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PREPARATION AND CHARACTERISATION OF POROUS SILICON AND POROUS SILICON BASED COMPOSITE MATERIALS

A thesis submitted to the University of Dublin, Trinity College
for the degree of Doctor of Philosophy

By

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Abbreviations

AFM	Atomic Force Microscopy
aqu	aqueous
bd	break down
BE	Binding Energy
BET	Brunauer-Emmet-Teller
BJH	Barrett-Joyner-Halenda
bsi	back side illumination
BuLi	n-butyl lithium
CB	conduction band
CBM	Current burst model
Cp	Cyclopentadienyl
CpNa	Sodium cyclopentadienide
CTAC	Cetyltrimethylammonium chloride
CVD	Chemical Vapour Deposition
Cz	Czochralski
DMF	Dimethyl formamide
DMSO	Dimethyl sulfoxide
EL	Electroluminescent
EtOH	Ethanol
FA	formamide
FcLi	Lithiated ferrocene
FESEM	Field Emission Scanning Electron Microscope
fsi	front side illumination
FTIR	Fourier Transform infrared
FZ	floating zone
HF	Hydrofluoric acid
IS	Isomer shift
i-V	current-voltage
J	Current density

JCPDS	Joint Committee on Powder Diffraction Standards
MCT	Mercury Cadmium Telluride
MeCN	Acetonitrile
MEMS	Micro-Electro-Mechanical-Systems
MG-Si	Metallurgical-grade silicon
MR	Magnetoresistance
NaOBu ^t	Sodium <i>tert</i> -Butoxide
NEt ₃	Triethyl amine
nm	nanometres
org	organic
PL	Photoluminescence
ppba	parts per billion atomic
PS	Porous silicon
QC	quantum confinement
RE	Rare earth
rpm	rotations per minute
RT	Room temperature
SCR	Space charge region
SEM	Scanning Electron Microscopy
SIMS	Secondary Ion Mass Spectroscopy
SQUID	super-conducting quantum interference device
TBAP	Tetrabutylammonium perchlorate
TEM	Transmission Electron Microscopy
TEOS	Tetraethylorthosilicate - Si(OEt) ₄
THF	Tetrahydrofuran
UHV	Ultra high vacuum
VB	Valence band
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray diffraction

Summary

The main aim of the thesis was to develop new advanced materials based on porous silicon. In chapters II and III, the fabrication of porous silicon by electrochemical etching using different aqueous and organic electrolytes have been explored. The structure and properties of porous silicon such as porosity, thickness and pore depth were studied as a function of etching parameters and anodisation conditions which include HF concentration, current density, silicon resistivity etc. We have demonstrated that using conductive salts (here TBAP) in HF-DMF solution allows the etching of silicon samples with higher current density. A similar process without conductive salts would result in electropolishing.

The development of new composite material based on porous silicon is the highlight of this thesis. In chapter IV, magnetite-porous silicon composite materials were developed and characterised by Mössbauer, Magnetoresistance and magnetic measurements (SQUID magnetometer). We have prepared iron oxide layers on hydroxyl-terminated porous silicon using metallorganic precursors and sol-gel processing. We have demonstrated that magnetite-porous silicon composites can also be prepared by in situ co-precipitation of magnetic nanoparticles from the mixture of iron ($\text{Fe}^{3+}/\text{Fe}^{2+}$) salts taken with ammonia solution. We have found that this process results in the self-organisation of magnetite nanoparticles into dendrite- or fractal-like magnetite structures on porous silicon samples. We believe that the formation of fractal structures may be influenced by several factors such as dipole-dipole interaction of nanoparticles, solvent evaporation effects and pore morphology of the silicon substrate. The sintering of porous silicon-magnetite composites in vacuum resulted in the formation of the micron size linear arrays of magnetite microparticles on porous silicon. The formation of these arrays can be explained by the grain growth and fusion of magnetite nanoparticles. Sintered magnetite-porous silicon samples demonstrated relatively low room temperature magnetoresistance. The as-developed magnetic-porous silicon composite materials showed temperature dependent magnetoresistance properties, which may be useful for sensor applications.

In chapter V, the porous silicon-glass composite materials have been prepared by a sol-gel technique. The preparation of porous silicon-rare earth doped xerogel (glass) by the vacuum filtration method has been explored for the first time. We have also invented a new

method of producing xerogel and glass microtubes or capillaries using micro-channel glass substrates and sol-gel processing techniques. To the best of our knowledge this technology has not been previously reported or patented. The microtubes, which are produced by this method, showed the whispering gallery mode phenomenon, which has not been reported for aluminosilicate xerogel microtubes to date. The xerogel microtubes produced in this work might have potential applications as microcylindrical light emitters for optical communication components. The porous silicon acts a good matrix for the preparation of different xerogel composites, which can have potential applications in photonics.

In chapter VI, we have developed two approaches to functionalise silicon surfaces with ferrocene or cyclopentadiene *via* spacer groups and by direct bonding to silicon surfaces. We demonstrated that the functionalised silicon surfaces could be conveniently characterized by XPS, FTIR and PL (where appropriate) spectroscopy. All these techniques have proven the formation of new species and their covalent binding to the silicon surfaces after their treatment. Further studies using advanced STM and AFM techniques in combination with computer simulation will be necessary to understand these systems in more details. This is beyond the scope of this project and should be done in the future.

Chapter VII contains the experimental details of the procedures and techniques described in this thesis. Chapter VIII presents conclusions and the future outlook for the research performed in this project.

In overview, a number of very interesting porous silicon composites, which might have different potential applications in the near future. We also believe this work should contribute to both materials chemistry and technology.

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Dedicated to my mother

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I

Introduction

1.1 General introduction

Silicon is the one of the most technologically important materials known to mankind, dominating the microelectronic industry which influences our everyday lives. It is the most widely used material in the semiconductor industry, after replacing germanium in the early fifties.¹ Silicon has a number of advantages over germanium. Germanium has limited availability and it is impossible to grow a stable oxide on it that could passivate the surface, act as an etch protector and, most important, be used as a high-quality gate insulator. Silicon, on the other hand, gained from the ability to grow silicon dioxide, a material with properties precisely matched to the needs of the semiconductor industry. Add to this the relatively low junction breakdown voltage of germanium, and it is easy to understand why it was soon outshone by silicon as the major semiconducting substrate. Furthermore, the low cost compared to other semiconducting materials and the ease of processing has certainly contributed to the success of silicon in integrated circuit technology. According to prediction of G. E. Moore, which later became known as Moore's law,² *"with the unit cost falling as the number of components per circuit rises, by 1975 economics may dictate squeezing as many as 65,000 components on a single silicon chip"*. This observation about silicon integration has fuelled the worldwide technology revolution. Currently there are silicon based transistors of 90 nm and size moving towards less than 65 nm.

1.1.1 From sand to electronic grade silicon

The history of silicon starts with its discovery by Berzelius³ in 1823, but Deville⁴ is credited with preparing the first crystalline silicon in 1854. Silicon is always found in a compound form in nature, usually combined with oxygen (for example sand is mainly SiO_2). Starting from SiO_2 , silicon must undergo various chemical and physical processing before it reaches the material state of semiconductors or in other words, electronic grade silicon. High-purity polycrystalline silicon, often referred to as poly-silicon, is the essential feedstock for the growth of large silicon single crystals. Polysilicon is produced from the readily available SiO_2 using carbon, H_2 and HCl . The first stage is the production of metallurgical-grade silicon (MG-Si), which is produced by the carbothermic reaction between quartz and carbon in an electric furnace at temperatures up to 2000°C , according to the basic reaction:



Finely crushed MG-Si is reacted with anhydrous HCl in a fluidised bed at a temperature around 300°C to produce gaseous trichlorosilane, SiHCl₃.



The purest SiHCl₃ is separated from other chlorosilanes and further purified by distillation. This yields a purity of < 1ppba with respect to electrically-active impurities and is a suitably pure form for either deposition of bulk polysilicon or thin-layer epitaxial deposition.

Polysilicon deposition is achieved by reduction with hydrogen of trichlorosilane at temperatures around 1100°C,



From polysilicon rods, single crystal silicon rods can be prepared by making use of two techniques⁵ – i) Floating Zone [FZ] technique and ii) Czochralski [Cz] technique. FZ technique uses defect-free polysilicon rods, while crushed pieces can be used for Cz process and this technique is inexpensive compared to FZ technique. In the FZ technique, the polysilicon rod is mounted vertically over a piece of single crystal silicon seed. Radio-frequency (RF) induction coil heating is used to melt the top of the seed and the bottom of the polysilicon rod and form a molten float zone. If the RF coil is now moved very slowly upwards, the bottom of the molten zone would start to solidify on top of the seed, continuing its single crystal structure and orientation. As the molten zone transverses the polysilicon rod, it transforms the rod's polycrystalline structure into a single crystal. About 95% of the world's production of silicon single crystals is manufactured from the Czochralski⁶ procedure. Figure 1.1 shows a schematic representation of the Cz procedure.

