon networks (Fig. 4.7 c). When the current density is increased beyond this, the surface once again becomes scattered with less pore size or with wider silicon network. This may be due to the dissolution of top silicon PSi layer at higher current densities and the bottom surface near to the silicon is exposed. The associated silicon nanoparticle size may also increase. Fig. 4.7 d and e shows the SEM surface morphology of PSi formed at current densities of 45 and 60 mA/cm² respectively. It reveals increasing pore size with etching current density.

4.6.2 AFM Analysis

The nanocrystallite size in PSi layers and its distribution depend on the etching current density. The surface morphology observed by AFM for these PSi structures formed at current densities of 5, 10, 30, 45 and 60 mA/cm² are shown in Fig. 4.8 a, b, c, d and e respectively.

The silicon nanorods are vertically aligned and evenly distributed over the entire surface as seen in Fig. 4.8 c and d. The average diameter of these nanorods is about 30 nm. Both three dimensional and two dimensional (inset) morphologies are presented in Fig. 4.8 c and d. Fig. 4.8 a shows the initiation of silicon etching a 5 mA/cm² with larger grains. In Fig. 4.8 b, the etching process at 10 mA/cm² has produced surface hillocks, possibly generated from the removal of silicon leaving this non-uniform nanostructure. In Fig. 4.8 c, uniform and very fine needle like silicon (nanorods/nanopillars) nanostructures are observed, which is the result of the best PSi structure formed at 30 mA/cm². The surface topography is the top portion of the first etched silicon surface which shows a mixed feature with less asperities and incipient porous structure. Fig. 4.8 d shows thicker silicon pillars which are observed after the dissolution of the top fine porous layer at higher current densities beyond 30 mA/cm² [26, 27].

This shows that the average pore depth increases with current density as explained by Chang and Chen [28]. These observations confirm the formation of nano-crystalline silicon particles inside the pores and all over the etched layers. It gives rise to photoluminescence at room temperature, which can also be attributed to the quantum confinement effects (QCEs) owing to the presence of silicon nanocrystals in the etched layers [29]. Fig. 4.8 e shows a single pit morphology with its thick silicon network. The
horizontal cross section shows a pore diameter of about 4.5 μm formed at a high current density of 60 mA/cm². This type of larger silicon wall or thick silicon feature formation is observed after the dissolution of the top layer of the PSi structure at higher current densities. This will further lead to polishing of the silicon surface rather than forming porous structure.

4.7 RAMAN STUDIES OF PSi STRUCTURES

Raman spectroscopy is a powerful tool that can be used to determine the solid state structure. Raman measurements were performed on the PSi layers using a Renishaw Invia Laser Raman microscopy system. The Raman spectra were recorded in the backscattering configuration at room temperature employing an He-Ne gas laser excitation line (632.8 nm).

The p-type silicon crystal wafer of orientation (100), used in the present study, has a Raman peak at 521 cm⁻¹ (Si peak) which is highly symmetric and shown in Fig. 4.9 a. The photograph of the larger laser illuminated Si single crystal surface is shown as an inset. Electrochemical etching form porous structure whose Raman studies show that Si peak position of the Raman line gets shifted towards lower wave numbers and the line shape becomes asymmetric on etching. The larger laser illuminated PSi surface (inset) and the recorded Raman spectrum with asymmetric feature are shown in Fig. 4.9 b. The PSi regions are seen as golden brownish (deep etched) while bluish area are lightly etched silicon networks. The cross wire intersection indicates well developed porous area with silicon nanocrystals inside. Raman spectra are recorded for the single crystal silicon wafers, etched at current densities 5, 10, 30, 45, 60 mA/cm² and shown in Fig. 4.9 a, b, c, d and e respectively. The Raman peak shifts to a lower frequency of 519 cm⁻¹ after etching at 5 mA/cm² and becomes asymmetric and wide. The line shape asymmetry increases with the increase of current density and also the Raman peak position shifts. The inherent asymmetric broadening of the Raman peaks and the shift of their maxima towards lower frequency are the confirmative evidences of nanocrystalline nature of the developed PSi structures. Further these Raman results show that nanocrystallites in PSi structures prepared in the present study, at different current densities, have various dimensions of PSi structures which is confirmed by the shift of the Raman peak to lower wave number side.

