PHOTOLUMINESCENT PROPERTIES OF POROUS SILICON

（質性光發致光的硅孔多）

by

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（輝志簡）

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Finally, I should thank Dr Wong Hung Kit for his invaluable encouragement.
Abstract

Visible photoluminescence of porous silicon can be obtained in our laboratory. Photoluminescence varies from red to orange and even green when porous silicon is excited with ultraviolet radiation. Porous silicon prepared in 49.5% hydrofluoric acid gives higher energy photoluminescence than those prepared in less concentrated hydrofluoric acid. Under small anodization current, porous silicon prepared on 1 and 10 Ω-cm wafers gives stronger photoluminescence than those prepared on less resistivity wafers. The relationship between the intensity and peak energy of the photoluminescence of porous silicon support the excitonic enhancement effect predicted by the quantum confinement model.

Besides photoluminescence studies, transmittance and reflectance spectra of porous silicon were also studied. The results show that the porous silicon preserves, to a various degrees which depend on its porosity, the properties of bulk silicon. Infrared transmittance spectroscopy shows that siloxene is not important in the mechanism of the visible photoluminescence of porous silicon. Annealing studies and infrared transmittance spectroscopy show that the presence of silicon hydride is necessary, but not sufficient in the mechanism.
In 1956 the Uhlirs undertook a research at Bell Laboratory to develop a technique for polishing and shaping the surface of silicon. The technique they used was anodization of silicon by hydrofluoric acid in a simple electrochemical cell. They discovered thick films on their samples when low current densities were applied. The films, which consisted of many pores, were later known as porous silicon, and are now classified as microporous, mesoporous and macroporous when the pore widths are smaller than 2nm, between 2 and 50nm and larger than 50nm respectively. Because only passivated silicon surface was sought after, the formation of porous silicon was avoided by suitably controlling the etching parameters.

In the 1980’s, porous silicon was used to make dielectric isolation for silicon on insulator (SOI) technology because of its property of rapid oxidation at low temperatures. To fabricate the SOI structure, buried porous layer is made by lateral etching from an opening at the surface. With suitable choices of dopant types and concentrations, the surrounding layers act as etch stops so that only the buried layer will be etched. A buried silicon dioxide insulator layer will be formed within the silicon by oxidization of the porous layer. It is a good insulator for eliminating crosstalks between devices in very large scale integrated circuits (VLSI). A fully isolated 16k byte random access memory had been reported in 1982. For practical applications, the formation of silicon dioxide layers should be obtained without volume change. As silicon expands into silicon dioxide during oxidation, the volume can be controlled by choosing the initial porosity, the optimal of which
is 56%. Layers with porosities greater than 70% have therefore been considered of little interest, particularly because they present poor mechanical properties. However, it was recently discovered that highly porous silicon permits light emission far above the band gap of bulk silicon. This may be ascribed to quantum size effect as porous silicon is composed of crystallites of sizes about one nanometre. Pickering had reported visible photoluminescence at low temperatures\(^{[P3]}\), but his results did not catch much attention until Canham proposed the quantum confinement model to explain his own result of room temperature visible photoluminescence of porous silicon.\(^{[C3]}\)

Porous silicon has a high quantum efficiency of photoluminescence and acts like a direct band gap semiconductor. Until now only gallium arsenide is widely used in optoelectronics because of the indirect band gap nature of silicon. Gallium arsenide is a more complex and expensive semiconductor; while silicon is abundant, cheap, and whose physical and chemical properties are known thoroughly from years of microcircuit fabrications. The integration of opto-electronic devices onto a silicon-based chip is the recent topic of material research. Porous silicon is a potential candidate for this purpose. Although radiative transitions in silicon can be enhanced by doping suitable impurities or by alloying, the room temperature luminescence obtained in these ways is still weak and thus not suitable for optoelectronics.

Room temperature visible photoluminescence of silicon is also obtained in ultrafine silicon particles prepared by hydrogen sputtering\(^{[P3]}\) and by microwave plasma deposition of SiH\(_4\).\(^{[M1]}\) However, if silicon is ever to be the basis of optoelectronics, anodization is the most attractive among existing methods. It does not
need expensive instrument and complex setup for its preparation.

Recently the study of porous silicon has become a hot topic for physicists. The quantum confinement model of the room temperature visible photoluminescence of porous silicon is of great interest. They wonder how an indirect band gap semiconductor can have such a high quantum efficiency in photoluminescence and how the band gap energy of bulk silicon is shifted up from the bulk value of 1.1eV to 2eV, corresponding to the visible range.

Canham\cite{Canham} suggested a quantum wire model in which high porosity porous silicon is believed to consist of many columns of silicon, of diameter several nanometres. The two dimensional confinement of electrons and holes in the columns causes the upshift. Vial\cite{Vial} proposed a quantum dot model in which high porosity porous silicon is believed to have nanometre size silicon clusters surrounded by silicon dioxide. The three dimensional confinement of electrons and holes in the clusters is then the reason of the upshift. Spatial confinement of carriers leads to the spread out of their wavefunctions in momentum space; overlapping wavefunctions enhance the probability of radiative transitions. Besides the correctness of the quantum confinement model, physicists are also interested in why the photoluminescence peak is so broad and radiation efficiency so high, despite the enormous amount of dangling bonds expected on the surface of porous silicon. For quantum confined systems, energy levels are discrete and hence the corresponding photoluminescence spectra should be very narrow. The presence of dangling bonds provides non-radiative recombination paths for electron-hole pairs which compete with photoluminescence.

Besides quantum confinement model, there are other explanations for the room
temperature visible photoluminescence of porous silicon. It has been suggested that it is not due to the fine structure of silicon, but the chemicals formed on the surface. Detailed descriptions are given in Chapter 2.

The studies presented here focus mainly on the optical properties of the porous silicon because the measurements are non-destructive and the results are directly related to the band structure and the mechanism of photoluminescence.
Chapter 2

Proposed mechanisms of the visible photoluminescence of porous silicon

For simplicity the pores of the porous silicon layer can be treated as having a regular shape of fixed radius and running perpendicularly down the surface without branching, variations in size and separation. Figure 2.1 shows the plan views of cylindrical and rectangular pores of porosities of 25, 50 and 80%. For high enough porosity, nearest-neighbour pores will merge and isolated columns of silicon will be left among the merged pores. Carriers in these columns can no longer move in three dimensions as in bulk silicon, but are confined in the two dimensions parallel to the porous layer. Canham\textsuperscript{[C3]} and Lehmann\textsuperscript{[L1]} independently suggested that the columns acted like quantum wires, provided that the diameter of the columns was small enough, in the order of several nanometres. Vial\textsuperscript{[V1]} suggested that the highly porous silicon had many fine silicon clusters surrounded by silicon dioxide. The sizes of the clusters are in the order of nanometres. Carriers inside are confined in three dimensions. This is the quantum dot model. In either case, the band structure is modified by the quantum confinement and hence the optical properties change. The quantum confinement models lead to two important consequences. The first one is the raise of energy levels. As in the well known case of a particle in an one dimensional quantum well of infinite potential barrier, the lowest energy level is no longer at the bottom of the well, but at an energy which depends on the reciprocal of the product of the mass of the particle and the square of the width of the quantum well. The upshifts of energy levels are larger for narrower wells. The upshifts of
Figure 2.1 Idealized plan view of an anodized (100) silicon wafer containing (a)-(c) cylindrical holes, (d)-(f) rectangular holes. The indicated changes in porosity are achieved by pore enlargement through chemical dissolution\(^{[c3]}\)
energy levels in two and three dimensional wells are qualitatively similar. The other consequence is the zone folding effect.\textsuperscript{[3]} The lattice constant of bulk silicon is 5.43Å. In the direction on the surface of the porous layer, the primitive distance of repetition of silicon or pore is longer than the lattice constant of the bulk silicon. The first Brillouin zone is then a portion of that of bulk silicon. Under reduce zone scheme the bands in higher Brillouin zone can be transformed to the first Brillouin zone. Figure 2.2 shows a case in which the primitive distance of repetition is five times the lattice constant of the bulk silicon.\textsuperscript{[3]} The first minimum of the conduction band is now at the zone centre. The system may have quasi-direct vertical transition. The raise of energy levels and zone folding do not automatically lead to efficient luminescence. Read et al. suggested that high external radiative efficiency is enhanced by localization of exciton, low refractive index of the highly porous silicon and hydride passivation of surface.\textsuperscript{[R1]} At room temperatures exciton is unstable in bulk silicon, but quantum confinement increases its binding and localization energies. Localization of exciton suppresses migration to non-radiative centres. Hydride passivation of surface also reduces the number of non-radiative centres per unit area. The non-radiative recombination rate is therefore comparatively low. The luminescence can arise from the excitonic, in addition to the band to band recombination. These make the photoluminescence efficient. Theoretical calculations of the electronic structure and optical properties of quantum wires in porous silicon have been carried out for wire widths from 7.7 to 31Å by Sanders.\textsuperscript{[52]} Buda et al.\textsuperscript{[B4]} have presented a first-principles calculation of electronic structures silicon wires of diameters up to 1.5nm. Ohno et al.\textsuperscript{[O2]} have presented similar studies of ab initio electronic structure of porous silicon. These calculations
Figure 2.2 Illustration of zone folding in the case of Si(100). By folding in submultiples of one-fifth of the zone boundary, one can fold the conduction-band minimum, 0.2π/a from the zone boundary, to zone centre. This transition is now called quasi-direct.\textsuperscript{[L3]}
suggest the quantum confinement as the main cause of the efficient photoluminescence of porous silicon.

Brandt et al.\cite{32, 37} have presented an alternative explanation. Siloxene is a compound containing hexagonal rings and is composed of silicon, oxygen and hydrogen in the ratio of 2:1:2. It has many derivatives. The molecular structures of three of the derivatives are shown in Figure 2.3. Brandt et al.\cite{32, 37} have showed the similarities between the photoluminescence, photoexcitation, Raman scattering and infrared absorption spectra of siloxene derivatives and porous silicon. The siloxene derivatives they used were Kautsky and Wohler compounds and some were annealed at 400°C. The structural model of Kautsky compound is shown in Figure 2.3a and the structural models of Wohler compound are shown in Figures 2.3b and 2.3c. The Kautsky compound consists of layers of hexagonal silicon rings interconnected by oxygen bridges. The remaining silicon dangling bonds are terminated by hydrogen. The Wohler compound consists of either linear silicon chains interconnected by oxygen or pure silicon layers with alternating OH and H bond terminators. During annealing hydrogen groups were substituted by OH groups. From the similarities in optical and structural properties of porous silicon and siloxene derivatives, Brandt et al. concluded that the visible luminescence of the porous silicon was due to the presence of compounds of silicon, oxygen and hydrogen formed on the surface rather than the quantum confinement effect. Deak et al.\cite{41} have carried out semi-empirical quantum chemical calculations of the siloxene derivatives. They concluded that hexagonal silicon rings and linear silicon chains isolated by oxygen in siloxene derivatives acted like quantum dots and quantum wires respectively and called the effect as chemical quantum confinement.
Figure 2.3 Structure models for siloxene (Si₄O₃H₆). (a) Monolayers formed by hexagonal silicon rings interconnected by oxygen bridges. The fourth bond of silicon is terminated by hydrogen. (b) Monolayers formed by linear silicon chains interconnected by oxygen, terminated by hydrogen. (c) Silicon monolayers with alternating OH and H bond terminators.\[82\]
Although their calculations also deal with quantum wires or quantum dots, the point of view is very different from the quantum confinement proposed by Canham.\textsuperscript{[C3]} Quantum confinement model preserves the band structure of silicon, but chemical quantum confinement is mainly derived from electronic structures of chemical species.