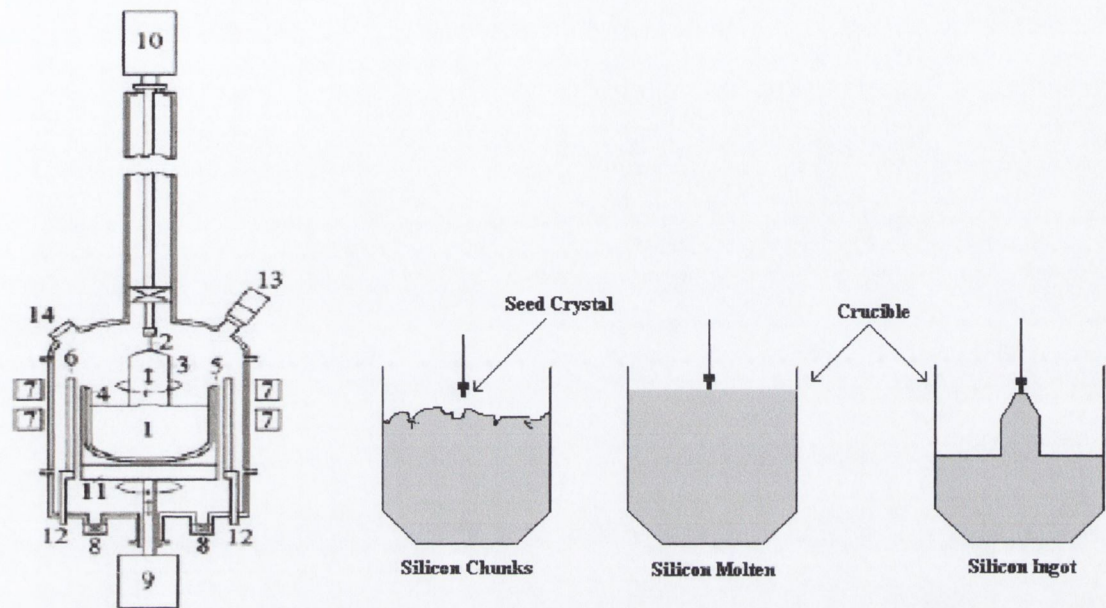


Figure 1.1 The schematic diagram of the Czochralski process.⁶

The Czochralski process is based on heating silicon chunks in a silica crucible, which is supported by a graphite crucible. A seed crystal is used to withdraw silicon single crystal from the melt at about 1420°C. During the preparation, the molten silicon is in contact with the crucible material (SiO₂) which causes the release of SiO₂ particles from the crucible wall into the silicon melt, which in turn lead to dislocations in the silicon crystal. The reaction of the silica with liquid silicon leads to the doping of the melt with oxygen.



Oxygen is transported in part by convection and diffusion to the melt-gas surface where it evaporates as SiO and is blown off with high-purity argon [purging from the top of the furnace] and pumped away. Some of the oxygen dissolved in the melt is transported to the melt-crystal phase boundary and incorporated into the crystal lattice, which leads to

oxygen doping of the crystal and wafer. The silica crucible and the single crystal are usually counter-rotated at rates between 0 and approximately 30 rpm to reduce the effect of any temperature inhomogeneities in the furnace and melt. In the Czochralski process, crystal ingot growth is mainly controlled by the two operation variables – heating rate and pulling speed of the molten polysilicon.

The single crystal FZ/Cz silicon ingots undergo shaping (*e.g.*, grinding, slicing), damage removal (*e.g.*, etching, polishing), cleaning (mechanical/chemical) and surface modifications (gettering and epitaxy) before being used for device processing. Gettering is defined as the process of removing device-degrading impurities from the active circuit regions of the silicon wafer. Epitaxy is a high temperature process by which a single crystal semiconductor layer of controlled thickness, composition and doping is grown on a single crystal silicon substrate. The overall process⁵ is shown in figure 1.2.

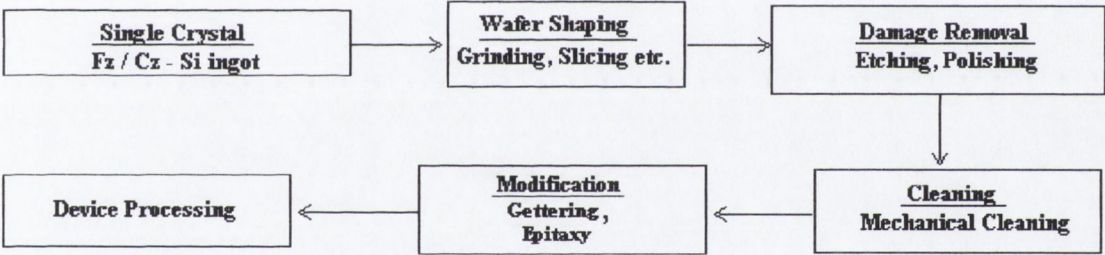


Figure 1.2 The schematic presentation of crystalline silicon processing.⁵

1.1.2 Crystalline silicon and its properties

Silicon has an energy band structure with electronic states, which are completely filled at zero Kelvin. This is separated from one which is completely empty at absolute zero by a narrow region of forbidden energies;⁷ Semiconductors generally have properties in between insulators and conductors. The electronic properties of a semiconductor are dominated by the highest partially empty band and the lowest partially filled band; it is often sufficient to

only consider those bands. This leads to a simplified energy band diagram for semiconductors as shown in figure 1.3.

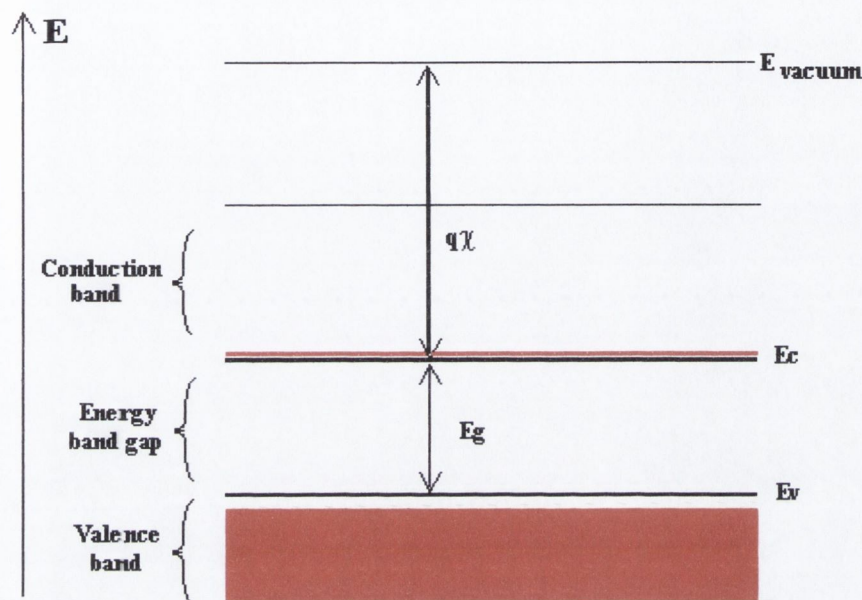


Figure 1.3 Energy band gap diagram of silicon.

In figure 1.3 the energy terms E_c , E_v and E_g represent the bottom edge of the conduction band, the top of the valence band and the band gap energy of conduction band and valence band respectively. The distance between the conduction band edge, E_c , and the energy of a free electron outside the crystal (known as vacuum level, E_{vacuum}) is quantified by the electron affinity, χ multiplied by the electronic charge q . The free electrons in the lattice are at a temperature dependent equilibrium state called the Fermi level.

The important feature of an energy band diagram (which is not included on the simplified diagram) is whether the conduction band minimum and the valence band maximum occur at the same value for the wave number. If so, the energy band gap is called direct. Silicon and Germanium are indirect band gap materials.⁸ This means that in order for a charge transition to occur, there must be a change in momentum as well as an energy change. The difference between direct band gap and indirect band gap is illustrated in figure 1.4.

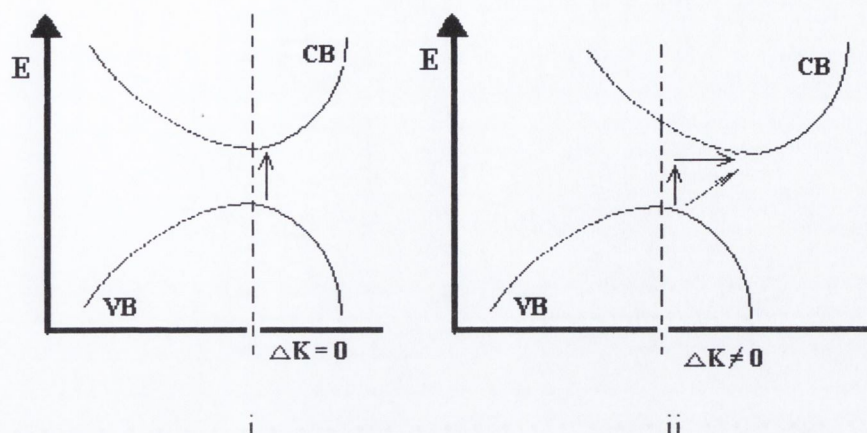


Figure 1.4 (i) A direct band gap and **(ii)** an indirect band gap semiconductor.

A semiconductor in an extremely pure form is termed as *intrinsic*. A doped semiconductor is termed as *extrinsic*. Doping is the process of adding impurities to silicon to make it more conductive. Doped silicon can be used for electronic device applications. Two types of extrinsic semiconductors exist: *n*-type (negative) and *p*-type (positive). When silicon is doped with group 15 elements, the impurity atom donates an extra electron, so the material is called *n*-type Si. This extra electron occupies an energy level known as the donor level in the forbidden energy gap below the empty conduction band. When group 13 elements are used the result is *p*-type Si. In this case, the Fermi level goes down in energy close to the valence band.

1.1.3 Surface chemistry of silicon

Silicon is a covalent solid that crystallises into the diamond cubic lattice structure as shown in figure 1.5. Like carbon, its group 14 homologue, silicon atoms hybridise into a tetrahedral bonding configuration. In the bulk solid, the diamond cubic lattice allows silicon atoms to achieve this tetrahedral configuration. At the surface of the material, however, the bulk is truncated, so the stable bulk tetrahedral is distorted.⁹ The reactivity of the silicon surface is controlled in part by the unsatisfied bonding orbitals, or so-called “*dangling bonds*”,⁹ that remain upon truncating the bulk.