This sharp peak shows that the Si surface is just being etched at very low current densities and represent the PSi/bulk silicon interface. Such behaviour could be due to the
decrease of the crystallite size up to 10 mA/cm² and the increased peaks intensity at 519 and 498 cm⁻¹ as seen from Fig. 4.10 b. The splitted peak correspondingly indicates the presence of moderately increased PSi depth and silicon interface developed at 10 mA/cm². Figure 4.10 c shows a very broad single peak at 490 cm⁻¹ with highest peak intensity. This confirms that this Raman peak solely originates from the thick PSi structure, formed at 30 mA/cm² [30] with quantum dots or quantum sized crystallites or amorphous phase. On increasing the current densities further to 45 and 60 mA/cm² (Fig. 4.10 d and e), the width and intensity of the shifted peak at 499 cm⁻¹ decreases while the other peak intensity at 519 cm⁻¹ increases enormously. This confirms our early discussions that at higher current densities some PSi structures at the top are dissolved and the underlying silicon substrate with slight etching is exposed, which is accompanied with larger silicon grains.

Such observations are in good agreement with the observations of Bessais et al [31] that at higher current densities the presence of hydrogen bubbles into the deepness of the PSi layer prevents further etching and PSi crystallites are larger. At the same time, the top surface small crystallites are removed where the interconnected dots are more opened [32-34]. These results show that PSi structure formed at 30 mA/cm² may give the maximum PL as it is observed with quantum sized silicon crystallites.

4.8 PHOTOLUMINESCENCE (PL) ANALYSIS

PL analysis has been carried out for the freshly prepared PSi structures at different current densities. Also, effect of heating the PSi structure at high temperature in air has been studied from the PL results of heated and aged PSi structure.

4.8.1 Bandgap Tuning Observation from PL Studies

PL spectra probe crystallites where the emission process occurs. PSi structures are reported to luminescence in the near infrared (0.8 eV) and in the whole visible range called S-band [35]. Visual observation of the PSi showed a golden brownish area for various current densities. The observed PL spectra at room temperature at all the current densities confirm the formation of PSi structures with nanocrystalline features. PL spectra were recorded using 425 nm excitation spectrum corresponding to energy of 2.7 eV.

Figure 4.11 shows the PL spectra of PSi structures formed at 5, 10, 30, 45, 60 mA/cm² for 30 min. The corresponding peaks are observed at 699, 656, 630, 651 and 645 nm respectively. It shows a bandgap tuning with etching current (1.77 to 1.97 eV). The intensity increases up to 30 mA/cm² and then decreases. The initial shift in the
luminescence towards the blue region can be explained in terms of the formation of smaller silicon grains at 30 mA/cm² compared to 5 mA/cm² and 10 mA/cm² where the pore formation had just begun. Further shift of the luminescence peak towards red region at current densities greater than 30 mA/cm² may be due to the dissolution of top silicon PSi layer and the bottom surface near to the silicon being exposed, containing larger grains. Similar type of variation has been observed earlier [36].

At 30 mA/cm², a single-peak with nearly symmetric profile (Fig. 4.11 c) shows the formation of silicon nanocrystallites uniformly distributed over the entire surface. The PSi samples prepared at current densities above and below 30 mA/cm² show PL spectra with asymmetric and overlapped peaks. It means that, in such PSi surface profile, there is the presence of a set of semi-isolated silicon nanocrystallites with different dimensions or shapes [37]. Each set of such silicon crystals consists of a narrow distribution of similar dimensions and contribute to one of the PL peaks in the broad PL spectra [34, 38, 39].