Some studies have shown a correlation of the photoluminescence and the abundance of hydrogen.\textsuperscript{[P4, T5, T6]} Noting the presence of large amount of silicon hydride in porous silicon, it has been suggested that the visible photoluminescence of porous silicon was due to the presence of silane rather than the quantum confinement effect. Silane polymers contain hydrogen and silicon atoms catenated together to form a linear backbone. Low molecular weight silanes are often called oligosilanes while high molecular weight silanes are designated as polysilanes.\textsuperscript{[M1]} Based on the existing experimental evidence of silicon hydride peaks in the infrared-absorption spectra, Takeda et al.\textsuperscript{T2} proposed an oligosilane bridge model as another possibility for the explanation of the room temperature visible photoluminescence of porous silicon. They calculated both the cases of oligosilanes isolated in free space and pinned at both ends. Figure 2.4 shows the molecular structures they studied and the corresponding energy level diagrams. The light-emission energy varies a lot for different types of oligosilanes and geometrical conditions, but the photoexcitation is insensitive to these factors. Although the calculation showed oligosilanes pinned at both ends might emit visible light, it is not the whole story. The electronic states of the silicon clusters at both ends of the oligosilane bridge may also play an important role. If the indirect gap of silicon is preserved, energy may transfer to the clusters and be consumed in non-radiative recombinations and no visible
Figure 2.4 Total energy-level diagrams (A) before and (B) after the relaxation of the molecular structure caused by photoexcitation for two types of oligosilanes connecting two silicon clusters. Cb: capped bond.[72]
luminescence will be observed. If the endings of the oligosilane bridge are nanometre size silicon clusters, the quantum size effect will lead to band-gap widening and stop the energy transfer and the competitive non-radiative process. Figure 2.5 shows the oligosilane bridge model. The black and white circles stand for the nanometre size silicon clusters of various sizes and silicon oxide regions converted from nanometre size silicon crystallite respectively. The zigzag lines connecting the circles stand for various types of oligosilane bridges. In the quantum confinement model nanometre size silicon crystallite or cluster is the origin of the visible photoluminescence; in oligosilane bridge model it is a requisite to minimize non-radiative recombination.

In addition to the quantum confinement models, siloxene, polysilane and oligosilane models, it has been suggested that the photoluminescence is due to the amorphous phase presented in the porous layer.\cite{P3} The enhancement of the band gap of amorphous silicon passivated by hydrogen is well known and will not be discussed here.\cite{S6}

The origin of the visible photoluminescence of porous silicon has caused much controversy; which of the models mentioned above is the appropriate one is still not conclusively decided. However, the quantum confinement effect and the oligosilane bridge model seem to have more experimental supports than others.
Figure 2.5  A schematic representation of the model structure for the light-emitting porous silicon.\textsuperscript{[72]}

nanometre size silicon crystallite

silicon oxide

oligosilane bridge
Chapter 3
Sample Preparation

3.1 Anodization of porous silicon in an electrochemical cell

Porous silicon layers were prepared by the anodization of silicon wafers in a single cell containing hydrofluoric acid. The constructions of the cell and the circuit used are shown in Figure 3.1.1. Due to the corrosive nature of hydrofluoric acid, polyvinyl chloride (PVC) was used to make the cell. Two-inch-diameter, boron-doped, p-type, silicon (100) wafer was cut into four roughly equal quarters. A quarter was sandwiched between the bottom of the cell and a compression plate which provided the electrical connection for the anode. An aluminium foil with sponge backing was placed on the plate and under the wafer as the electrical contact. The wafer and the aluminium foil were pressed against the Neoprene O-ring by the plate with nylon screws. The O-ring sealed off the leakage and defined the anodized area. An immersed platinum wire was used as the cathode. The area of silicon exposed to aqueous hydrofluoric acid solution was 1.8cm², corresponding to a hole of 1.5cm diameter. The concentrations of hydrofluoric acid used were 11.1%, 26.6% and 49.5% by weight. The 26.6% hydrofluoric acid was made from the dilution of 49.5% hydrofluoric acid with an equal volume of deionized water. The 11.1% hydrofluoric acid was made from mixing one part of the 49.5% hydrofluoric acid with four parts of deionized water in volume. A series of samples was prepared using different combinations of concentrations of hydrofluoric acid and average current densities. Four kinds of p-type silicon wafers of resistivities 0.01, 0.1, 1 and 10Ω-cm were used in the studies. The samples were etched with constant currents;
Fig 3.1.1a  Single cell for anodization.
Fig 3.1.1b  Circuit for anodization of silicon.
their designations and their conditions of anodization are listed in Table 3.1.1. Current was supplied by a Keithley K220 current source and the voltage was monitored by a Keithley K197 digital multimeter. Both the current source and the multimeter were connected to a personal computer through an IEEE-488 interface. After anodization, the samples were dried with an air blower. The samples were weighted before and after the anodization using a Sartorius 2474, electric balance. The precision of the balance is ±0.01mg. Mass losses due to anodization were calculated from the difference of the weights recorded.

Mr Cheung’s samples were prepared by a similar setup. The conditions of anodization are listed in Table 3.1.2. Sometimes he used a double cell instead of the single cell. The setup consisted of a voltage source and two multimeters. The voltage source was used in the current limited mode as a constant current source. The current and voltage across the cell were recorded directly from the multimeters. After anodization, the samples were rinsed with deionized water and then dried in dry nitrogen.

3.2 Appearances of samples

The appearance of porous silicon obtained as a result of anodization depends on the resistivity of the wafer, as well as on the current density. When low current density was used, the resultant porous layer usually appeared smooth. However, its colour was determined by the resistivity. Shiny grey porous silicon was often found from anodization of 0.01 Ω-cm silicon wafer; dark brown or black from 0.1 to 1 Ω-cm and yellow from 10 Ω-cm. Interference fringes were always found on samples from the anodization of silicon wafers of resistivity larger than 0.01 Ω-cm. When
Table 3.1.1a  Samples prepared with 1mA, anodization current and 90 min, etching time

<table>
<thead>
<tr>
<th>Sample</th>
<th>Resistivity of substrate, ( \rho ) (( \Omega \text{cm} ))</th>
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<th>0.1</th>
<th>1</th>
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<td>Concentration</td>
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<td>D5</td>
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<td>of hydrofluoric</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>acid (wt%)</td>
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<td>A6</td>
<td>B6</td>
<td>C6</td>
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<tr>
<td></td>
<td></td>
<td>A7</td>
<td>B7</td>
<td>C7</td>
<td>D7</td>
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Table 3.1.1b  Samples prepared with 2mA, anodization current and 50 min, etching time

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<th>0.1</th>
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<td>Concentration</td>
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<td>D9</td>
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<td></td>
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<td>acid (wt%)</td>
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<td>A10</td>
<td>B10</td>
<td>C10</td>
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<td></td>
<td>A11</td>
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<td>C11</td>
<td>D11</td>
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Table 3.1.1c  Samples prepared with 26.6 wt% hydrofluoric acid and 0.35-0.7\( \Omega \text{cm} \) p-type wafers

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<td>K28</td>
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<tr>
<td>K53</td>
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Table 3.1.2 Sample prepared at constant current by Mr Cheung W.Y.

<table>
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<tr>
<th>Sample</th>
<th>Concentration of hydrofluoric acid (wt%)</th>
<th>Anodization current (mA)</th>
<th>Etching time (min)</th>
<th>Resistivity of substrates (Ωcm)</th>
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<td>88</td>
<td>26.6</td>
<td>26.9</td>
<td>8</td>
<td>0.35-0.7</td>
</tr>
<tr>
<td>89</td>
<td>26.6</td>
<td>26.9</td>
<td>30</td>
<td>0.35-0.7</td>
</tr>
<tr>
<td>91</td>
<td>11.1</td>
<td>26.9</td>
<td>30</td>
<td>0.35-0.7</td>
</tr>
<tr>
<td>92</td>
<td>26.6</td>
<td>26.9</td>
<td>15</td>
<td>0.35-0.7</td>
</tr>
</tbody>
</table>
high current density was used, as in the study of current voltage characteristics, the surfaces of the resultant porous silicon were rough. The samples prepared from 0.01 Ω-cm wafers had many pits on their surfaces, because small chips of silicon were lifted off. Those prepared with 0.1 and 1 Ω-cm wafers had a dark brown or black rough surface. The samples prepared with 10 Ω-cm wafers often had a yellowish rough surface.

3.3 Uniformity of samples

In principle anodized porous silicon can have a uniform surface, provided the current density used is uniform everywhere. To achieve this, one needs to design an etching cell by solving Maxwell's equation with appropriate boundary conditions. This is obviously not a practical approach. Even if one carries out the design and a perfect cell is constructed, there still is the problem of hydrogen bubbles. Hydrogen bubbles always form on the sample surface during anodization and, as a result, perturbs current flow. The area covered by the bubble is not in contact with hydrofluoric acid until the bubble grows to a size and floats away. The bubbles leave behind concentric ring patterns on the surface of porous silicon. Therefore we decided that the construct of a perfect cell costs too much effort and may not contribute much in preparing uniform samples. To reduce the effect of hydrogen bubbles, we have tried many approaches. The single cell was placed in an ultrasonic bath to shake off the bubbles, but there was no great improvement. Magnetic stirrer was also tried, but it could not remove bubbles efficiently either. Better results were obtained by mixing the hydrofluoric acid with ethanol. The samples prepared with a mixture of ethanol and aqueous hydrofluoric acid had more uniform appearance.
However, the porous silicon layers were very loose and had some unknown powder deposited on the surface. For easy handling, storage and comparison of results with other groups, the "classical" aqueous hydrofluoric acid solution was used. The samples etched with our cell have a weakly etched ring on its rim, which is due to the dead space adjacent to the O-ring and between the wafer and the cell. Bubbles tend to be trapped in that space. Other than the occasional small ring patterns, the central portion of our porous silicon is however more or less uniform.

3.4 Formation mechanism

There are three proposed models for the formation of porous silicon: the Beale model\(^{[81]}\), the diffusion-limited model\(^{[84]}\) and a quantum-based model.\(^{[1-1]}\) Beale suggests that electric field lines concentrated at surface irregularities, focus current flow to the pore tips, and locally enhance dissolution there. The dissolution is a positive feedback process. Moreover, Schottky barrier is present at the silicon/solution interface. The interpore regions are devoid of mobile carriers because of overlapping depletion regions.\(^{[83]}\) Current is then selectively directed to the pore tips as a result of the high-resistance, depleted porous structure.

The diffusion-limited model describes the formation of porous silicon in terms of a stochastic random walk process. During pore generation, a hole diffuses to the silicon surface and oxidatively reacts with a surface silicon atom. The nature of the random walk presents the pore tips as the most likely contact sites for a hole diffusing from the bulk of the semiconductor, and provides a similar selective dissolution at surface irregularities as does the Beale model. A characteristic diffusion length, which is a function of the dopant concentration, voltage, etc.,
controls the different pore morphologies. The Beale model is based on the presence of Schottky diode, but the diffusion-limited model can be applied to electrochemical phenomena universally. Even if a diode analogy is to be used to describe porous silicon formation, it is more applicable to consider diffusion in describing the limiting current in a forward-biased p-n diode and the semiconductor portion of a Schottky diode rather than depletion regions. However, both the Beale and diffusion-limited models can be represented by the same mathematical equation.