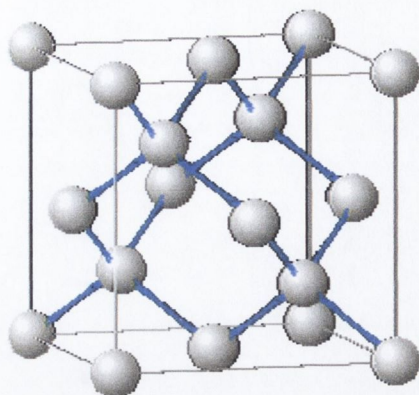


Figure 1.5 The face centred cubic diamond structure of silicon.

The surface silicon atom is bonded only to two other silicon atoms thereby creating two dangling bonds per silicon atom on the surface. The dangling bonds which have single electrons readjust to minimise the total surface free energy by a process called “*reconstruction*”.⁹ The energy minimisation is a trade-off between energy gained by forming new local bonds (to eliminate dangling bonds) with energy lost because of bond strain that results from its new configuration.¹⁰⁻¹²

Lattice planes in silicon are usually described by their Miller index. The crystallographic faces of silicon that are most important industrially are Si(100) surface and Si(111) surface. The Si(100) surface reconstructs into a (2x1) structure, where (2x1) designates the new periodicity of the surface atoms. The Si(100) – 2x1 surface consists of pairs of atoms in adjacent rows and bonded to each other, thereby reducing the number of dangling bonds. A term used for bonding pairs of silicon atoms is – *Silicon dimers*.¹³ Chemists can visualise it, as formed from a sigma bond (σ bond) and a pi bond (π bond). The energy of the Si(100) – 2x1 surface can still be lowered if the dimer moves from a symmetrical configuration to one where the dimer is tilted. Hence at low temperature the dimers of the Si(100) – 2x1 surface are observed to be tilted.¹¹ But at higher temperature, the thermal energy induces a rapid change in the direction of the tilt, which causes the dimers to appear symmetric.

Both Si(100) – 2x1 and Si(111) – 7x7 surfaces are very reactive even after surface reconstruction, so they are typically cleaned and prepared under ultra-high vacuum (UHV) conditions (pressure $\sim 10^{-10}$ Torr) by bombarding the surface with argon ions to sputter

away the surface atoms and/or by heating to temperatures near 900°C. The resulting surface is very reactive and an exposure to air oxidises the surface very fast.

There is an alternative way to functionalise the silicon surface using wet bench chemistry. The silicon surface can be rendered relatively stable by passivating the surface with hydrogen. The most common methods involve exposure of silicon to dilute aqueous hydrofluoric (HF) acid solution. The reaction with dilute HF not only terminates the surface with Si-H atoms but also changes the surface structure due to the replacement of the relatively weak Si-Si bonds with rather strong Si-H bonds. This results in the relaxation of the reconstructed surface.⁹

The silicon surface can be modified with organic or metallorganic moieties starting from both bare and hydrogen passivated surfaces. Most reactivity studies of bare silicon are performed under UHV conditions while reactions with hydride-terminated silicon frequently involve wet chemical methods.

It is worth to mention other forms of silicon: (i) *Amorphous silicon* – a non-crystalline allotropic form of silicon, which does not form a continuous crystalline lattice as in crystalline silicon. (ii) *Nanocrystalline silicon* – similar to amorphous silicon but differs due to small grains of crystalline silicon in the amorphous phase. (iii) *Polycrystalline silicon* or polysilicon closely related to nanocrystalline silicon differs from the crystalline form in that polysilicon consists solely of crystalline silicon grains separated by grain boundaries.

Finally, our project is focused mostly on porous silicon, which is discussed below in details.

1.1.4 Porous silicon

The discovery of porous silicon dates back to 1956 when the husband and wife team of Ingeborg and Arthur Uhlir at Bell Laboratories reported the material for the first time,¹⁴ followed by D. R. Turner two years later.¹⁵ As the name porous silicon indicates, the bulk crystalline silicon during electrochemical etching process changes into a kind of sponge structure of silicon with interconnected and hydrogen-covered silicon columns and pores. As mentioned earlier porous silicon was prepared fifty years ago but it was only in the 1970's that some interest started to develop in the morphology of porous silicon and its complex microstructure began to be studied.¹⁶ Porous silicon regained some interest during 1980's after Imai's article in Solid State Electronics,¹⁷ where his so called "full isolation by porous oxidized silicon (FIPOS)" process was described. Even though in 1970's and 1980's the material caught some attention but it was in 1990's only the attention came to its peak, when L. T. Canham reported visible room temperature photoluminescence of porous silicon.¹⁸ Although the visible photoluminescence of porous silicon at 4.2 K was reported by Pickering,¹⁹ it was Canham's article that marked a turning point in the history of this material.

After Canham's report¹⁸ on visible room temperature photoluminescence in porous silicon, a tremendous increase in numbers of papers on porous silicon has been observed with thousands of science publications were published in the subsequent 13-year period.²⁰ The stage after the 1990s can be described as a *golden era* for porous silicon. A brief report by Chabal in 1990²¹ contributed greatly to the field of wet-chemical monolayer formation on crystalline silicon surfaces. Soon after that in 1993 Chidsey *et.al.*, demonstrated the pyrolysis of neat diacyl peroxides in the presence of hydrogen-terminated silicon leading to the formation of monolayers covalently bonded directly to the silicon surface.²² This was the first report of a densely packed, organic monolayer on a silicon surface. The functionalisation of silicon surfaces with organic groups lead to a new branch of silicon-based molecular electronic, which can have better properties when compared to its metallic counterpart.²³ Additionally a lot of research has been focused on the modification of porous silicon surfaces, using organic and organometallic species mainly to stabilize the luminescence characteristics of porous silicon.²⁴ The fabrication of porous silicon with different pore morphologies came up as a different line of research investigation. The

periodic array of porous silicon for photonics applications and the microstructuring of porous silicon gained attention due to potential technological importance.²⁵

1.1.5 The chemical formation of porous silicon

An electrochemical etching cell for the preparation of porous silicon is presented in figure 1.6. A metal contact (an aluminium plate) is made to the backside of the wafer and sealed so that only the frontside of the sample is exposed to the electrolyte. In figure 1.6 the anode is a silicon wafer (*anodization*) and the cathode is a platinum wire. O-rings (usually rubber or teflon) are used to make tight contact and also prevent HF leakage.

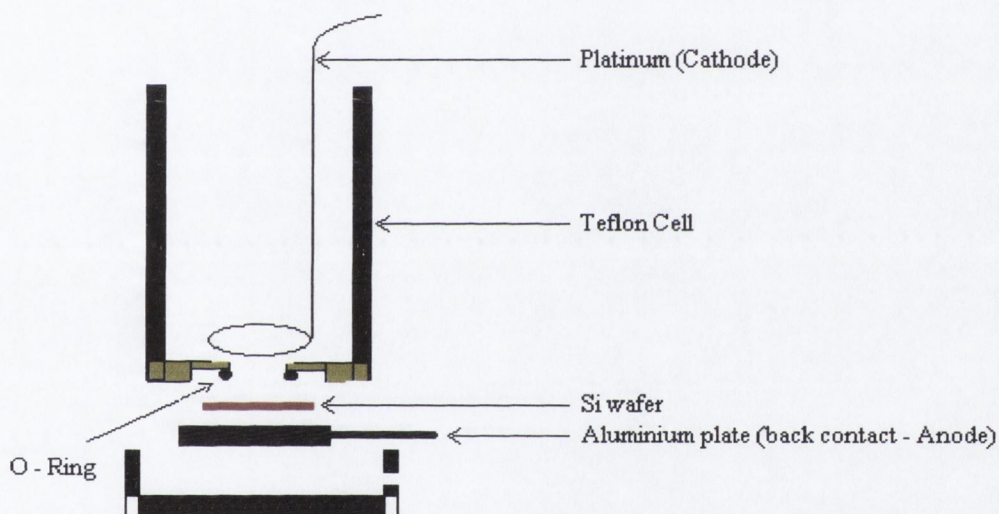


Figure 1.6 Electrochemical etching cell for the preparation of porous silicon.

The simplest technique for the formation of porous silicon is the electrochemical etching of silicon by using an ethanolic solution of HF. The dilution is necessary due to the hydrophobic nature of the bare Si surface. The ethanol-HF solution will reduce the surface tension on the interface and in addition the ethanol-HF can penetrate to the pores, whereas pure aqueous HF cannot. The cell is designed to prevent the accumulation of hydrogen bubbles, which are produced during the course of the reaction. Ethanol or similar surfactants can remove some of the hydrogen gas.²⁶ It has been reported that the lateral

inhomogeneity and the surface roughness can be reduced by increasing the electrolyte viscosity and also by decreasing the temperature.²⁷ Electrochemical etching can be performed either by keeping a constant current (*galvanostatic*) or by keeping a constant voltage (*potentiostatic*). In the galvanostatic method the current is more constant over a wide area, which allows a better control of porosity, porous layer thickness, and reproducibility.²⁸

The electrochemistry of silicon is still not fully understood²⁹ and different mechanisms for etching such as the Current Burst Model (CBM) and the Space Charge Region (SCR) models have been proposed.²⁹ The Current Burst Model postulates that current flow across the solid silicon/HF-containing electrolyte interface is spatially and temporally inhomogeneous. Local current (called the current burst) starts to flow whenever the local field strength is high enough. This current generates some oxide growth and it stops the flow at certain thickness of the oxide. Then, the oxide is dissolved (by chemical means) and whenever the oxide layer is thin enough, the cycle starts again.