Further, the size variation of the nanocrystallites was determined on the assumption that each particle constituting the PSi gives a sharp luminescence peak. XRD results show the particle size variation increasing with current density, which is maximum for the PSi structure formed at 30 mA/cm² in the present study. These detailed studies of PL conclude that PSi structure formed at 30 mA/cm² for 30 min can produce uniform and high quality PSi substrates with maximum photoluminescence.

4.8.2 Thermal Stability of Heated PSi Structures

The effect of rapid thermal treatment in air and exposure to open atmosphere for two months is studied. This has been done to asses the stability of PSi structure to heating, since SnO₂ and ZnO coatings will be formed after heating the sol-gel coated PSi structure at high temperature (400 °C). PL spectra of freshly prepared PSi layer, heated at 600 °C for 5 h, aged for one month and two months are shown in Fig. 4.12 (a-d), respectively. Heating reduces the PL intensity and shifts the peak to higher wavelength side from 630 to 700nm with some humps in the lower wavelength side as well. After aging for one month and two months, pronounced PL peaks are observed on both sides of the peak of the fresh PSi layer. This is in accordance with the reported PL drop in some cases [40-42]. Even after oxidation at higher temperature, the PL is observed and found to be stabilised in our study as reported by Petrova-Koch et al [43]. In order to assess the PSi based optoelectronic devices for various applications, the device should have high
efficiency and good stability over a long period of time under oxidizing atmospheric conditions.

4.9 FT-IR ANALYSIS

FTIR spectra studies have been performed on the anodically etched PSi structures to identify the species present at the freshly prepared PSi surfaces and also at the oxidized surfaces after aging. The spectral peaks give information about the changes in chemical composition of the PSi structure.

Fig. 4.13 a shows the FTIR spectra of the freshly prepared PSi at 30 mA/cm². It shows that the PSi structures formed in the present study have been mainly hydrogen passivated when freshly analyzed as reported by Moreno et al [44]. The presence of distinct peaks with good intensities confirms the fact that the signal from PSi is larger and easier to measure due to its very high specific area [45]. The peak at 610 cm⁻¹ is very strong which is assigned to Si-H bending mode in Si₃-SiH bond. The peak at 658 cm⁻¹ indicates the presence of Si-H wagging mode. These two peaks are the strong evidence that the PSi surface is hydrogen passivated for the as-prepared layers.

Figures 4.13 b and c show the FTIR spectra of PSi layer exposed to atmospheric air for four and eight weeks respectively. The absorption peaks at 817 cm⁻¹ is assigned to Si-O bending mode in O-Si-O and the peak at 895 cm⁻¹ is related to SiH₂ scissor mode or Si-O-H stretching mode [46]. The band observed between 900 to 1300 cm⁻¹ along with distinct peaks is due to the presence of Si-O bonds. The prominent peak at 1107 cm⁻¹ is the characteristic form of Si-O-Si bonds [46]. The peak at 1018 cm⁻¹ is related to Si-O stretching in O-SiO. These spectral regions also provide information about the concentration of surface oxides with aging time. The oxidation during aging is important and inevitable which is confirmed by the appearance of shoulder on the 1107 cm⁻¹ peak and this absorption is related to the O-Si-Hₓ groups. In Fig. 4.13 (a) smaller peaks are observed in the 2000 to 2200 cm⁻¹ region which are assigned to Si-Hₓ bonds [47]. When aging period is increased these bands disappear as seen in Fig. 4.13 b and c. The peaks at 1454 cm⁻¹ is attributed to CH₃ asymmetric deformation mode. The peak at 2357 cm⁻¹ suggests Si-H stretching mode is O₃-SiH bond. The absorption peaks observed at 2820 and 2929 cm⁻¹ are the characteristic of the presence of Si-O-CH₃ groups with CH stretching mode. This might have resulted from the reaction with the residual water in the solvent. The broad absorption band around 3500 cm⁻¹ corresponds to the stretching mode for O-H in the Si-O-H bond.
These observations show that the as-prepared PSi surface is hydrogen passivated and may produce PL. After oxidation in open atmospheric air, Si-H groups are anchored with O-Si-H\textsubscript{x} type of bonds and they are also showing PL properties but with less intensity. These O-Si-H\textsubscript{x} group cover the silicon nano crystallites leading to an improvement in the internal PL emission efficiency [48]. Therefore, the PL observed from the PSi structure formed in this study may be both due to the nanocrystalline nature (QCE) mainly and to some extent to the chemical species present inside the porous structure.