The quantum model proposes that increase in the porous silicon band gap decreases the mobile carrier concentrations and produces a "depletion" similar to the depletion layer proposed by Beale. Since the diffusion-limited model provides all the basic elements to describe pore formation in both n- and p-type silicon, there is no need to made use of a quantum interpretation of the pore formation mechanism.

3.5 Measurements of current-voltage characteristics

To study the current-voltage characteristics of the anodization process, 15 quarters of wafers were anodized at varied currents. The same cell and setup used for preparing porous silicon were used for this study. The current was increased from zero to a preset current and then back to zero. A series of forward and backward sweeps were done with the preset current increasing from 1μA to 100mA and then decreasing back to 1μA. Designations, resistivities of wafers and concentrations of hydrofluoric acid used for this study are listed in Table 3.5.
Table 3.5  Sample used in study of current voltage characteristics

<table>
<thead>
<tr>
<th>Sample</th>
<th>Resistivity of substrate, $\rho$ (\Omega\text{cm})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.01</td>
</tr>
<tr>
<td>Concentration</td>
<td></td>
</tr>
<tr>
<td>of hydrofluoric</td>
<td></td>
</tr>
<tr>
<td>acid (wt%)</td>
<td></td>
</tr>
<tr>
<td>11.1</td>
<td>A4</td>
</tr>
<tr>
<td>26.6</td>
<td>A1</td>
</tr>
<tr>
<td>49.5</td>
<td>A3</td>
</tr>
</tbody>
</table>

3.6 Current-Voltage (I-V) Characteristics

The anodization of silicon is an irreversible, electrochemical reaction whose rate is controlled by the current. During the measurement of the I-V characteristic, the porous layer is constantly being modified, the longer the anodization time, the more substantial the change. Previous studies have shown that the I-V characteristics can be divided into three regions: pore formation, transition and electropolishing.\[^{22}\] There is no clear electropolishing region when 11.1% or more concentrated hydrofluoric acid is used.\[^{22}\] The I-V characteristics are essentially exponential, but show strong fluctuations when current is larger than 4mA. In these curves hysteresis and discontinuities are commonly observed, especially for currents larger than 4mA. The exponential portion of the I-V curve corresponds to the pore formation region. The other portion corresponds to the transition region. Typical forward sweeping I-V characteristics are shown in Figure 3.6.1. The DC conductance, indicated by the ratio of current to voltage, is substrate dependent. It is largest for 0.01\Omega\text{-cm wafer and smallest for 100\Omega\text{-cm wafer anodized under same conditions. The measured I-V characteristics are not always reproducible (see Figure 3.6.1a-c). However, the relative order of the DC conductance at the same current is not
Figure 3.6.1a I-V characteristics of anodization of porous silicon in 11.1% hydrofluoric acid.
Figure 3.6.1b  I-V characteristics of anodization of porous silicon in 26.6% hydrofluoric acid.
Figure 3.6.1c  I-V characteristics of anodization of porous silicon in 49.5% hydrofluoric acid.
significantly affected by the anodization conditions. Similar results have been reported by Smith.\textsuperscript{[54]}

Figure 3.6.2 shows the typical forward and backward sweep I-V characteristics. The hysteresis reflects the history dependent nature of the anodizing process. Sharp changes in the I-V characteristics were found to correlate with sudden bursts of hydrogen bubbles and small pieces of silicon chipping off, indicative of electropolishing instead of anodizing were occurring. These effects are more severe at high current densities. Once a large current, say larger than 4mA, has been passed, the DC conductance increases. At low current, such as below 2mA, chemical reactions are sufficiently slow that the nature of the porous silicon has not changed drastically before the I-V measurement is completed, allowing essentially reproducible I-V characteristics curve to be obtained. Therefore, the currents used for the preparation of samples for our optical studies were chosen to be 1 or 2mA.

Typical I-V characteristics at low current densities are shown in Figure 3.6.3. The pore formation region is exponential and can be fitted to a Schottky diode-resistor model. There is a Schottky barrier at the silicon/electrolyte interface similar to a semiconductor/metal junction. The resistance of the setup is modelled as a resistor in series. The cell acts as a battery if a load replaces the voltage supply, thus the electromotive force \( E \) is included. The equivalent circuit is a battery, a resistor and a diode connected in series with an applied current source as shown in Figure 3.6.4. The potential drop across the resistor and the diode equals to the difference of the total voltage and the electromotive force of the battery such that

\[
V_t - E = I \ R + V_d \tag{3.6.1}
\]
Figure 3.6.2  Forward and backward sweep I-V characteristics of sample D1.
Figure 3.6.3a  I-V characteristics of sample A3.

( * = measured value, solid line : fitted result )
Figure 3.6.3b  I-V characteristics of sample B3.

(* = measured value, solid line : fitted result)
Figure 3.6.3c  I-V characteristics of sample C3.

( * = measured value, solid line : fitted result )
Figure 3.6.3d  I-V characteristics of sample D3.

(* = measured value, solid line: fitted result)
Fig 3.6.4 Equivalence circuit of anodization.
where \( V_t \), \( E \), \( I \), \( R \) and \( V_d \) are the total voltage across all the components, the electromotive force of the cell, the current flowing through the circuit, the resistance of the series resistor in the model and the voltage across the diode respectively. For the diode, the relation between \( I \) and \( V_d \) is, i.e.

\[
I = I_o \{\exp[(e V_d) / (\eta k T)] - 1\}
\]  (3.6.2)

where \( k \), \( T \), \( \eta \), \( I_o \) and \( e \) are the Boltzmann constant, the temperature, the ideality factor, the reverse saturation current and the charge of an electron respectively. Substituting Equation 3.6.2 into 3.6.1 and rearranging, the equation used for fitting becomes

\[
V_t = (\eta k T / e) \ln \{I / I_o + 1\} + I R + E
\]  (3.6.3)

The curves shown in Figure 3.6.3 are fitted to Equation 3.6.3, using \( \eta \), \( I_o \), \( R \) and \( E \) as adjusting parameters. Good fits were obtained. The parameters obtained from the fit are shown in Table 3.6. The series resistance increases as the resistivity of wafer used. Other results vary with the etching conditions, but have no simple relation to them. In our cell, the contact between the wafer and the aluminium foil is determined by the pressure exerted by the bottom plate. It is not easy to apply a uniform and reproducible pressure through four tightening screws. The junction between the wafer and the aluminium foil may also act like a diode which is not included in our Schottky diode-resistor model. Furthermore, we found that there is no simple relation between the photoluminescence and the fitted parameters.
Table 3.6 Fitting result of current voltage characteristic up to 1mA

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\eta$</th>
<th>$I_o$ (µA)</th>
<th>$R$ (Ω)</th>
<th>$\epsilon$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>3.29</td>
<td>0.58362</td>
<td>158.13</td>
<td>-0.2295</td>
</tr>
<tr>
<td>B1</td>
<td>8.16</td>
<td>3.2613</td>
<td>620.54</td>
<td>-0.2116</td>
</tr>
<tr>
<td>C1</td>
<td>5.70</td>
<td>2.44693</td>
<td>977.08</td>
<td>-0.1509</td>
</tr>
<tr>
<td>D1</td>
<td>296.57</td>
<td>32.40288</td>
<td>3595.99</td>
<td>-0.8210</td>
</tr>
<tr>
<td>B2</td>
<td>13.50</td>
<td>17.8610</td>
<td>650.40</td>
<td>-0.1490</td>
</tr>
<tr>
<td>C2</td>
<td>30.75</td>
<td>55.14273</td>
<td>1552.15</td>
<td>-0.0940</td>
</tr>
<tr>
<td>D2</td>
<td>46.72</td>
<td>43.28659</td>
<td>3662.05</td>
<td>-0.1439</td>
</tr>
<tr>
<td>A3</td>
<td>3.29</td>
<td>0.63819</td>
<td>329.64</td>
<td>-0.2544</td>
</tr>
<tr>
<td>B3</td>
<td>4.74</td>
<td>1.64808</td>
<td>719.03</td>
<td>-0.1794</td>
</tr>
<tr>
<td>C3</td>
<td>3.85</td>
<td>0.40363</td>
<td>877.18</td>
<td>0.2034</td>
</tr>
<tr>
<td>D3</td>
<td>99.33</td>
<td>145.13134</td>
<td>5345.32</td>
<td>-0.0496</td>
</tr>
<tr>
<td>A4</td>
<td>3.52</td>
<td>0.14637</td>
<td>42.63</td>
<td>-0.3659</td>
</tr>
<tr>
<td>B4</td>
<td>3.53</td>
<td>0.05295</td>
<td>147.86</td>
<td>-0.3048</td>
</tr>
<tr>
<td>C4</td>
<td>20.64</td>
<td>21.32339</td>
<td>2026.03</td>
<td>-0.0374</td>
</tr>
<tr>
<td>D4</td>
<td>26.60</td>
<td>1.74832</td>
<td>13359.94</td>
<td>-0.4790</td>
</tr>
</tbody>
</table>
3.7 Voltage monitored at constant anodizing current

Figure 3.7.1 shows a voltage versus time curve obtained at a current of 20μA. The voltage increases rapidly in the initial anodization stage and reaches a more or less stable value. Almost periodic modulation of the voltage is observed. The small modulations may be caused by bubble formations. When bubbles formed on the surface expand in size and increase in number, the resistance of the cell increases and thus the voltage increases at the constant current condition. The rate of bubbles leaving the silicon surface is direct related to the density and size of the bubbles. When both are small, the rate of bubbles leaving is small and the predominant effect is the growth of bubbles in size and density. This causes the measured voltage to increase. When the voltage increases to a critical value, rate of increase of density and size of bubbles become slow and the rate of bubbles leaving becomes dominant. More bubbles leave than form on the surface and hence the voltage decreases. The voltage decreases until the number of bubbles drops to a value such that the rate of formation of bubbles becomes dominant again. Successive cycles thus lead to voltage oscillations. Another possible explanation of the oscillations is the competition between surface islands of oxide dissolution and free silicon dissolution.\[54\]

3.8 Mass lost due to anodization

The mass losses of different samples are shown in Table 3.8.1. The losses are very close to each other because the total amount of charges transferred in the anodization process, which is the product of anodization currents and etching times, are nearly equal. Mass losses are about 1mg for samples anodized in 11.1% and
Figure 3.7.1 Voltage monitored at anodization.
26.6% hydrofluoric acid. For samples anodized in 49.5% hydrofluoric acid mass losses are in the range between 0.4 and 0.8mg. Smaller losses are observed for samples anodized in 49.5% hydrofluoric acid than others and the data are more scattered. The difference in mass losses indicates the domination of different reactions. The porosity is defined as the ratio of the total volume of the pores to the volume of the layer. The total volume of the pores is given by \( m / \rho \), where \( m \) is the mass loss and \( \rho \) the density of silicon. The porosity can then be written as

\[
p = \frac{m}{\rho A d}
\]  

(3.8.1)

where \( A \) and \( d \) are the area and thickness of the porous layer respectively. The only unknown in the determination of porosity is the thickness. The measurement of thickness will be discussed in Chapter 4.