In the Space Charge Region (SCR) model³⁰ the pore formation involves a SCR, which acts as a passivating layer. This model is supported by the fact that *n*-type, as well as *p*-type, silicon electrodes are under depletion in the pore formation regime.³¹ A *p*-type silicon is under forward conditions during macropore formation. Close to the interface to the electrolyte an SCR exists in the semiconductor electrode. The width *W* of the SCR depends on the difference between the Fermi levels of the electrolyte and semiconductor, called the built-in potential V_{bi} , on the *p*-type density, on the applied bias *V* and on the interface geometry.³² With the Poisson's equation, the width of the space charge region can be calculated for different geometries and it was determined that the space charge width is minimal at the pore tip compared to the pore wall. A *p*-type silicon electrode anodised in HF behaves like a solid-state Schottky diode under forward conditions. The forward current of a Schottky diode is dominated by diffusion, or thermionic emission or tunneling of holes. At zero bias and under forward conditions the SCR is not fully depleted of holes and so a diffusion current I_{diff} exists that is caused by the concentration gradient of holes dn_h/dr , according to Schottky's theory. At thermal equilibrium and with no applied bias, I_{diff} is compensated by the field current I_{field} and $I_{diff} = I_{field}$ is fulfilled at the pore walls as well as at the pore tip. However, the absolute values of I_{diff} and I_{field} are larger at the pore tip,

because concentration gradient dn_h/dr , as well as the electric field strength, increases with decreasing W . If a forward bias V is applied, I_{field} decreases, while I_{diff} increases. The total current density at the pore tip, $I_{\text{tip}} = (I_{\text{diff}} - I_{\text{field}})_{\text{tip}}$ is always larger than the current density at the pore wall $I_{\text{wall}} = (I_{\text{diff}} - I_{\text{field}})_{\text{wall}}$. Therefore a depression in the electrode etches faster than a planar area. If the distance between the two neighbouring pores becomes less than $2W$ their SCRs overlap and the pore wall becomes passivated due to depletion of holes.

It has been proposed that the change from a diffusion-dominated charge transfer to a thermionic emission-dominated is responsible for the observed suppression of macropore formation in aqueous electrolytes for p -type doping densities in excess of 10^{16} cm^{-3} .³³ According to the theory of Bethe, the thermionic emission current I_{therm} is due to holes that have sufficient energy to overcome the potential barrier E_b and are traversing normal to the interface.

When a potential is applied to silicon in aqueous solution a measurable external current flows through the system. For an electric current to pass the Si/electrolyte interface it must first change from an electronic to an ionic current. In other words it shows that a specific chemical redox reaction must occur at the Si interface, the nature of which is important for the formation of porous silicon.²⁸ Typical i - V curves for p - and n -type silicon in aqueous HF are shown in figure 1.7.³⁴

The i - V curves demonstrate some basic similarities to the normal Schottky diode behaviour expected from a semiconductor/electrolyte but there are some important anomalies.³⁵⁻³⁹ For example, even though the sign of the majority carriers changes between n - (electrons) and p - (electronic holes) type silicon, the chemical reactions at the silicon/electrolyte interface remains the same. Although reverse-bias dark currents as low as $0.3 \mu\text{A}/\text{cm}^2$ have been reported for p -type silicon,⁴⁰ these currents are still three orders of magnitude higher than those observed for Schottky diodes, which possibly indicates that there are possible surface-state contributions. J_{PS} in figure 1.7 is the critical current density in mA/cm^2 below which porous silicon is formed.

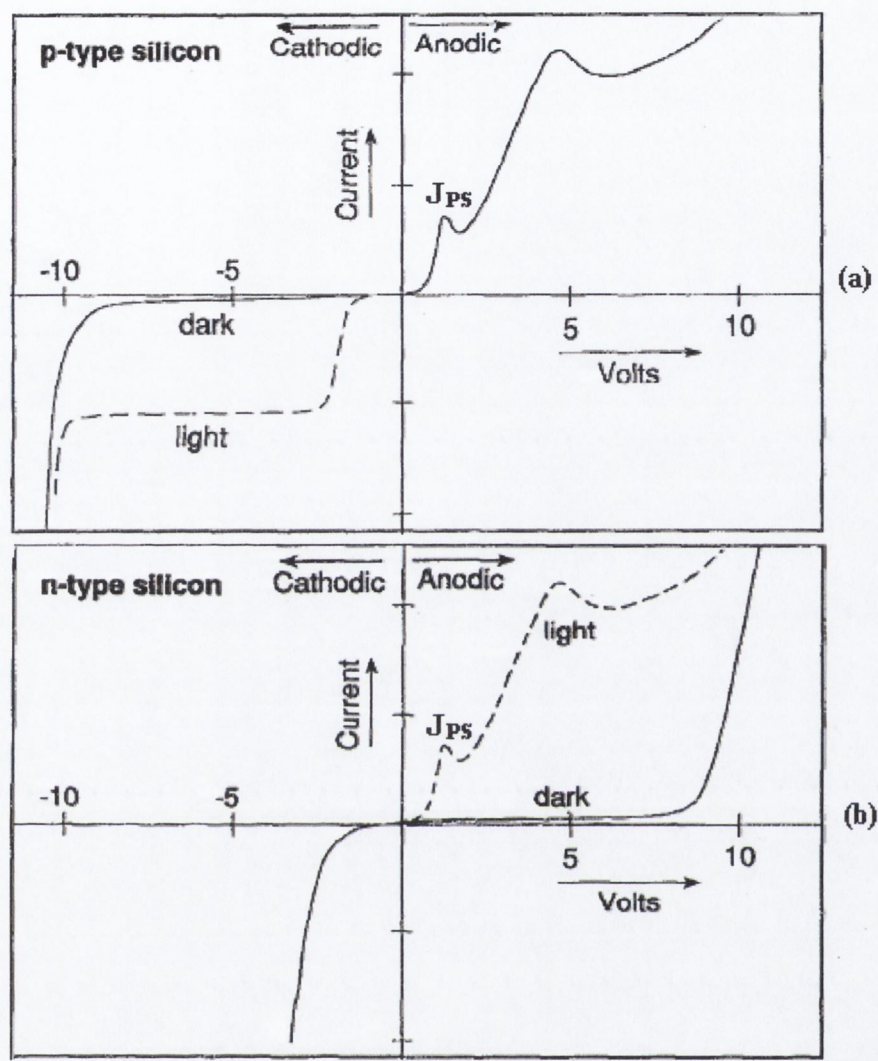


Figure 1.7 Typical i - V curves for p - and n -type silicon,³⁴ (a) p -type silicon (b) n -type silicon.

Silicon is normally stable (does not dissolve) under cathodic polarizations for both n - and p -type. The only important cathodic charge transfer reaction is the reduction of water and liberation of hydrogen gas. This usually occurs only at high cathodic over potentials for p -type material or in other words at *reverse-biased breakdown*²⁸ (using Schottky diode terminology). Under anodic polarizations, silicon dissolves, but depending on the magnitude of anodic potential, divergent surface morphologies result.³⁴ At high anodic potentials electropolishing occurs on the silicon surface resulting in smooth and planar

morphologies, whereas at low anodic potential, the surface morphology is something like a vast labyrinth of channels that can penetrate deep into the bulk silicon. This phenomenon leads to the formation of porous silicon.

There is an additional factor in the electrochemical etching process. When the current density is high, there are many electronic holes at the surface. In this case, electrochemical etching is limited by the fluoride ions migrating under the influence of the electric field, and hitting surface protrusions. These regions are then preferentially etched and surface is smoothed (conditions for electropolishing). In the case of low current density, there are enough fluoride ions, but less holes so the etching is limited by hole diffusion.⁴¹ If the surface has a pit, the holes will be forced to go there by the electric field, leading to the enlargement of the pit or in other words, the formation of a pore.

The size, shape, thickness and density of channels (pores) in silicon are determined by the exact anodization conditions *i.e.*, the HF concentration, temperature, dopant concentration, anodization time, electrolytes used for the reaction. For *n*-type silicon illumination is a major factor because hole supply is needed for the etching process to initiate the dissolution process since *n*-type silicon is under reverse conditions during anodic etching. Illumination, which is generally needed for pore formation in *n*-type silicon, can be given either from the frontside (*fsi*) of the sample or from the backside (*bsi*). The etching reaction that occurs during porous silicon formation by anodic etching in HF requires electronic holes which have to be supplied by silicon.³⁵ The basic conditions for electrochemical pore formation in a homogenous electrode are a passive state of pore wall and an active state of pore tips. A surface area that is depleted of holes will be passivated. Hole depletion occurs only if all holes that reaches the interface is immediately consumed in the dissolution reaction. In general, pore growth in silicon is best described as a phase separation of silicon into two areas: i) pore tips, where most or all of the current is flowing and ii) pore walls and rest of silicon, where no current is flowing or in other words, areas which are passivated against dissolution.

Lehmann and Gösele have presented an entirely surface bound oxidation scheme with hole capture and subsequent electron injection to produce the divalent silicon oxidation state.⁴²

Figure 1.8 depicts the mechanism proposed by Lehmann and Gösele. This mechanism of silicon dissolution is considered to be the most acceptable to date.