4.10 COMPOSITIONAL ANALYSIS BY XPS

Fig. 4.14 displays the fitted Si 2p XPS results acquired from the prepared porous silicon. The Si 2p peak of the porous silicon is fitted by three peaks. The peak at 99.3 eV is due to elemental silicon, the one at 98.9 eV arises from Si-H, and the one at 100.4 eV correspond to surface Si-OH. The chemical shift towards low energy indicates that porous silicon has a stronger reducibility than silicon due to the existence of Si-H dangling bond which make porous silicon react with slightly alkalescent solution [49]. This result is in good agreement with the FTIR results presented in section 4.9.

4.11 CONCLUSION

In this work, PSi has been formed from p-type silicon wafer by the electrochemical etching method. PSi structure with nano silicon pillars/dots was obtained at 30 mA/cm\textsuperscript{2} current density and 30 min etching. X-ray diffraction studies indicated that the peak intensity decreased with increase of electrochemical etching and reached a minimum intensity and broadening the peak width for 60 mA/cm\textsuperscript{2} current density. The lattice parameter, lattice strain and dislocation density were estimated from the X-ray diffraction pattern. The width of the Raman peak increased with increase of current density. Photoluminescence spectra indicated an increase in height of the PL peak with increase of current density. The AFM analysis indicates that this oscillatory behavior can be associated with the competitive process observed during the porous layer formation, where smaller crystallites always appear on top of the larger ones. FTIR and XPS results confirm the presence of Si-H and Si-OH bonds, which may also contribute to the PL from PSi structure.
REFERENCES


Fig. 4.1 Electrochemical etching experimental set-up:
   (a) Anodization set-up showing the power supply and the etching cell
   (b) Silicon electrode
Fig. 4.2 Reaction mechanisms for dissolution of Si and silicon fluoride and silicon hydroxide (oxyhydride) bond formation in aqueous HF etching solutions
Fig. 4.3 Current – Voltage (I-V) analysis of Si wafer with a scan rate of 5 mV/Sec
Fig. 4.4 Current – Voltage (I-V) analysis of PSi electrode with a scan rate of 5 mV/Sec
Fig. 4.5 XRD pattern of (a) Single crystal silicon and PSi structures formed at (b) 5 (c) 10 (d) 30 (e) 45 (f) 60 mA/cm²
Fig. 4.6 Reflectance spectra of PSi samples anodized with different current densities (a) 5, (b) 10, (c) 30, (d) 45 and (e) 60 mA/cm²
Fig. 4.7 SEM images of uncoated PSi structures formed at different current densities: (a) 5, (b) 10, (c) 30, (d) 45 and (e) 60 mA/cm²
Fig. 4.8 AFM pictures of PSi structures formed with current densities: (a) 5, (b) 10, (c) 30, (d) 45 and (e) 60 mA/cm²
Fig. 4.9 Raman peak and Laser illuminated surface (inset): (a) single crystal silicon wafer and (b) Porous Silicon structure
Fig. 4.10 Raman spectra of PSi structures formed with current densities: (a) 5, (b) 10, (c) 30, (d) 45 and (e) 60 mA/cm²
Fig. 4.11 Photoluminescence spectra of PSi structures formed at (a) 5, (b) 10, (c) 30, (d) 45 and (e) 60 mA/cm$^2$
Fig. 4.12 Photoluminescence emission spectra of PSi structures (a) freshly formed, (b) heated at 600 °C for 5 h, (c) aged for one month and (d) aged for two months
Fig. 4.13 FT-IR spectra of PSi structures: (a) fresh formed, (b) aged for one month and (c) aged for two months
Fig. 4.14 Si 2p XPS spectrum of PSi structure anodized at 30 mA/cm²