Table 3.8.1 Mass loss against resistivity

<table>
<thead>
<tr>
<th>Mass lost (mg)</th>
<th>anodization current, etching time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1mA, 90min</td>
</tr>
<tr>
<td></td>
<td>Conc. of HF (wt%)</td>
</tr>
<tr>
<td>11.1</td>
<td>26.6</td>
</tr>
<tr>
<td>49.5</td>
<td></td>
</tr>
<tr>
<td>0.01</td>
<td>0.95</td>
</tr>
<tr>
<td>0.1</td>
<td>1.07</td>
</tr>
<tr>
<td>1</td>
<td>0.97</td>
</tr>
<tr>
<td>10</td>
<td>0.95</td>
</tr>
</tbody>
</table>

The number of electrons, \( Z \), needed to release a silicon atom for different samples are shown in Table 3.8.2. It is calculated from:

\[
Z = \frac{M}{(N_A \times e)} \times \frac{I \times t}{m}
\]

(3.8.2)
Table 3.8.2 Z of sample of different resistivity

<table>
<thead>
<tr>
<th>Z</th>
<th>anodization current, etching time</th>
<th>1mA, 90min</th>
<th>2mA, 50min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conc. of HF (wt%)</td>
<td>11.1</td>
<td>26.6</td>
</tr>
<tr>
<td>resistivity</td>
<td>0.01</td>
<td>1.7</td>
<td>1.6</td>
</tr>
<tr>
<td>of substrate</td>
<td>0.1</td>
<td>1.5</td>
<td>1.7</td>
</tr>
<tr>
<td>Ω-cm</td>
<td>1</td>
<td>1.6</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1.7</td>
<td>1.5</td>
</tr>
</tbody>
</table>

where M is the molar mass of silicon, $N_A$ the Avogadro number, $t$ the time for anodization and $m$ the mass loss of the sample. We have found that $Z$ is around 3 for samples prepared in 49.5% hydrofluoric acid and between 1.4 and 2 for samples prepared in 10% and 26.6% hydrofluoric acid. The chemical reactions involved in the anodization are complex, but are believed to be a competition of three main reactions: oxide formation, oxide dissolution and direct dissolution of silicon. The corresponding chemical formulae are written as^{22}:

oxide formation

\[
Si + 4 OH^- + n \text{ h} \rightarrow Si(OH)_4 + (4 - n) \text{ e} \quad (3.8.3.a1)
\]

\[
Si(OH)_4 \rightarrow SiO_2 + \text{ H}_2\text{O} \quad (3.8.3.a2)
\]

oxide dissolution

\[
SiO_2 + 6 \text{ HF} \rightarrow \text{ H}_2\text{SiF}_6 + \text{ H}_2\text{O} \quad (3.8.3.b1)
\]

direct dissolution of silicon

\[
Si + 2 \text{ F}^- + v \text{ h} \rightarrow SiF_2 + (2 - v) \text{ e} \quad (3.8.3.c1)
\]

\[
SiF_2 + 2 \text{ HF} \rightarrow SiF_4 + \text{ H}_2 \quad (3.8.3.c2)
\]

\[
SiF_4 + 2 \text{ HF} \rightarrow \text{ H}_2\text{SiF}_6 \quad (3.8.3.c3)
\]
where h and e are hole and electron respectively and \( n < 4 \), \( v < 2 \). In all the above reactions \( Z \) should be smaller than 4, the valency of silicon. Its actual value depends on the current density and the concentration of hydrofluoric acid, which affects the balance of the competition of the reactions. In the preparation of porous silicon in 49.5% hydrofluoric acid, \( Z \) is around 3, which indicates the domination of oxide formation. In the preparation of porous silicon in 11.1% and 26.6% hydrofluoric acid, \( Z \) is between 1.4 and 2, which indicates the domination of direct dissolution of silicon. Zhang had reported the increase of concentration of hydrofluoric acid led to the increase of rates of different reactions under different current and voltage combinations.\(^{[22]}\) Our result is opposite to Zhang’s result. We have not understood this clearly yet. Although different values of \( Z \) indicate different dominant reactions, the results of photoluminescence show no direct relation with the value of \( Z \).
Chapter 4

Transmittance and reflectance studies

4.1 Transmittance and reflectance studies in the ultraviolet to near infrared range

4.1.1 Experimental setup of transmittance and reflectance spectroscopic studies

Transmittance spectra were obtained from a double beam recording spectrophotometer, Hitachi UM-3501. The working spectral range of UM-3501 is from 187 to 3200nm i.e. 0.39 to 6.6eV. The wavelength accuracy is ±0.2nm for the ultraviolet to visible region and ±1.0nm for the near infrared region. The photometric accuracy is ±0.3% transmittance. The slit width was fixed at 2nm in the ultraviolet and visible, and varied from 0.1 to 36nm in the near infrared range. To eliminate the effect of the substrate, the spectra of the samples were measured with reference to a silicon wafer of the same type in the reference beam. In addition, transmittance spectra of porous silicon layers referenced to air were also taken.

The UM-3501 was also used to measure the reflectance spectra, with the 5° specular reflectance accessory installed. Reflection from an aluminium mirror was used as the standard reference.

4.1.2 Transmittance spectra

The thickness of the silicon wafers used in our studies is 280µm. After anodization, about 10µm of the top surface of the wafers becomes porous and the rest remains intact, acting as the substrate for mechanical support. Transmittance spectra obtained for the porous layers are strongly affected by the substrates which
are much thicker. The substrate is opaque for photons of energies above the indirect gap of silicon, which is 1.1eV. Below the band gap free carrier absorption, which depends on the impurity concentration and hence the resistivity of the wafer, plays a significant role, particularly when it is less than or equal to 0.01Ω-cm. The position of the free carrier absorption peak is inversely proportional to the square root of the concentration of dopants. The free-carrier absorption peak shifts to the high energy side as the concentration increases, i.e. resistivity decreases. Therefore a strong absorption peak is found in the transmittance spectra of the porous silicon layers on substrates of resistivity of 0.01 Ω-cm. Figures 4.1.2a-d show the transmittance spectra of porous silicon formed on substrates of resistivities from 10 to 0.01Ω-cm. The energy range of the transmittance spectra taken is from 0.39 to 1.44eV because transmittance is practically zero for energies higher than 1.4eV. The figures also show the transmittance of the corresponding wafers. For the 10Ω-cm silicon wafer, curve (ii) in Figure 4.1.2a, below band gap transmittance is about 7% and free electron contribution is negligible. The transmittance, which is lower than the theoretical value, may have been reduced by the scattering of rough back surface. The transmittance of porous silicon made from this wafer is seen to be higher by almost 10 to 15%. This shows that porous silicon is more transparent than silicon of the same thickness. Sagnes et al. observed that a dramatic shifts of the absorption edge of porous silicon towards higher energies with respect to that of silicon. Base on the increase of the shift with porosity and decrease of substrate doping, they interpreted the shift as arising from the quantum confinement of carriers in the porous silicon crystallites. Another salient feature to note is the interference effect. The fact that interference is observed suggests porous silicon layer has fairly
Figure 4.1.2a  Transmittance spectra of (i) sample D11 and (ii) silicon wafer of resistivity of 10Ωcm.
Figure 4.1.2b Transmittance spectra of (i) sample C11 and (ii) silicon wafer of resistivity of 1Ωcm.
Figure 4.1.2c Transmittance spectra of (i) sample B6 and (ii) silicon wafer of resistivity of 0.1Ωcm.
Figure 4.1.2d  Transmittance spectra of (i) sample A6 and (ii) silicon wafer of resistivity of 0.01Ωcm.
uniform optical thickness. Interference patterns are sometimes also observed for porous silicon formed on other wafers, although they are not shown in the Figures 4.1.2b-d. Figures 4.1.2b-d also show clearly that, just like that on 10 Ω·cm wafer, porous silicon layers on 0.01 and 0.1 Ω·cm wafers are less absorbing than silicon. For reasons unknown, may be it is related to the complicated electrochemistry of anodization, transmittance of porous silicon on 1 Ω·cm wafer is quite different. As shown in Figure 4.1.2c, it is significantly less transparent between 0.6 and 1.2eV than silicon, suggesting a high concentration of gap states, possibly originated from unpassivated surface of porous silicon. Absorption peak between 3120 and 4000cm⁻¹ (0.39 and 0.5eV) was found and is shown in Figure 4.1.2c. It indicates the presence of O-H bonds. The transmittance spectra of porous silicon etched in 49.5% aqueous hydrofluoric acid often have that absorption peak.

4.1.3 Reflectance spectra

Because of the strong absorption of the substrate, transmittance spectra give no information on porous silicon at energies above 1.4eV. Moreover, as we have mentioned, transmittance spectra of porous silicon on low resistivity substrates are affected by the free carrier absorption. Therefore, we sought for other methods to study the above gap optical properties. Reflectance spectroscopy is a powerful tool for the analysis of the optical properties of material. It is not strongly affected by the thickness of the porous silicon layer and the presence of the substrate as in the transmittance spectroscopy. As shown in Figure 4.1.3.1 the reflectance spectra of silicon wafers are almost identical, within an error of ±1%, and independent of resistivity. The peaks at 3.4 and 4.5eV are identified to be the E₁ and E₂.
Fig 4.1.3.1 Reflectance spectra of silicon of resistivity of
(a) 0.01 Ωcm, (b) 0.1 Ωcm, (c) 1 Ωcm and (d) 10 Ωcm.
From (a) to (d) have 5% offset
transitions.\textsuperscript{[G2]} It is because the two peaks correspond to energies much larger than the band gap energy and the dopants mainly affect the states near band gap. The energy range of reflectance spectra taken is from 0.39 to 5eV. The sudden change at 1.5eV is due to the coincidental dip in the reflectance of the aluminium reference mirror and to the change of detectors, which also occurs at this energy. The reflectance spectra of porous silicon have different shapes, depending on the substrates and the conditions of anodization. Those made from 0.01 $\Omega$-cm wafers have two peaks near the positions of $E_1$ and $E_2$ peaks of silicon. Figure 4.1.3.2a shows the reflectance spectrum of sample A6. It is very close to the reflectance spectrum of silicon wafer of same resistivity, but has slightly lower reflectance near the $E_2$ peak and below the band gap, and has ripples due to the interference effect. The similarity of the two spectra, especially near the $E_1$, shows the preservation of silicon-like properties in porous silicon on substrates of resistivity of 0.01 $\Omega$-cm, despite the anodization. Reflectance spectra of porous silicon on substrates of resistivity higher than 0.01 $\Omega$-cm have only a broad peak or no peak at all in the energy range between 2 and 5eV. These deviations from the reflectance spectra of silicon are a measure of porosity and crystalline size. Figure 4.1.3.2b shows the reflectance spectrum of sample B6. Comparing with the reflectance spectrum of silicon wafer of 0.1 $\Omega$-cm resistivity, the reflectance is considerably lower in the measured range and there is only a very broad peak in the range between 2 and 5eV. Figure 4.1.3.2c shows the reflectance spectrum of sample C10 which is almost identical to that of sample B6 in Figure 4.1.3.2b, despite the fact that C10 is made from 1 $\Omega$-cm wafer. Figure 4.1.3.2d shows the reflectance spectrum of sample D11. The peak near $E_1$ and $E_2$ nearly disappear. The relation of these peaks to the
Figure 4.1.3.2a  Reflectance spectra of (i) sample A6 and (ii) silicon wafer of resistivity of 0.01Ωcm.
Figure 4.1.3.2b Reflectance spectra of (i) sample B6 and (ii) silicon wafer of resistivity of 0.1Ωcm.
Figure 4.1.3.2c Reflectance spectra of (i) sample C10 and (ii) silicon wafer of resistivity of 1Ωcm.
Figure 4.1.3.2d Reflectance spectra of (i) sample D11 and (ii) silicon wafer of resistivity of 10Ωcm.
In general, the reflectance of porous silicon is small, as compared with that of crystalline silicon in the range between 2 and 5eV. The reflection coefficient, \( R \), is given by