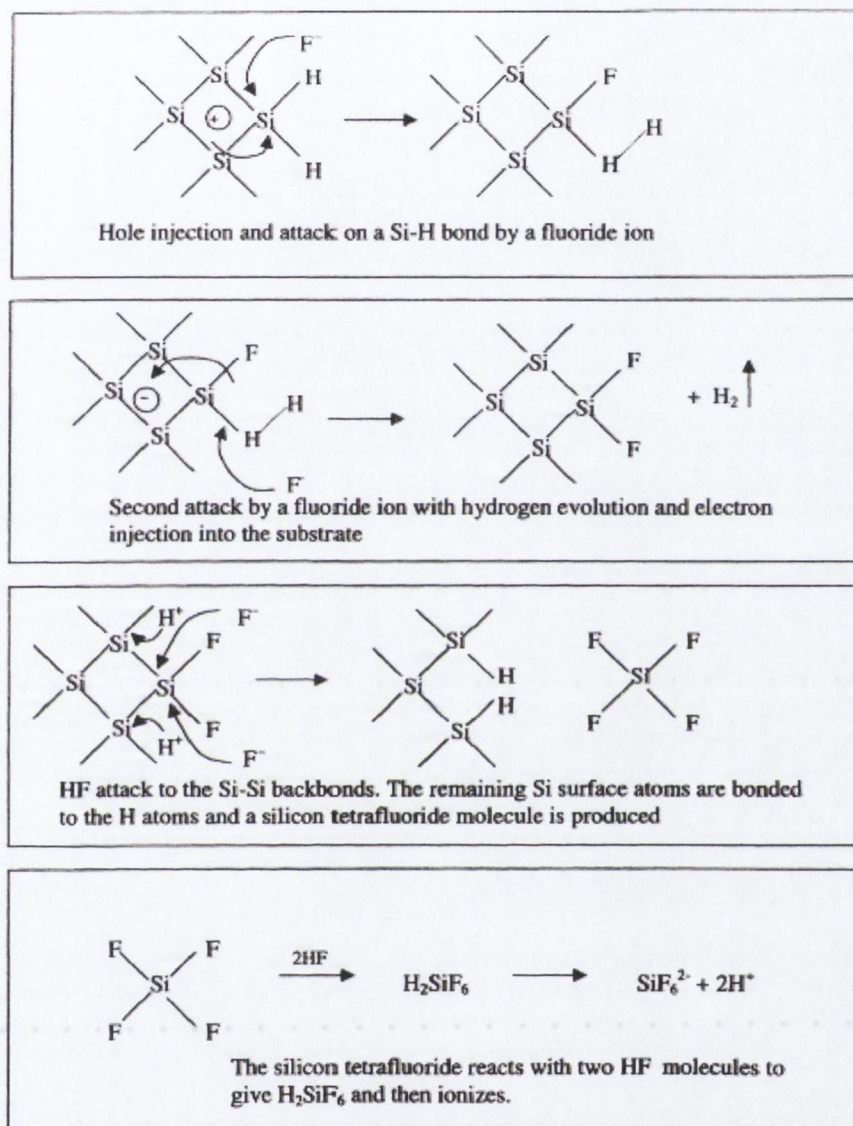


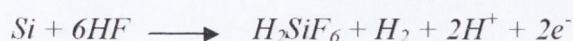
Figure 1.8 Silicon dissolution scheme proposed by Lehmann and Gösele.⁴²

According to the figure 1.8, the Si hydride formation passivate the silicon surface unless a hole is available. This hypothesis is supported by the experimental observation that hydrogen gas continues to evolve even after the removal of the applied potential. Also, the

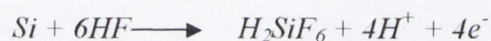
presence of Si-H bonds have been spectroscopically confirmed during the porous silicon formation.^{43,44} Both the formation of SiF_6^{2-} ions and molecular hydrogen have been confirmed experimentally.^{14,15}

The overall equation for the porous silicon formation can be presented as

during pore formation:



during electropolishing:



According to IUPAC classification porous silicon can be classified into three pore ranges:

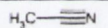
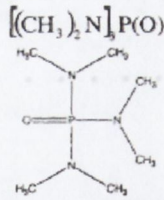
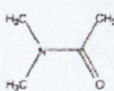
- | | | | |
|------|-------------|---|-----------------------------|
| i) | Microporous | - | $\leq 2\text{nm}$ |
| ii) | Mesoporous | - | $\geq 2 \leq 50 \text{ nm}$ |
| iii) | Macroporous | - | $\geq 50 \text{ nm}$ |

New terminology such as “*nanoporous*” is somewhat ambiguously defined but broadly defines a solid skeleton with nano-dimensions. The condition for the formation of porous silicon in the nanometer range or the micrometer range largely depends on the electrolyte used for electrochemical etching. The first paper dealing with organic solvent/HF containing electrolytes for *p*-macropore formation was published in 1994 by Propst and Kohl.⁴⁵ Electrolytes used for silicon etching can generally be classified as organic and aqueous. Electrolytes combining HF and an organic solvent are termed “*organic electrolytes*” whereas ones without any organic solvent are generally termed “*aqueous electrolytes*,” which normally includes HF/ethanol mixtures. The organic electrolytes *i-V* characteristics curves do not show a J_{PS} peak as is shown by aqueous electrolytes in figure 1.7. It is possible that the J_{PS} peak is actually present but masked due to the large resistance

of organic electrolytes.²⁹ Föll *et al.*, distinguished organic electrolytes from aqueous electrolytes with the aqueous electrolytes having J_{PS} peak in the i - V curves.

The organic solvents commonly used for electrochemical etching together with HF are dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), formamide (FA), acetonitrile (MeCN), hexamethylphosphoric triamide (HMPA) and dimethyl acetamide (DMA). Table 1.1 shows the organic electrolytes used in silicon electrochemistry and their major properties.²⁹ DK in the table 1.1 represents the dielectric constant of the electrolyte and it determines to which degree HF will be dissociated. The oxidising power of the electrolyte in the table tells how well they form an oxide on silicon.²⁹ The values were determined from the slope of voltage versus time curves for each organic electrolytes.

Table 1.1 Organic electrolytes used in Si electrochemical etching.²⁹

Symbol	Formula name	Polarity (DK)	Oxidizing power
MeCN	 Acetonitrile	6.2	Very weak; slope of anodic oxide, 0 a.u.
DMF	 Dimethylformamide	6.4	Slightly oxidizing, 0.5 a.u.
FA	 Formamide	7.3	Strong, 3.5 a.u.
DMSO	 Dimethylsulfoxide	6.5	Mild oxidizing, 2.5 a.u.
HMPA	 Hexamethylphosphoric triamide	6.6	Oxidizing, 6.5 a.u.
DMA	 Dimethylacetamide	6.3	Mild oxidizing, 2.1 a.u.

It can generally classify the pore formation in *n*-type and *p*-type silicon in to different categories for example, macropore formation in *n*-type silicon using aqueous electrolyte with backside illumination (*bsi*).

- a) Macropores in *n*-type silicon obtained in aqueous/organic electrolytes with frontside illumination and backside illumination

Macropores formed in *n*-type Si with *aqu/bsi* are mostly known as “perfect” pores.³⁰ “Perfect” pores – a term used by Lehmann and Föll to describe smooth cyclindrical pores with large aspect ratios and constant diameter at all depths.³⁰ The terms “good” and “bad” or “poor” were coined for pores terminology. The former corresponds to pores with more or less constant pore diameter with depth and latter corresponds to the pores with constantly changing pore diameters with pore depth.⁴⁶ The space charge region model²⁹ can plays a role in explaining the formation of macropores in *n*-type Si (*aqu/bsi*). The theory is that the system *n*-Si/electrolyte is reversely biased in electrical terms and that any bending of the prominent SCR in the Si by original-pores would focus some of the holes produced by light onto the pore tip. If the holes were available from the backside they would be focused by the SCR on the pore tips and macropores should grow with constant diameters to considerable depths. Also, another facet which needs to be mentioned is the dependence of pore morphology on the sample orientation.⁴⁷ Levy-Clement *et.al.*, reported a systematic study on the existence of *n*-macropores (*aqu/fsi*).⁴⁸ The frontside illumination (*fsi*) it has been ruled out that the light penetrating a pore generates carriers at the pore tip and thus promotes pore growth.⁴⁸ General accord is that carriers must diffuse from the surface (near the region where they are generated) to pore tips.

Macropores formed in *n*-type formed under *fsi* are more or less the same as in *p*-type silicon where holes are present in the silicon-electrolyte interface under high illumination. But under low illumination levels, the current is limited by the concentration of holes. Macropore formation in *n*-Si obtained using an organic electrolyte and *bsi* was first reported in 2000.⁴⁶ As it is a recent report there is little data available about *n*-macropores

(*bsi*) and no pore formation model besides the Current Burst Model (CBM)²⁹ has attempted for an explanation so far.

b) Macropores in *p*-type silicon obtained in aqueous/organic electrolytes

Macropore formation in *p*-type silicon is based on forward biased conditions. An extended SCR model is not expected for a *p*-type electrode in the anodic regime. As a result, most models for macropore formation on *p*-type Si electrodes are based on passivation effects, rather than SCR.²⁹ The *p*-macropores (*org*) tend to become more “perfect” if the oxidizing power of the electrolyte is not too small – at least 0.5 a.u., (see table 1.1). Electrolytes with low oxidizing power, *e.g.* MeCN, will produce hardly any macroporous at all, whereas electrolytes with strong oxidizing powers produce micropores instead of macropores.

It is well understood now that in order to obtain “good” macropores, the electrolyte should have the following properties:

- Medium oxidation of silicon
- Good H donor capacity
- Large polarity

Electrolytes with a low dielectric constant tend to have reduced HF activity, which slows down the direct dissolution process and the oxide dissolution. In other words, we can explain that if the electrolyte is not highly polar it cannot easily dissolve HF to make it chemically available at the silicon-electrolyte interface.⁴⁹

The conductivity of the organic electrolyte, temperature, circulation of the electrolyte are of considerable importance in the preparation of *p*-macropores silicon. The orientation dependence of *p*-macropores (*org*) is similar to that of *n*-macropores (*aqu*). The *p*-macropores (*aqu*) were first reported by Lehmann and Rönnebeck,³³ after several hundred papers had been published exclusively on *p*-micropores (*aqu*). *P*-macropores (*aqu*) are found at current densities much lower than J_{ps} and for medium to low HF concentrations. Although not many properties of *p*-macropores (*aqu*) are known at present,^{32,50} it can be

concluded that they are rather easily obtained for HF concentration less than 15 wt% and current density less than 0.05 J_{PS} if nucleation is provided for, *e.g.* by KOH etch pits.

c) Mesopore and micropore formation in *n*-type and *p*-type silicon

Mesopores are formed by etching of either highly doped silicon or moderately doped silicon in aqueous electrolytes. The former case always produces n^+/p^+ -mesopores (*aqu*). n^+ and p^+ are generally used to describe heavily or highly doped *n*-type or *p*-type silicon respectively.²⁹ No light is required in the case of n^+ Si because avalanche breakthrough (a form of current multiplication occurring because of very large currents flowing in situations where this would normally not be possible) occurs easy and enough current is produced even at small voltages. Avalanche breakdown occurs when the voltage applied across a material is great enough that free electrons are accelerated and where in turn they knock atoms to make their electron free. The moderately doped silicon produces, break down (*bd*) pores, which are usually denoted as *n*-mesopores (*aqu/bd*). The break down pores are formed when the applied voltage increases above the breakdown potential resulting in the generation of electronic holes near the pore tips by interband tunnelling of holes.⁵¹ Etching of highly doped silicon in organic electrolytes produce n^+/p^+ -mesopores (*org*) similar to their n^+/p^+ -mesopores (*aqu*).^{52,53} With regard to pore formation models, there are no convincing models at present.

Micropores can be generally formed using aqueous electrolytes with large HF concentrations. This can be explained by two reasons: i) microporous layers grow rather rapidly and uniformly and ii) their porosity is high ("porosity tends to increase with the HF concentration and the etching current"⁵⁴). If the current and/or the HF concentration are too small, macropores (*aqu*) will result. There has been some reports on the transition from micropores (*aqu*) to mesopores (*aqu*) {if the doping level is increased} or from micropores (*aqu*) to macropores (*aqu*) {if the current and/or HF concentration are lowered}. At the present time, no model can explain micropore formation satisfactorily.²⁹ While quantum wire effects seem to be necessary, they only could account for the distance between the micropores but not for the diameters. The quantum wire model utilises the quantum interpretations to explain pore generation.^{35,42} The basic premise of the quantum model uses the proposed increase in the porous silicon band gap to substantially decrease the mobile

carrier concentrations and produce a “depletion” similar to the depletion layer proposed by Beale.^{19,55} The current is then limited to the pore tips by electric-field enhancement, and the porous structure is passivated by the quantum effect.

1.1.6 Photoluminescence in porous silicon

Hydrogen-terminated silicon oxidizes slowly in air, often resulting in loss of photo- or electroluminescent properties. Many studies have been directed at understanding the chemical properties of H-terminated silicon surfaces in order to protect porous silicon from loss of its luminescent properties. Papers appeared in large numbers in the last few years on the stabilization of photoluminescence in porous silicon by forming more stable Si-C bonds.⁵⁶ The chemistry of silicon etching has been studied and several models explaining the formation of porous silicon ranging from micro to macro are known.^{29,34} The Photoluminescence (PL) of porous silicon and its correlation with the formation of chemical bonds was explained satisfactorily.⁵⁷

Photoluminescence is the spontaneous emission of light from a material under optical excitation. The excitation energy and intensity are chosen to probe different regions and concentrations in the sample. The intensity of the PL signal provides information on the quality of surfaces and interfaces. The basic principle of photoluminescence can be outlined as when light of sufficient energy is incident on a material, photons are absorbed and electronic excitations are created. Eventually, these excitations relax and the electrons return to the ground state. If the radiative relaxation occurs, the emitted light is called PL. This light can be collected and analysed to yield a wealth of information about the photo-excited material.

The current world-wide interest in porous silicon primarily started from the report,¹⁸ in 1990, that efficient visible light emission from high porosity structures arises from quantum confinement effects. Tuneable efficient room temperature photoluminescence reported in porous silicon makes it a more applicable for sensing than any other porous materials.⁵⁸ The origin of photoluminescence however became a very controversial topic and a horde of models emerged⁵⁹ each supported by specific observations of the microstructure of the material and the spectroscopic nature of the light emission process.

Porous silicon structures demonstrate luminescence efficiently in the near infrared (0.8 eV), in the whole visible range and in the near UV range.⁶⁰ This broad band of energies arises from a number of clearly distinct luminescent bands. We can categorize the PS luminescence simply into three different bands:

1. The blue band, centred around 2.3 to 2.6 eV (F-band)
2. The visible band, centred between 1.4 and 2.2 eV (S-band)
3. The IR band centred typically at 0.8 eV (IR band)

1. *F-band*

The F-band or fast band shows decay times in the nanosecond regime. It is commonly known as the green-blue band and was first proposed by Harvey *et.al.*, in 1992.⁶¹ It has been established that porous samples which are left in HF electrolyte developed a weak green PL and a quenching of red PL. The green PL shows a blue shift and an increase in intensity with illumination time. A green-blue photoluminescence (peak energy 2.3-2.7 eV) is observed from samples that have been exposed to some kind of oxidizing treatment, like formation in an HF-H₂O₂ mixture, storage under ambient air for a prolonged period or oxidizing with H₂O₂. The silanol group (Si-OH) has been proposed as the luminescent center responsible for this blue band, although the origin of this photoluminescence is still under discussion.^{28,62}

2. *S-band*

This band has been tuned across the entire visible range from deep red to blue. Porous silicon substrates have now been reported to yield relatively efficient S-band luminescence under a wide variety of conditions (Table 1.2).⁵⁹

Table 1.2 Conditions for S-band photoluminescence⁵⁹

Conditions of porous Si	Chemical termination of skeleton surface
<i>In situ</i> in HF during and after formation	Si F _x H _y
Freshly etched in inert ambient air	SiH _x
Chemically or anodically oxidized	Si O _x H _y
Aged in ambient air for months to years	Si O _x H _y C _z
Rapid thermally oxidized at high temperatures	Si O _x H _y

It is worth to mention that, while PL efficiency is high under blue or UV excitation, in the range from red to yellow region, the emission is rather low.⁶³ The S-band large spectral width is due to inhomogeneous broadening, and its spectral position depends on porosity. It was found that S-band efficiency is not proportional to the inner surface area, but that there exists a threshold porosity that has to be exceeded in order to achieve an efficient luminescence.⁵⁹

3. The IR photoluminescence band

The IR PL band centred between 0.8 and 1.3 eV is usually present in most PS samples. At room temperature (RT), the intensity of the IR band is weak. But at cryogenic temperatures it became much stronger and intense than even the red band.⁶⁴ The IR band has been ascribed to radiative recombination from the CB (conduction band) to DB (dangling bond) center. So, the origin of this radiation could be silicon dangling bond related, although no direct correlation has yet been demonstrated.²⁸

1.1.7 Porous silicon composite materials

The intense development of modern optoelectronics calls for a wide investigation and application of new materials and technologies. Porous materials with their excellent properties to host various materials are important for development of new composites. Porous silicon has shown to be a promising host for rare earth containing materials because

it has a large surface area allowing the easy infiltration of the ions into a matrix.⁶⁵ Emission from lanthanide ions have high efficiency, low temperature quenching, sharp spectral bands and high coherence.⁶⁶ The distinguishing features of the synthesis of films doped with erbium and europium in meso/macroporous materials is when the properties of the matrices as well as the properties and spectral characteristics of rare earths were considered. The luminescence spectrum of lanthanides in the trivalent state caused by ionization of $6s$ - and $5d$ -electrons and intracenter transitions of $4f$ -electrons shielded by outer $5s$ - and $5p$ -electrons consists of a set of fairly narrow spectral lines from UV to the IR range. Because of this, the synthesis of materials doped with lanthanides and their investigations with porous matrices are of increasing interest for modern optoelectronics.

There are various reports on the incorporation of rare earth ions into a porous matrix like ion implantation,⁶⁷ electrochemical migration,⁶⁸ or spin-on techniques.⁶⁹ Compared to other techniques, the sol-gel method attracts much attention as an alternative low cost technology for fabrication of a variety of materials. In the last seven to eight years, interest in the application of the sol-gel method in combination with porous matrices has increased because the sol is capable of penetrating into pores and forming an oxide film with desired properties.⁷⁰ Thus owing to the comparatively low viscosity of colloidal solutions, the sol-gel method allows the production of xerogel films of different chemical composition, not only on the smooth surface of semiconductors, but also in meso/macro porous structures. This opens up a number of prospects for the use of this method, for example, for a change of the chemical composition, specific surface and optical properties of mesoporous specimens.⁷¹ The sol-gel method in combination with porous matrices allows to form fairly thick xerogel films in which the role of a "load-carrying structure" (skeleton) is played by initially stronger porous specimens. The xerogel films synthesised in (rough) porous structures have a thickness of several microns. It is technologically difficult to obtain films of several micron on a smooth surface, because this requires the applications of multilayer (>100 layers) coatings to obtain the desired micro layer.⁷²⁻⁷⁴