\[
R = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2}
\]

where \( n \) and \( k \) are the refractive index and extinction coefficient respectively. Low in reflectance often implies that extinction coefficient is small and refractive index is close to one, i.e. the medium is transparent. However, this is not the case for porous silicon. One cannot see the substrate through the porous silicon film, otherwise the measured reflectance spectra will resemble that of silicon. Also strong visible photoluminescence must be preceded by strong absorption of energies. Photoluminescence excitation experiments have shown that there is strong absorption above 3-5eV. The low reflectance of porous silicon is therefore due to scattering of ultrafine silicon particles. As the wavelength of light becomes shorter, the scattering becomes stronger. Interference fringes are observed in all the reflectance spectra of porous silicon prepared for optical studies. They often have uniform depth, which suggest they are due to the presence of single layer of film. Some have modulated interference patterns (Figure 4.1.3.2e). In such case, there are two thin films formed on the substrate. The optical thicknesses determined from the fringes are consistent with those found in the transmittance and photoluminescence spectra as will be discussed in Section 4.1.4. To see if the spectra obtained are stable, some reflectance measurements were repeated after two months. Figures 4.1.3.3a-c show the reflectance spectra of samples A10, C10 and D11 and the corresponding reflectance spectra taken earlier. The interference pattern of the reflectance spectra
Figure 4.1.3.2e Interference patterns found in the reflectance spectra of samples B6 and C10.
Figure 4.1.3.3a  Reflectance spectra of sample A10

(i) as prepared and (ii) two months later.
Figure 4.1.3.3b  Reflectance spectra of sample C10
(i) as prepared and (ii) two months later.
Figure 4.1.3.3c  Reflectance spectra of sample D11

(i) as prepared and (ii) two months later.
of the sample, D11 prepared from 49.5% hydrofluoric acid changed a lot, indicating
the optical thickness had changed. Besides this, the peak in the range between 2 and
5eV had disappeared. Theiss\(^{[3]}\) had reported the similarly flattening of this peak
after thermal and anodic oxidation. The change in optical thickness is mostly due
to change in refractive index rather than the change in thickness. The change in
thickness only leads to a change in the separation of interference peaks, but not the
features of the reflectance spectra. The change in the refractive index may be
related to the oxidation of porous silicon. The reflectance spectra of porous silicon
prepared from hydrofluoric acid of concentrations other than 49.5% show little
change in the two months as shown in Figures 4.1.3.3a and 4.1.3.3b.

4.1.4 Optical thickness of the porous silicon layer

Interference patterns are found in the reflectance and the corresponding
transmittance\(^{[3]}\) spectra of porous silicon. They indicate the presence of a thin layer
of transparent material, most likely, the porous silicon layers, on top of the silicon
substrate. The conditions for constructive interference in reflectance and
transmittance spectra are

\[
2n d = m \lambda \quad (4.1.4.1)
\]

and

\[
2n d = (m + \frac{1}{2}) \lambda \quad (4.1.4.2)
\]

where \(n\) is the refractive index, \(d\) the thickness of the porous silicon layer, \(m\) an
integer, the order of interference and \(\lambda\) the wavelength. In a series of interference
peaks, if the first of the series at the longest wavelength is assigned to order

\[m = m' + 1,\]

where \(m'\) is an integer to be determined, then the \(q^{th}\) interference peak will be of
order \( m' + q \). Equation 4.1.4.1 becomes

\[
2 \frac{n d}{\lambda} = m' + q.
\]

The gradient of the plot \( q \) versus \( 1/\lambda \) gives the quantity \( 2nd \) and the intercept gives \( m' \). The order of each interference peak in the series is thus determined. Adjacent interference peaks in the reflectance spectra are equidistant in the energy scale from the visible to the near infrared range, suggesting the constancy of the refractive index of the porous layer in that range as shown in Figure 4.1.3.2e. Figure 4.1.4.1 shows the relation of the order of peaks, \( m \), to the reciprocal of wavelength, \( 1/\lambda \). The optical thickness, \( nd \) is found from the slope of the graph. The fact that all the graphs extrapolate to zero, confirms the correct assignment of the order of interference. Interference peaks observed in photoluminescence spectrum of sample C5 are marked with a "P" in the Figure 4.1.4.1. Please refer to Section 5.1.9 for the discussion of interference pattern observed in photoluminescence. Figure 4.1.4.2 shows the variation of optical thickness with the resistivity of the silicon wafers used to prepare porous silicon. For the heavily doped wafers, the optical thicknesses of porous silicon layer are larger.

4.1.5 Effective medium approximation

The effective optical properties of heterogeneous or composite systems can be described by a suitable mixture model incorporating the optical properties of the components making up the system. The effective medium approximation follows this idea. The dielectric constant of the heterogeneous system is related to the dielectric constants and the volume or mass fractions of the components of the system. Many such models, of different sophistication, have been proposed. For simplicity, two
Figure 4.1.4.1 Order of interference versus reciprocal of wavelength for samples A10, B9, C5 and D6.
- sample anodized in 11.1% HF with 1 mA for 90 minutes
○ sample anodized in 26.6% HF with 1 mA for 90 minutes
△ sample anodized in 49.5% HF with 1 mA for 90 minutes
● sample anodized in 11.1% HF with 2 mA for 50 minutes
△ sample anodized in 26.6% HF with 2 mA for 50 minutes
* sample anodized in 49.5% HF with 2 mA for 50 minutes

Figure 4.1.4.2 Optical thickness versus resistivity.
phase Bruggeman model was used to analyze our data. In the model, it is assumed that each component is spherical in shape and embedded in a sea of an effective dielectric medium. The effective dielectric constant has to satisfy the expression

\[ f_a \left( \frac{\varepsilon_a - \varepsilon}{\varepsilon_a + 2\varepsilon} \right) + f_b \left( \frac{\varepsilon_b - \varepsilon}{\varepsilon_b + 2\varepsilon} \right) = 0 \]  

(4.1.5.1)

where \( f_a, f_b, \varepsilon_a \), and \( \varepsilon_b \) are the volume fractions of phases a and b and their dielectric constants respectively. The sum of volume fractions equals to unity. In its application to porous silicon, \( f_a, \varepsilon_a \), and \( \varepsilon_b \) are taken as the porosity, dielectric constants of air and silicon respectively. \( f_b = \text{1} - f_a \) is the volume fraction of silicon. Figure 4.1.5 shows the variation of effective refractive index with porosity as determined from Equation 4.1.5.1. The square root of the effective dielectric constant is taken as the effective refractive index, assuming the extinction constant is negligible. For silicon, the extinction coefficient is often less than \( 10^{-4} \) in the infrared range. Results for two of the other models are also plotted on the same graph. In one of the models, the two phases form infinite layers of different dielectric constants. This is equivalent to the case of capacitors in series. The effective dielectric constant is given by

\[ \varepsilon = \varepsilon_{si} - p (\varepsilon_{si} - \varepsilon_{air}) \]  

(4.1.5.2)

where \( \varepsilon \) is the effective dielectric constant, \( p \) porosity, \( \varepsilon_{si} \), \( \varepsilon_{air} \) dielectric constant of silicon and air respectively. In the other model, one considers columns of different dielectric media running parallel to each other. This is equivalent to the case of capacitors in parallel. The effective dielectric constant is given by

\[ \varepsilon = (\varepsilon_{si} \varepsilon_{air}) / [p (\varepsilon_{si} - \varepsilon_{air}) + \varepsilon_{air}] \]  

(4.1.5.3)

At zero porosity the three models give the refractive index of silicon. When porosity
Figure 4.1.5 Refractive index predicted by effective medium approximation.
(a) : capacitors in series model
(b) : Bruggeman effective medium approximation
(c) : capacitors in parallel model
is equal to one, these models give the refractive index of air. Therefore the three curves in Figure 4.1.5 end at \((p=0, n=3.4)\) and \((p=1, n=1)\). The basic assumption of those models is that only two phases are involved. The assumption will fail when more than two phases are present in the system. The three models are different only in terms of different geometrical considerations. Earlier studies often treated the porous layer as containing many vertical, cylindrical pores in a layer of silicon. Scanning electronic microscope (SEM) result\(^{[61]}\) showed that the "tree structure" of pores is observed in low porosity silicon and a random network of interconnected pores is observed in high porosity silicon.

4.1.6 Determination of refractive index, porosity and thickness

Substitute the optical thickness determined from the study of interference peaks in the reflectance and transmittance spectra into Equation 3.8.1, an equation involving the ratio of porosity to refractive index is obtained. The equation can be casted in the form

\[
p / n = m / [\rho A (n d)]
\]

(4.1.6.1)

Quantities on the right-hand side of Equation 4.1.6.1 are all measurable. Using the Bruggeman effective medium approximation, discussed in Section 4.1.5, we have Equation 4.1.5.1 which gives the relationship between the porosity and the effective dielectric constant. With the approximation mentioned in Section 4.1.5 the effective refractive index is given by the square root of the effective dielectric constant. By solving Equations 4.1.5.1 and 4.1.6.1 simultaneously, the refractive index, the porosity and the thickness are determined. The results are summarized in Table 4.1.6. The porosity and the refractive index are smaller and the corresponding
Table 4.1.6 Estimation of porosity, refractive index and thickness by effective medium approximation