The porous silicon matrices are widely used for the preparation of novel composite materials. There are a number of examples of composites made using porous silicon and polymers or liquid crystals. The concept of a reconstructable photonic crystal based on an insulating porous matrix filled with liquid crystal was first suggested in a theoretical study

by Busch and John.⁷⁵ Astrova *et al.*, reported the spectroscopic properties of liquid crystal-grooved silicon composite materials.⁷⁶ The nematic liquid crystal molecules which are in the grooves are predominantly aligned in a planar configuration with respect to the silicon walls which were then realigned homeotropically with respect to the groove walls under the influence of an electric field. The porous silicon-polymer composite materials gained attraction in recent years due to the conducting properties of polymer as an appropriate optical interface to porous silicon.^{77,78} The idea to use a conductive polymer as an optical or electrical interface to porous silicon has become popular and many scientific papers and technical patents were issued world wide.⁷⁹ Electrochemical polymerization of polyaniline (PANI) and other conductive polymers were studied and methods like spin casting,⁸⁰ soaking⁸¹ or thermal evaporation⁸² were tested and patents based on conductive polymers/porous silicon structures were obtained.⁸³ Further the fabrication of porous-silicon/polymer nanocomposite photonic crystals formed by microdroplet patterning has been reported by Sailor.⁸⁴ The micrometer-sized photonic crystals consisting of a porous-silicon/polymer nanocomposite have also been prepared by spray-coating of a polymer solution onto a porous silicon photonic-crystal layer.⁸⁴

The incorporation of magnetic nanoparticles into porous silicon can lead to the development of new magnetic composite materials.⁸⁵ Also, the incorporation of organic materials into porous silicon substrates imparts some property of the organic material to the semiconductor device. Such hybrid organic-inorganic semiconductor materials might find some use as chemical or biological sensor or for the generation of new-generation dielectric materials for surface passivation and protection.⁹

1.1.8 Applications of porous silicon

The application of porous silicon arises mainly from utilising some of its optical and surface properties. Here are some of the important applications of porous silicon:

1. Sensors

Silicon based sensors can generally be classified as physical, chemical or biological depending on the parameter to be measured. The variation in PS properties with the adsorption of molecules at the large internal surface area is exploited for their use as

chemical sensors. For example, photoluminescence efficiency decreases when porous silicon is exposed to various chemicals and the final photoluminescence efficiency depends on the dipole moment of the physically absorbed molecules.⁸⁶ The conductivity and the capacitance of PS changes dramatically upon exposure to gases or ambient atmosphere.⁸⁷ The reason for this is thought to be due to both the change in the dielectric constant of the matrix and from the dielectric-induced changes in the carrier concentration in the porous silicon nanostructures.

2. *Reflectors*

Porous Silicon can be used as a base material for passive or active optical devices like Bragg reflectors, Fabry–Perrot filters, planar waveguides, planar microactivities, *etc.*⁸⁸ Because of its porous nature, the effective refractive index of porous silicon is lower than that of bulk silicon. Therefore, porous silicon can also be used as an antireflection coating for silicon solar cells.⁸⁹ It has been shown that *p*-type porous silicon thin layers can be described with a refractive index mainly dependent on the porosity. The possibility of covering a large range of refractive indexes n , from 1.25 to 3, was revealed.⁹⁰

3. *Silicon lithography*

In the lithography process, porous silicon can be used as sacrificial layer for the convenient preparation of micro- and nano-lithographic structures. Free standing 3D structures such as geometric pits, walls and cantilever beams can be galvanostatically formed by using backside illumination during etching.⁹¹ Polysilicon strain-free membranes can be created by thin-film deposition over porous silicon layers, followed by selective dissolution of the porous silicon.⁹²

4. *Biomedical applications*

While porous silicon has been the dominant material for electronic and micro-mechanical devices,³² it has only recently been used for medical and biological applications.⁹³ It has been demonstrated that porous silicon may be used to treat a wide range of ailments *e.g.*, from broken bones to cancer. Porous silicon compares favourably with titanium, ceramics, composites, polymers and others materials commonly used for biological implants.⁹⁴

Porous silicon based structures are finding potential application in *in-vivo* sensing as well as interfacing with biological tissues. Porous silicon structures have been used for the nucleation of hydroxyapatite, a major component of human bone.⁹⁵ Porous silicon “biochips”⁹⁶ find another application in micro array technology, where the molecular recognition elements are arranged on a silicon chip.⁹⁶ The state of each element on the biochip is determined by the abundance of the complementary analyte in a sample mixture. Biochip recognition elements and analytes can be small molecules, nucleic acids or proteins, such as ligand receptor antibodies and enzymes.

1.1.9 Methods of characterisation of porous silicon

The main methods of characterization used in this thesis for the characterisation of porous silicon are: FT-IR spectroscopy, Raman/photoluminescence spectroscopy, XPS, Scanning Electron Microscopy and SIMS.

i. FT-IR spectroscopy

Fourier Transform Infrared (FT-IR) spectroscopy is a good tool for an investigation of the surface species on porous silicon. The high surface area of porous silicon makes it easy to characterise, even with simple transmission infrared spectroscopy. The peak positions of hydride-terminated silicon will not interfere with that of other organic groups or in other words Si-H_x ($x = 1, 2, 3$) peaks usually appear in regions, are easily detected in a spectrum. Figure 1.9 shows an FT-IR spectrum for a freshly etched porous silicon sample. Depending on the intensity of the IR peaks, it is possible to determine the percentage of each Si-H_x peak on the porous silicon. IR spectral analysis also gives an insight into various types of bonding to the porous silicon surfaces and thus it acts as a preliminary technique to characterise an organically modified porous silicon sample.

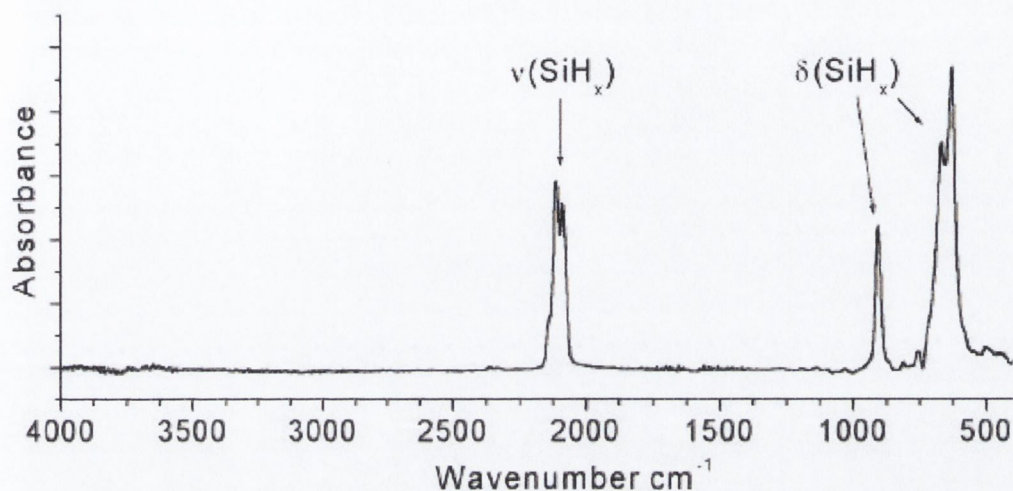


Figure 1.9 Absorbance FT-IR spectrum for a freshly etched porous silicon sample.⁹⁷

ii. Raman spectroscopy

Like FT-IR, Raman spectroscopy also gives valuable information on the bonding of various organic or organometallic species on porous silicon surfaces. Raman spectroscopy, and especially micro-Raman spectroscopy, can also give indirect information on the microstructure of porous silicon. Micro-Raman is further useful to study stresses in porous silicon.

iii. XPS (X-ray Photo electron Spectroscopy)

XPS is frequently used for chemical analysis by detecting core-level emissions. Each element has core levels with definite values of energy levels (though slight shifts occur, due to changes in the chemical environment, including surface chemical shifts). Surface chemical shifts in core-level emissions are used to distinguish the adsorption sites on the surface. When several different adsorption sites exist, one can determine the number of the sites by deconvoluting the emission spectra into different shifted components. This can be done by tuning the incident photon energy to realize the so-called surface-sensitive condition. The escape depth of the electrons, and thus the mean free path in the solids,

strongly varies as a function of their kinetic energy. For photoelectrons from core levels, surface- and bulk-sensitive conditions may thus be achieved by properly adjusting the photon energy. Thus the principle lies in the absorption of a photon by an atom, followed by the ejection of a core or valence electron with characteristic binding energy.

iv. Scanning Electron Microscopy (SEM)

SEM is an excellent tool for an investigation of the microstructure of porous silicon. Not only the morphology of porous silicon, but also the geometry of pores can be studied in details using SEM. Investigations of microporous silicon generally require both TEM and SEM.

v. SIMS (Secondary Ion Mass Spectroscopy)

Secondary ion mass spectroscopy (SIMS) is by far the most sensitive surface technique, but also the most difficult to quantify. SIMS is very popular in materials research for making concentration depth profiles and chemical maps of the surface. The principle lies in the fact that when a surface is exposed to a beam of ions (Ar^+ , Cs^+ , Ga^+ or other elements with energies between 0.5 and 10 keV), energy is deposited in the surface region of the sample by a collisional cascade. Some of the energy will return to the surface and stimulate the ejection of atoms, ions and multi-atomic clusters. In SIMS, secondary ions (positive or negative) are detected directly with a mass spectrometer.