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\rho$($\Omega$cm)</th>
<th>$p$/n</th>
<th>$p$($%$)</th>
<th>$n$</th>
<th>$d$($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A5</td>
<td>0.01</td>
<td>0.086</td>
<td>24</td>
<td>2.8</td>
<td>9.6</td>
</tr>
<tr>
<td>A6</td>
<td>0.01</td>
<td>0.086</td>
<td>24</td>
<td>2.8</td>
<td>9.7</td>
</tr>
<tr>
<td>A7</td>
<td>0.01</td>
<td>0.033</td>
<td>10</td>
<td>3.2</td>
<td>10.3</td>
</tr>
<tr>
<td>A9</td>
<td>0.01</td>
<td>0.11</td>
<td>29</td>
<td>2.7</td>
<td>8.6</td>
</tr>
<tr>
<td>A10</td>
<td>0.01</td>
<td>0.056</td>
<td>17</td>
<td>3.0</td>
<td>13.3</td>
</tr>
<tr>
<td>A11</td>
<td>0.01</td>
<td>0.034</td>
<td>11</td>
<td>3.2</td>
<td>13.3</td>
</tr>
<tr>
<td>B5</td>
<td>0.1</td>
<td>0.30</td>
<td>57</td>
<td>1.9</td>
<td>4.6</td>
</tr>
<tr>
<td>B6</td>
<td>0.1</td>
<td>0.20</td>
<td>44</td>
<td>2.3</td>
<td>5.3</td>
</tr>
<tr>
<td>B7</td>
<td>0.1</td>
<td>0.18</td>
<td>42</td>
<td>2.3</td>
<td>4.5</td>
</tr>
<tr>
<td>B9</td>
<td>0.1</td>
<td>0.26</td>
<td>53</td>
<td>2.0</td>
<td>4.9</td>
</tr>
<tr>
<td>B10</td>
<td>0.1</td>
<td>0.18</td>
<td>41</td>
<td>2.4</td>
<td>6.7</td>
</tr>
<tr>
<td>B11</td>
<td>0.1</td>
<td>0.15</td>
<td>37</td>
<td>2.5</td>
<td>4.4</td>
</tr>
<tr>
<td>C5</td>
<td>1</td>
<td>0.39</td>
<td>65</td>
<td>1.7</td>
<td>3.6</td>
</tr>
<tr>
<td>C6</td>
<td>1</td>
<td>0.32</td>
<td>59</td>
<td>1.8</td>
<td>4.1</td>
</tr>
<tr>
<td>C7</td>
<td>1</td>
<td>0.20</td>
<td>44</td>
<td>2.3</td>
<td>2.8</td>
</tr>
<tr>
<td>C9</td>
<td>1</td>
<td>0.28</td>
<td>55</td>
<td>2.0</td>
<td>4.3</td>
</tr>
<tr>
<td>C10</td>
<td>1</td>
<td>0.28</td>
<td>55</td>
<td>2.0</td>
<td>4.7</td>
</tr>
<tr>
<td>C11</td>
<td>1</td>
<td>0.20</td>
<td>45</td>
<td>2.3</td>
<td>3.1</td>
</tr>
<tr>
<td>D5</td>
<td>10</td>
<td>0.39</td>
<td>65</td>
<td>1.7</td>
<td>3.6</td>
</tr>
<tr>
<td>D6</td>
<td>10</td>
<td>0.64</td>
<td>82</td>
<td>1.3</td>
<td>3.2</td>
</tr>
<tr>
<td>D9</td>
<td>10</td>
<td>0.45</td>
<td>70</td>
<td>1.6</td>
<td>3.6</td>
</tr>
<tr>
<td>D10</td>
<td>10</td>
<td>0.68</td>
<td>84</td>
<td>1.2</td>
<td>3.2</td>
</tr>
<tr>
<td>D11</td>
<td>10</td>
<td>0.49</td>
<td>72</td>
<td>1.5</td>
<td>1.9</td>
</tr>
</tbody>
</table>
thickness is larger when heavily doped substrates are used in the preparation of porous layer. The result of the dependence of porosity on doping concentration is consistent with previous scanning electron microscope (SEM) result\textsuperscript{[60]} and Beale’s result.\textsuperscript{[81]} Figures 4.1.6a, 4.1.6b and 4.1.6c show the variations of determined refractive index, thickness and porosity with the resistivity of the substrates. The porosities of those samples, with two peaks ($E_1$, $E_2$) in the reflectance spectra are found to be less than 30%. It may be concluded that low porosities samples still retain the crystalline properties of bulk silicon and effective medium approximation is valid for this range of porosities. In Ferrieu’s spectroscopic ellipsometry studies\textsuperscript{[51]} of porous silicon, he showed that the imaginary part of the dielectric function of porous silicon of porosity lower than 31% formed on 0.01 Ω-cm substrates had two peaks at same energies as the $E_1$ and $E_2$. For porosity greater than 48%, on 10 Ω-cm substrates, he found only one peak between the positions of $E_1$ and $E_2$.

4.1.7 Thickness measured by optical microscopy

To check the validity of applying the Bruggeman effective medium approximation to porous silicon, nine samples were cleaved and the cross sections of the porous layer were studied under an Olympus BH2 microscope. Thicknesses of the porous layers were measured with the aid of an OSM-4 filar micrometer eyepiece. The scale uncertainty is ±0.1μm and the magnification is 1000×. The thickness varies from point to point. Three readings were taken in the central portion of the porous silicon film for each sample. Once the thickness is obtained. Refractive index can be determined without invoking effective medium
Figure 4.1.6a  Determined porosity of porous Si versus resistivity of wafer.
Figure 4.1.6b Determined refractive index of porous Si versus resistivity of wafer.
- sample anodized in 11.1% HF with 1mA for 90 minutes
○ sample anodized in 26.6%HF with 1mA for 90minutes
△ sample anodized in 49.5%HF with 1mA for 90 minutes
● sample anodized in 11.1%HF with 2mA for 50 minutes
□ sample anodized in 26.6%HF with 2mA for 50 minutes
* sample anodized in 49.5%HF with 2mA for 50 minutes

Figure 4.1.6c  Determined thickness of porous Si versus resistivity of wafer.
approximation. Thicknesses measured and refractive indices determined this way are compared with the corresponding values obtained from the effective medium approximation in Figures 4.1.7a and 4.1.7b respectively.

4.1.8 Validity of the effective medium approximation

The calculations in Section 4.1.6 were based on the results of mass loss and optical thickness. In the calculations of porosity it was assumed that all the removed silicon came from the pores and the removal of a complete layer was neglected. This tends to overestimate the porosity. In some of our samples very high porosities and refractive indices close to one were obtained from the calculation. However, results based measurements with optical microscopy show deviations from those calculated. Pickering had reported the wide scatter of optical density for the same gravimetric density of porous silicon layer. Pickering[P3] and Theiss[T3] had used the effective medium approximation in their optical studies of porous silicon independently. Pickering[P3] concluded that the approximation did not describe the results of porous silicon prepared from non-degenerate substrates. Theiss[T3] claimed that the approximation was not suitable for high porosity porous silicon. We had assumed fine spheres of different dielectric constants in the model. However, it may not be the true case. In the Figure 4.1.8 the refractive indices determined from optical thicknesses and thicknesses directly measured by optical microscope are close to the curve described by Bruggeman effective medium approximation at low porosity, but scatter much more at high porosity. The deviations are probably due to the breakdown of the assumption of having only two phases. Pickering and Thesis suggest that it is more precise to include silicon dioxide in the effective
Figure 4.1.7a  Thickness versus optical thickness.
Figure 4.1.7b Comparison of refractive indices.

$n$ : from prediction of EMA

$n'$ : from measured thickness and optical thickness
Figure 4.1.8 Refractive index versus porosity.

(*) : refractive index from thickness measured
(a) : capacitors in series model
(b) : Bruggeman effective medium approximation
(c) : capacitors in parallel model
medium approximation, but there is no simple expression for the effective medium approximation in this case.

4.2 Infrared transmission studies

4.2.1 Experimental setup

Two infrared spectrophotometers were used for this purpose. One is a PYE UNICAM SP1100ES whose spectral range is from 400 to 4000cm\(^{-1}\). It has three linear ranges because of the gratings and filters used. They are 400 to 1215cm\(^{-1}\), 1215 to 2150cm\(^{-1}\) and 2150 to 4000cm\(^{-1}\). The other infrared spectrophotometer used was JASCO A-100 in the Chemistry Department which scans from 4000cm\(^{-1}\) down to 650cm\(^{-1}\).

4.2.2 Infrared spectra

There are no measured infrared spectra for porous silicon on substrates of resistivity of 0.01 \(\Omega\)-cm because of the nearly null transmittance due to free carrier absorption. For porous silicon on substrates of resistivity of 0.1 and 1 \(\Omega\)-cm there are often found absorption peaks at 650, 870 and 2100cm\(^{-1}\), corresponding to the Si-H bending, Si-H\(_2\) scissor and Si-H stretching mode respectively. For porous silicon on substrates of resistivity of 10 \(\Omega\)-cm there are absorption peaks at 650, 835, 870 and 2100cm\(^{-1}\). The absorption peak at 835cm\(^{-1}\) corresponds to the Si-H\(_2\) wagging mode. The absorption band from 1040 to 1160cm\(^{-1}\) is often found in the spectra of porous silicon prepared in 49.5% hydrofluoric acid. This broad absorption band corresponds to the Si-O-Si stretching mode. Figures 4.2.2.1a-c show the infrared spectra of the porous silicon on substrates of resistivities of 0.1 to 10 \(\Omega\)-cm prepared.
Figure 4.2.2.1a    Infrared transmittance spectra of porous silicon sample B5 to B11 on 0.10 cm substrate. The spectra are shifted up in transmittance by the percentage indicated.
Figure 4.2.2.1b: Infrared transmittance spectra of porous silicon sample C5 to C11 on 1Ωcm substrate. The spectra are shifted up in transmittance by the percentage indicated.
Figure 4.2.2.1c  Infrared transmittance spectra of porous silicon sample D5 to D11 on 100μm substrate. The spectra are shifted up in transmittance by the percentage indicated.
in different concentrations of hydrofluoric acid. There is no obvious relation between the vibration modes and the etching conditions. The transmittance of the porous silicon is slightly higher than that of the same type of wafer, except at the absorption peaks, because of its porous nature.

The hydride peaks at 870 and 2100 cm\(^{-1}\) were always observed. Although Tsai\[^{16}\] reported the correlation of photoluminescence intensity and magnitude of hydride peaks, there is no obvious relation between the hydride peaks and the photoluminescence from our studies. The broad oxygen peak is always found in the spectra of aged porous silicon. In the spectra of as-prepared porous silicon or those that had been dipped in hydrofluoric acid just prior to infrared transmission measurement the broad oxygen peak is not observed. Removal of the broad oxygen peak after dipping in hydrofluoric acid shows the presence of oxide overlayer on the surface of aged porous silicon. Figure 4.2.2.2 shows the infrared spectra of sample #92 before and after immersion in 49.5% hydrofluoric acid for one minute. Enhanced photoluminescence was observed with naked eye after immersion. Correlation of the vanishing of Si-O-Si bonds and enhancement of photoluminescence shows that siloxene is not the origin of the visible photoluminescence of porous silicon. Moreover, the absorption peak due to Si-O-Si bonds is much larger than the one due to silicon hydride bond, while oxygen and hydrogen in siloxene are in the ratio of one to two.
Figure 4.2.2.2 Infrared transmittance spectra of sample #92 (a) before (b) after dipped in 49.5% hydrofluoric acid for one minute.
Chapter 5
Photoluminescence and Photoexcitation

5.1 Photoluminescence studies

5.1.1 Experimental setup

Photoluminescence spectra were measured by the setup shown in Figure 5.1.1. The excitation source was the 4579Å line from an argon ion laser, (Coherent Innova 70). The incident power used was about 0.08mW, which was measured by a calibrated silicon p-i-n detector at the position of the sample. The laser beam was modulated by a chopper which also provided the reference signal for the lock-in amplifier, (Stanford Research Systems SR530). A small mirror was used to direct the laser beam to the sample and the beam was focused by the objective lens, L1. The focal length of L1 was 50mm. Schott GG475 longpass filter was used to cut off scattered and specularly reflected laser light. The focal length of the lens, L2, was 250mm, which was chosen to match the F number of the spectrometer (f/6.8). The spectra were collected through a 0.75m Czerny-Turner scanning spectrometer, (SPEX1702 with a 1200 grooves/mm grating blazed at 5000Å). The reciprocal linear dispersion of the grating for the first order diffraction is 10Å/mm. The entrance and exit slits were set at a width of 2mm and masks with rectangular aperture of a height 1cm were placed before the entrance and after the exit slits. Photoluminescence was detected by a photomultiplier tube, (Hamamatsu R2658). The typical average anode dark current of R2658 was 1nA at a tube voltage of 1250V. The signal current of the anode of the photomultiplier tube was converted by a preamplifier, (ORIEL 70710) at a gain of 1MV/A and with a bandwidth of
Fig. 5.1.1 Setup for Photoluminescence measurements.
100kH. To improve the signal to noise ratio, the preamplifier signal was fed into a lock-in amplifier. A line filter, a line × 2 filter and a bandpass filter of the lock-in amplifier were used to filter out unwanted noise further. The output of the lock-in amplifier was scaled to 10V full scale and was recorded in a personal computer through a 12 bit analog to digital interface card (DAS8-pga, Keithley).

For quick visual observation of the photoluminescence, porous silicon samples were placed in CC-20, a chromato-vue cabinet (Ultra-violet Products) which was designed for observing the fluorescence of gem stones. It has a 3650Å ultraviolet source inside.

5.1.2 Calibration of the spectral response of setup

The spectral response of the setup was calibrated by using a tungsten-halogen quartz lamp as a standard light source. The temperature of the lamp was measured by a Pyro Micro-optical Pyrometer to be 3013K when 12V was supplied. The spectrum of the tungsten-halogen quartz lamp recorded with the setup is shown in Figure 5.1.2a. Assuming the lamp is a black body radiator, the energy density of radiation follows the Planck’s Law, i.e.

\[ P_\lambda = \frac{8 \pi h c}{\lambda^5 \left( e^{\frac{h c}{\lambda k T}} - 1 \right)} \]

where \( P_\lambda \) is the energy density of radiation at wavelength \( \lambda \), \( h \) the Planck constant and \( c \) the speed of light. The spectrum calculated for a black body radiator at \( T = 3013K \) is shown in Figure 5.1.2b. The peak is arbitrarily normalized to 1, since we are only interested in the spectral shape and the relative response of the optical setup. The response is obtained by dividing the spectrum of Figure 5.1.2a by the
Figure 5.1.2a  Spectrum of the tungsten-halogen quartz lamp.
Figure 5.1.2b  Ideal black body radiation at 3013K.
Figure 5.1.2c  Response of photoluminescence measurement system.
spectrum of Figure 5.1.2b, and the result is shown in Figure 5.1.2c. It is found that the peak response is at 430nm (2.88eV) which is between 400nm (3.1eV), wavelength of the maximum response of the R2658 photomultiplier tube and 500nm (2.48eV), the blazed wavelength of the grating.

5.1.3 The photoluminescence and the appearance of the porous silicon

The black, smooth samples of porous silicon were often found to have weak or no photoluminescence at room temperature. The yellow samples were often found to have strong visible photoluminescence. However, there were exceptions. There is no relation between photoluminescence and the surface morphology down to the scale of one micrometre, as observed from an optical microscope. Interference colour band was often found on the samples under room light illumination. Interference effect was also observed in the photoluminescence spectra of some of the samples. Room temperature photoluminescence excited by the 4579Å argon ion laser line was seen to vary from bright red to orange in colour, depending on the sample. Under excitation of ultraviolet radiation at 3650Å, photoluminescence varies from bright red to green. Figures 5.1.3.1-6 show the appearance of porous silicon under room light and 3650Å excitation. Porous silicon samples prepared on wafers of different resistivities under same conditions are showed in same figure. In these figures, porous silicon samples formed on 0.01Ωcm wafers are placed on the upper right quadrant and those on 0.1, 1 and 10Ωcm wafers are placed one by one, following the clockwise sense.
Figure 5.1.3.1  Appearances of A5, B5, C5 and D5 (samples anodized with 1mA in 11.1% HF) under room light (upper photograph) and excitation of 3650Å (lower photograph)
Figure 5.1.3.2  Appearances of A6, B6, C6 and D6 (samples anodized with 1mA in 26.6% HF) under room light (upper photograph) and excitation of 3650Å (lower photograph)
Figure 5.1.3.3  Appearances of A7, B7, C7 and D7 (samples anodized with 1mA in 49.5% HF) under room light (upper photograph) and excitation of 3650Å (lower photograph)
Figure 5.1.3.4  Appearances of A9, B9, C9 and D9 (samples anodized with 2mA in 11.1% HF) under room light (upper photograph) and excitation of 3650Å (lower photograph)
Figure 5.1.3.5  Appearances of A10, B10, C10 and D10 (samples anodized with 2mA in 26.6% HF) under room light (upper photograph) and excitation of 3650Å (lower photograph)
Figure 5.1.3.6  Appearances of A11, B11, C11 and D11 (samples anodized with 2mA in 49.5% HF) under room light (upper photograph) and excitation of 3650Å (lower photograph)
5.1.4 Effect of laser radiation on porous silicon

We noticed that the photoluminescence was sometimes changing with illumination time. To rule out the possibility of the instability or drift of the laser, the photoluminescence and excitation beams were simultaneously monitored. The laser beam was divided into two by a beam splitter. One was monitored by a calibrated silicon p-i-n detector. The other was used as excitation, as in the case of the study of the photoluminescence described in Section 5.1.1. To determine the radiation damage threshold of the samples, the laser power was gradually increased until a rapid fall of photoluminescence was observed. The threshold power varied from sample to sample, but was always of the order of 10mW/mm².

5.1.5 Photochemistry

Studies of the effect of laser radiation in different ambients were carried out like regular photoluminescence measurements by placing the sample in a glass tube through which different gases were passed continuously. Sample #79 was used in this study. A transient change in photoluminescence intensity was observed when the ambient was changed. Figure 5.1.5 shows the time variations upon changing the ambient. In dry or wet air ambient the photoluminescence intensity dropped first and then increased linearly with the duration of illumination. In nitrogen or argon it rose rapidly first and then increased linearly with the duration of illumination. The steady state rates of changes of intensities were almost the same among different ambients, but with different baselines. During the study of the effect of laser power on sample #79 an increasing photoluminescence signal under constant excitation was observed. The increase can be recognized as a
Figure 5.1.5  Variation of photoluminescence intensity of porous silicon in different ambients
combination of a linear and an exponential curves. The initial transient is exponential and prolong increase is linear with time.

5.1.6 Aging and photoluminescence

After the porous silicon has been stored in the ambient of air, its photoluminescence changed. Samples K27 and K28 were prepared using small anodizing current for a short time. When freshly prepared, they had coloured appearance, but no visible photoluminescence under the excitation of 3650Å ultraviolet radiation. There is no obvious change in their appearance after almost one year of storage. Nevertheless, they showed a strong visible photoluminescence under the same 3650Å excitation. Figure 5.1.6 shows the appearance of K28 under room light and 3650Å excitation.

5.1.7 Annealing studies of porous silicon

Some samples from Mr Cheung were annealed by the Rapid Thermal Annealing (RTA) technique. The peak energies and intensities of photoluminescence can be plotted roughly along a linear band as shown in Figure 5.1.7.1. The band can be divided into different zones according to the conditions of annealing. In descending peak energies, the zones are: (1) annealed in oxygen at 200°C and then dipped in hydrofluoric acid, (2) annealed in nitrogen at 200°C and then dipped in hydrofluoric acid, (3) annealed in oxygen at 200°C, (4) unannealed and (5) annealed in nitrogen at 200°C. The spectral response of the setup of photoluminescence measurement is also drawn as the solid line in the figure. Obviously it is not the main cause of the stronger photoluminescence intensity of porous silicon at higher
Figure 5.1.6  Appearance of sample K28 under room light (upper photograph) and excitation of 3650Å (lower photograph)
Figure 5.1.7.1 Intensity versus peak energy.

(Solid line: spectral response of setup)
energies. The observation that photoluminescence intensity increase with peak energy is naturally explained by the quantum confined model. The photoluminescence of smaller size silicon clusters has higher peak energy and the intensity is stronger as the excitonic enhancement effect become significant. It is not so simple to explain this by chemical models such as those involve siloxene and oligosilane.

Sample #12 was cut into pieces and was annealed in forming gas (15% H₂, 85% N₂) at different temperatures. Figure 5.1.7.2 shows the photoluminescence spectra of these pieces. All of the spectra were normalized to the same scale. The piece annealed at 450°C has a weaker photoluminescence than the unannealed one. The pieces annealed at 600 and 800°C have no photoluminescence. Tsai et al. showed that the photoluminescence intensity of porous silicon significantly decreased for annealing temperature between 300 and 400°C, same temperature range when hydrogen desorption is important, changing the surface termination from mainly dihydride to predominantly monohydride species. As a result, it is believed that silicon dihydride plays a key role in the luminescence process.

5.1.8 Photoluminescence spectra

The photoluminescence spectra of the samples are all very broad. The peak energies vary from 1.5 to 2.1eV. The full widths at half maximum, FWHM vary from 0.28 to 0.5eV. There is no simple relation between the peak energy and FWHM. Figures 5.1.8a, 5.1.8b and 5.1.8c show the photoluminescence of porous silicon prepared on wafers of resistivities of 10, 1 and 0.1 Ω-cm respectively. The vertical scales of these figures are the same. Peak energies of the photoluminescence
Figure 5.1.7.2 Photoluminescence spectra of porous silicon annealed under different conditions
Fig 5.1.8a Photoluminescence spectra of porous silicon on 10 Ωcm substrates.
Fig 5.1.8b Photoluminescence spectra of porous silicon on 1 Ωcm substrates.
Fig 5.1.8c  Photoluminescence spectra of porous silicon on 0.1 Ωcm substrates.
of porous silicon (samples D7, C7, B7 in Figures 5.1.8a, 5.1.8b and 5.1.8c respectively) prepared in 49.5% hydrofluoric acid are around 2eV. The peaks tend to be symmetric in shape. Peak energies of other spectra shown are in the range of 1.5 to 1.7eV. These spectra have a longer tail on the high energy side than on the low energy side. The intensities of the photoluminescence of porous silicon prepared on 1 or 10 Ω-cm substrates are often found to be stronger and with higher peak energy, but of that prepared on 0.1 Ω-cm wafers are often weaker.

We have estimated the upshift of band gap based on the particle in a cubic-box model, using free electron mass. The upshifts of the ground state are 0.9eV and 0.4eV when the linear dimension of the cube are 11 and 17Å respectively. Read’s first principle calculations\(^{[81]}\) of quantum wires give upshifts of 0.9 and 0.4eV for 17 and 29Å thickness wires respectively. The size estimations obtained in Read’s calculations and simple particle in a cubic-box model are confirmed, at least in the same order of magnitude, by X-ray diffraction and Raman spectroscopy which will be discussed in Section 6.1.

Generally the width of the photoluminescence peak of the quantum well is expected to be very narrow. The broad photoluminescence peak of porous silicon is a result of heterogeneous broadening from a collection of quantum systems of various sizes. The shape of the peak shows that the distribution of sizes of quantum systems is asymmetric with respect to its peak and the side representing larger sizes has steeper distribution than that representing smaller sizes. For small sizes, the excitonic effect is more important.\(^{[01,02]}\) Therefore the photoluminescence spectra tend to pick out smaller silicon columns whose photoluminescence peaks are at higher energies.
5.1.9 Interference

Interference pattern was found in some photoluminescence spectra as shown in Figures 5.1.8a and 5.1.8b. The optical thicknesses deduced from the interference peaks are consistent with the corresponding result obtained from the reflectance and transmittance spectra. The occurrence of the interference patterns are not as common as those in the reflectance or transmittance spectra. Photoluminescence originates from the different depths of the thin layer which causes interference adds up with different phases. As a result the contrast of interference pattern in photoluminescence is worse than those observed in reflectance and transmittance spectra, especially for relatively thick film. Two of the interference peaks observed in photoluminescence have been plotted in Figure 4.1.4.1. They deviate from those obtained from transmittance and reflectance studies, because the refractive index of porous silicon in the visible is different from that in the near infrared.
5.2 Photoexcitation studies

5.2.1 Experimental setup

Light from an ORC XM-150, xenon lamp was focused onto the entrance of a 0.3m scanning monochromator (Model 218, GCA/McPherson) by a quartz lens. An iris diaphragm placed between the lamp and the lens was used as the aperture stop to match the F number of the monochromator and minimized the scattered light inside the monochromator. Monochromatic light from the exit of monochromator was focused onto the sample by two quartz lenses. Two iris diaphragms were placed between the lenses to ensure a parallel beam and reduce stray light. Lock-in detection scheme similar to the one used in photoluminescence setup was used to obtain photoexcitation spectra. Schott BG40, bandpass filter was used to further reduce the stray light. Luminescence was collected and directed to an EMI 9558QB photomultiplier tube by a lens. A long pass filter was placed before the lens to block reflected and scattered excitation light. The output of the photomultiplier tube was connected to a home-made transimpedance amplifier. The voltage signal was processed by the SR530 lock-in amplifier and output to Omegaline 640, a recorder. To eliminate the contributions of the spectral variations of the optical components and xenon lamp to the photoexcitation spectra, the spectral response of the optical setup was measured with the sample replaced by an aluminium mirror. In the measurement a personal computer equipped with a Metrabyte DAS8-pga, a 12 bit analog to digital interface card was used instead of the above lock-in detection. The photoexcitation spectrum of the sample was recorded first. The background stray light spectrum was also recorded. This was done with the output from the monochromator blocked off. Then an aluminium mirror was mounted instead of the
sample. The reflectance spectrum taken is the characteristics throughput spectrum of the whole setup with the xenon lamp as the source. The background noise spectrum reflected by the aluminium mirror was also recorded with the excitation beam blocked at exit of the monochromator. The differences of photoexcitation spectrum of the sample and the corresponding background noise were evaluated by the personal computer. The difference in the reflectance spectra of the aluminium mirror and the corresponding background noise were also evaluated by the personal computer. Normalized photoexcitation spectrum was calculated as the ratio of the two values.

5.2.2 Result

Figure 5.2.2.1 show photoexcitation spectra of a sample were taken with three longpass filters: OG570, RG630 and RG695. The longpass filters are named according to the wavelength at which the transmittance is 50%. For example, the transmittance of OG570 at 570nm is 50% and close to 1 for longer wavelength radiation. The corresponding intensities are approximately in the ratio of 3:5:9 which show the distribution of power in different ranges roughly. The peak is at 3.9eV (320nm) and the FWHM is 1.16μm. Normalized photoexcitation spectra (Figure 5.2.2.2) have a peak around 3.4eV (365nm) and FWHM of 0.9eV (1.2μm).
Figure 5.2.1 Setup for Photoexcitation measurement
Figure 5.2.2.1  Photoexcitation spectra of porous silicon through different longpass filters
Figure 5.2.2.2  Normalized photoexcitation Spectrum
Chapter 6
Discussions and conclusions

6.1 Information from peer groups

6.1.1 Raman scattering

Tse\[77\] had obtained a series of Raman\[11,85\] and photoluminescence spectra of porous silicon prepared by Mr Cheung. From the deviation of the Raman shift with respect to that of crystalline silicon he found that the grain sizes of the porous silicon vary from 25 to 200Å.\[11, 85\] The Raman and photoluminescence spectra were obtained from the same points on the samples, thus ensuring inhomogeneity of porous silicon is not an issue. He found no correlation between the Raman shift and the intensity or peak energy of the corresponding photoluminescence spectrum.

6.1.2 X-ray diffraction

Ling\[12\] had performed an experiment of grazing-incidence X-ray diffraction of sample K31. At 2θ = 69.2°, there is a broad peak of 5° FWHM which is the (400) diffraction. From the width and using Debye Scherrer formula crystallite size is estimated to be 20Å.

Both Raman scattering and X-ray diffraction show the presence of silicon clusters of size of several nanometres. Existence of silicon clusters of nanometre size is the necessary condition of both quantum confinement and oligosilane bridge model.
6.2 Photoluminescence and annealing

We have observed that the peak energies and intensities of the photoluminescence of porous silicon change with different annealing treatments. After annealed in oxygen at 200°C, porous silicon has stronger photoluminescence and blueshifted peak energies. Dipping in hydrofluoric acid for a few seconds further enhances the effect. There is no obvious difference in peak energies and intensities of our porous silicon, whether they are as prepared and annealed in nitrogen at 200°C. Nevertheless, dipping in hydrofluoric acid still leads to the blue shift of peak energies and increase in intensities of photoluminescence. It is clear why this is so in the context of quantum confinement model. The surface of the nanometre size silicon cluster is oxidized to form silicon dioxide during annealing in oxygen. So the photoluminescence peak blueshiftes and the intensities increase. Dipping in hydrofluoric acid dissolves the silicon dioxide on the surface. Silicon dioxide was formed when the sample is exposed to air again. The size of silicon cluster decreases at each cycle of oxidation and dipping. Therefore the photoluminescence peak energies will also blueshift and the intensities will increase.

The decrease of photoluminescence of porous silicon annealed over 400°C is also explainable by the quantum confinement model. It is related to the desorption of hydrogen. The increase of dangling bonds leads to the increase of non-radiative recombination centres and so the photoluminescence drops. The passivation of surface by hydrogen is a necessary condition for visible photoluminescence of nanometre size silicon. Prokes suggested that the disappearance of photoluminescence at high temperature is due to the destruction of polysilane on the surface. It is however more difficult to explain the blueshift of photoluminescence
after dipping in hydrofluoric acid with chemical models.

Similar argument may be applied to the observation of increased visible luminescence of aged porous silicon. When the samples were stored in air for a long time, silicon dioxide was formed on the surface and the silicon clusters became smaller. Therefore the photoluminescence becomes more intense.

6.3 Photoluminescence and the etching conditions

Same peak energies and order of intensities of photoluminescence are found for samples on 1 and 10 Ω-cm substrates which have undergone the same anodization conditions. Samples on 0.1 Ω-cm substrates prepared with the same conditions have almost the same peak energies, but with weaker intensities. Samples on 0.01 Ω-cm substrates have no significant photoluminescence. Figure 6.3.1 shows the results. The distribution of peak energy and intensity of samples on 1 and 10 Ω-cm is similar to the one shown in Figure 5.1.7.1. The variation cannot be explained by the relatively flat response of the setup. The most probable explanation is that the excitonic effect become significant as the size of the silicon cluster is smaller.

The variation of the peak energies with the concentrations of hydrofluoric acid is shown in Figure 6.3.2. The peak energies of porous silicon prepared from 25% hydrofluoric acid are lower than those prepared from 10 and 50% hydrofluoric acid. Zhang et al.[21] had presented their results of stepwise descend of photoluminescence peak energies of porous silicon when the concentration of hydrofluoric acid used in the preparation was increased from 12 to 33% and explained by a formation mechanism based on the quantum confinement of porous silicon walls.
Figure 6.3.1 Intensity versus peak energy.

( Solid line : spectral response of setup )
Figure 6.3.2 Peak energy versus concentration of hydrofluoric acid.
6.4 Consideration of different models in visible photoluminescence of porous silicon

Ferrieu's spectrometric ellipsometry studies\cite{Ferrieu} found no evidence of an amorphous phase in porous silicon. As discussed in Section 4.2.2, the vanishing of Si-O-Si absorption band in infrared transmission and the enhancement of photoluminescence of porous silicon after dipping in hydrofluoric acid show that siloxene does not play the key role in the photoluminescence of porous silicon. Recent extend X-ray absorption fine structure (EXAFS) measurement\cite{Friedman} also did not find any Si-O bond in porous silicon. Friedman showed that, in the photoexcitation and photoluminescence spectra, there are significant differences in the spectral shapes and the Stokes shifts for siloxene and porous silicon. Although there are many derivatives of siloxene, the presence of siloxene in porous silicon is not likely.

There are many common points in the quantum confinement model and silane model. Presence of hydride is necessary in both models. In the context of the quantum confinement model, the intensity and peak energy of photoluminescence are higher when the size of silicon cluster becomes smaller. Positive result in correlation of microstructure and the photoluminescence of porous silicon was published.\cite{Prokes} However, there exists opposite result. Prokes\cite{Prokes} observed that the intensity and the peak energy of photoluminescence depended on the surface area and the content of hydrogen respectively and concluded that the occurrence of visible photoluminescence is related to the polysilane/hydride complexes. It is difficult to distinguish between the effect of increasing surface area and diminishing of cluster size. The blue shift of photoluminescence after dipping in hydrofluoric acid is a consequence of the quantum confinement model alone, but some research groups\cite{Prokes} observed no such blue shift. Quantum confinement model can explain our results.
more satisfactorily.

Although both the quantum confinement model and silane model are the most accepted models, they have not included some of the experimental results. Lifetime of luminescence of porous silicon is several tens of microseconds long\textsuperscript{[RH, T4, VII]} while lifetime of luminescence of direct gap semiconductor is typically not more than a few nanoseconds. There is larger Stokes shift between photoexcitation and photoluminescence spectra which is characteristic of absorption by extended states and emission by trap of localized states.\textsuperscript{[P2]} The mechanism of visible photoluminescence of porous silicon would not base on either quantum confinement model or silane model only, but should be more complicated.

6.5 Conclusions

Current voltage characteristics of the porous silicon in the anodization setup were studied. In our results resistivity of the wafer used is the most important parameter. Interference fringes are observed in the transmittance and reflectance spectra. This shows that the porous silicon layer is uniform in thickness. The optical thicknesses found from the interference peaks in the transmittance and reflectance spectra also depend on the resistivities of substrates. Peaks alike $E_1$ and $E_2$ of bulk silicon were found in reflectance spectra of low porosity samples. As porosity is higher, there is greater difference in shape between the reflectance spectra of bulk and porous silicon. This leads us to analyse the result with the aid of Bruggeman effective medium approximation. The model seems too simple for porous silicon and cannot give very accurate results.

Visible photoluminescence of porous silicon has been reproduced in our
laboratory. Photoluminescence, which can be observed with the naked eyes, varies from red to orange and even green when porous silicon is excited with ultraviolet radiation. The etching conditions to precisely control the colour of photoluminescence have not been known thoroughly yet. Porous silicon prepared in 49.5% hydrofluoric acid gives higher energy photoluminescence than those prepared in less concentrated hydrofluoric acid. Using small anodization current, porous silicon prepared on 1 and 10 Ω-cm wafers gives stronger photoluminescence than those prepared on less resistive wafers.

The mechanism of the visible photoluminescence of porous silicon is still being actively studied. We think that siloxene is not involved in the mechanism of visible photoluminescence of porous silicon, but neither the quantum confinement model nor the presence of polysilanes/hydride complexes can be ruled out. The results from annealing porous silicon and the infrared transmittance studies show the presence of silicon hydride is necessary in the mechanism of visible photoluminescence, but it is not a sufficient condition. Further studies should be carried out to distinguish the two. The variation of photoluminescence intensity and the corresponding peak energy of photoluminescence of annealed samples and samples for optical studies is possibly excitonic enhancement effect which is an important consequence of quantum confinement models.
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