1.1.10 Objectives of the project

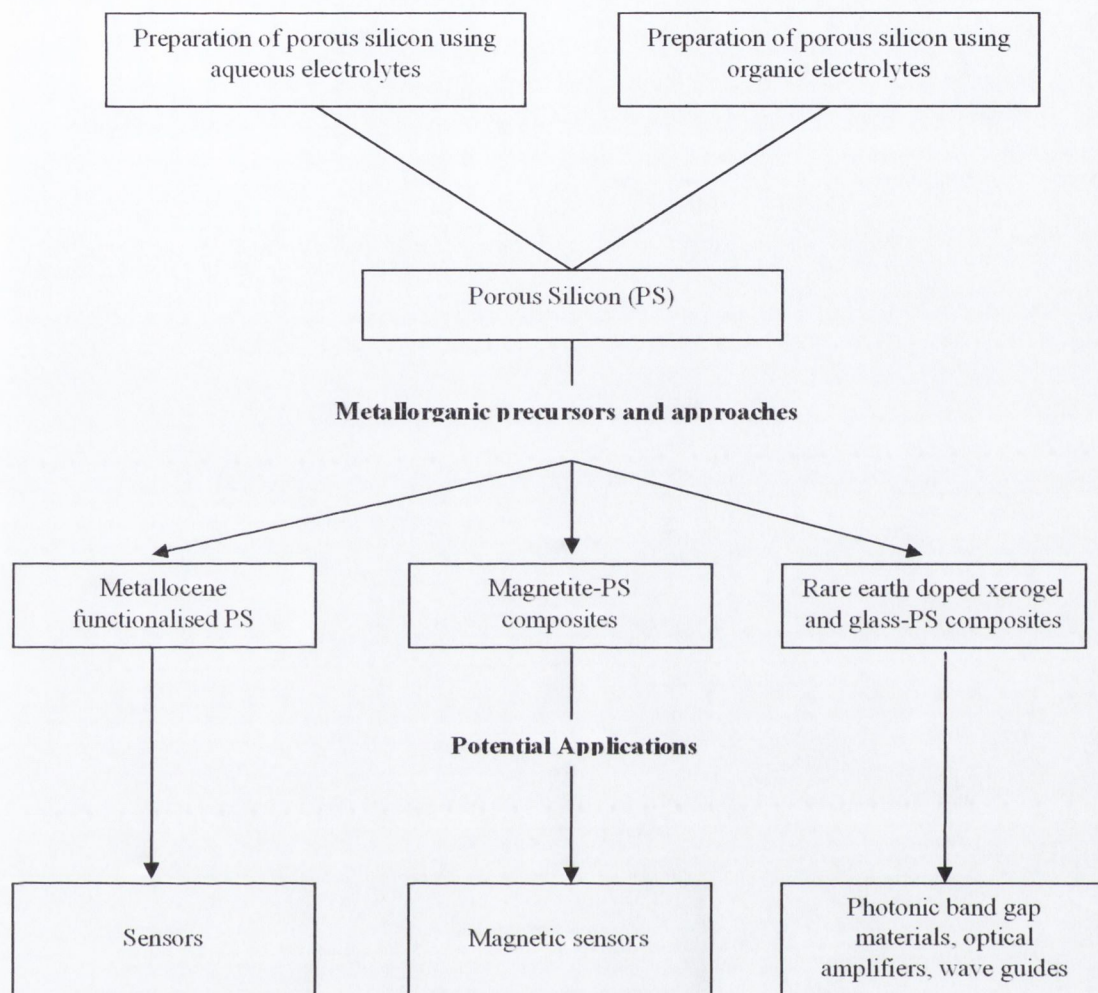
This thesis is mainly focused on the fabrication of *p*-type porous silicon using aqueous and organic electrolytes and the preparation of new composite materials based on porous silicon. Although there are many reports⁹⁸⁻¹⁰⁰ on composite materials prepared using various porous materials, the composite materials based on porous silicon is still in infantile stage of their development. In this work, we use metallorganic approaches and metallorganic precursors to modify porous silicon. The main advantage of using metallorganic species is the possibility of manipulating the properties of materials by controlling both the nature of the metal and the properties of the ligands. The main disadvantage is air- and moisture- sensitivity of some metallorganic intermediates during

processing. Porous silicon, which is chemically modified with organometallic compounds (e.g. metallocenes) might have a potential application as new optical sensor material. It has been shown that thin films of metallocene derivatives can be used as optical (photoluminescent) gas sensors.^{101,102} However there are only a few reports on silicon surface chemistry of metallocenes.^{103,104} Therefore one of the objectives of our work is to develop novel PS–metallocene composites using metallorganic chemistry approaches. The optical (photoluminescence) and electrical properties of the new composites are to be investigated. Another main objective of the project is to prepare magnetic iron oxide (magnetite- or maghemite-) PS composites and to investigate their magnetic properties (magnetisation and magnetoresistance). Magnetic-PS composite materials may have applications in magnetic sensors.^{105,106} Finally one more objective of the project is to develop new PS–rare earth doped glass composites using metallorganic precursors (TEOS, metallasiloxanes) and sol-gel processing. Porous silicon–glass composites might potentially be important as novel materials for optoelectronics.⁷⁰ For example they could be promising as photonic band gap materials, optical waveguides and compact optical amplifiers.¹⁰⁷

In summary the main aims of this project are:

1. To fabricate porous silicon using aqueous and organic electrolytes.
2. To develop and investigate new ways of specific chemical bonding of selected organometallic compounds (*e.g.* metallocenes) to the surface of porous silicon.
3. To prepare magnetic-porous silicon composites.
4. To develop novel porous silicon-based glass composites for photonic applications.

The structure of the project is also summarized in the Scheme 1.1



Scheme 1.1 Schematic presentation of the structure of this project.

The thesis comprised of several chapters and the chemical approaches used are described as follows:

First we planned to concentrate mainly on the fabrication of porous silicon using various aqueous and organic electrolytes. The luminescence properties and the morphology of porous silicon were investigated in detail. Works have been performed on the morphology changes occurred on porous silicon with both prepatterned and without prepatterned silicon. The dependence of various etching parameters with respect to silicon properties was investigated.

Then it is planned to prepare new magnetite–porous silicon composites *via* the synthesis of magnetite nanoparticles and further incorporation of the nanoparticles into porous silicon. We also plan to perform thermal processing of these magnetite–porous silicon composite materials their characterisation by various instrumental techniques, such as magnetic measurements (SQUID magnetometry), magnetoresistance and Mössbauer spectroscopy.

Further, the work is going to focus on aluminosilicate–porous silicon based composite materials. Rare earth doped aluminosilicate xerogel and glass materials are to be introduced into porous silicon using the sol-gel technique. This work is also going to involve the preparation and characterisation of xerogel and glass micro fibres using porous silicon as a template.

Finally, functionalisation of porous silicon using different metallorganic precursors and approaches is to be developed. The attachment of ferrocenyl- (Fc) and cyclopentadienyl- (Cp) moieties on to porous silicon is going to be investigated by FT-IR, Raman and XPS techniques.

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II

Preparation of *p*-type Porous Silicon using Aqueous Electrolytes and its Characterisation

2.1 Introduction

Electrochemical etching of silicon in hydrofluoric (HF) acid electrolyte is a well-known technique for the preparation of porous silicon.¹ The etching of silicon using different types of electrolytes has been subject of great interest since the last decade. Porous silicon can be prepared using HF based electrolytes in both aqueous and organic mediums. Most of the work to date was concentrated on the preparation of *n*-type porous silicon. There have been substantially fewer reports on the preparation of *p*-type silicon.² The first report on the formation of macropores on *p*-type silicon was published in 1994.³ The electrochemical formation of macropores on *p*-type Si in aqueous or alcoholic fluoride solutions was observed only for low-doped substrates.⁴ One of the main advantages of preparing *p*-type porous silicon is that it doesn't require any backside or frontside illumination,⁵ in contrast to the *n*-type silicon.

Fabrication of macropores in *p*-type silicon using organic electrolytes came as a surprise, similarly fabrication of macropores in *p*-type silicon using aqueous electrolytes was also unexpected.⁶ Lehmann and Rönnebeck published their reports on *p*-macropores by using aqueous electrolytes.⁶ These electrolytes were derived from the HF-H₂O system; termed "aqueous electrolytes" and abbreviated "aqu". This includes not only all mixtures of HF (commonly 49% p.w.) with water, but also fluorine bearing salts dissolved in H₂O (*e.g.* NH₄F), additions of ethanol (C₂H₅OH) and/or isopropanol (C₃H₈O), or anything else that serves to reduce surface tension, adjusts the pH-value, or the viscosity. The addition of surfactants to the aqueous electrolytes is also covered under the same definition as "aqueous" system. As explained in Chapter I, the main distinction between organic and aqueous electrolytes is that for the organic electrolytes *i-V* characteristics curves do not show a J_{PS} peak compared to the aqueous electrolytes which exhibit a J_{PS} peak in the *i-V* characteristics curves.²

The research on the formation of micropores in porous silicon using aqueous electrolytes with large HF concentrations are very important for two reasons: (i) microporous layers grow rapidly and uniformly and (ii) their porosity is high. If the current and/or the HF concentration are too small, macropores (aqu) will occur.² The transitions from micropores to mesopores depend on parameters such as doping level, current density, and HF concentration. These parameters are considered in detail in the present work. Knowledge of

the mechanism of formation of micropores is still in its infancy. No model can explain micropore formation satisfactorily.² While quantum wire effects⁷ seem to be necessary, they can only account for the distance between micropores (which must be so small as to produce quantum wire effects), but not for the diameters.

Following the discovery of the peculiar optical properties of microporous Si in 1990^{7,8} new research has focused on potential optoelectronic devices based on silicon, since then a large number of electro-luminescent (EL) devices have been presented.⁹ Most of them consists of a microporous layer with a contact layer on top. Although EL devices based on microporous silicon have been demonstrated to be stable, the lack of strong EL is a major problem to overcome.¹⁰ Further application of microporous silicon which emerged are Bragg reflectors and Fabry–Perot filters, made by a modulation of the PS porosity.¹¹ These applications are based on the variation of the optical properties with the porosity of the microporous (or mesoporous) films. Thönissen *et al.*, first showed that multilayers with controlled variations of the porosity and microstructure can be obtained by varying the doping concentration, or by varying the etching parameters (mostly the current density).^{11,12} For many electronic, electromechanical, optical and biological applications, it is highly desirable to pattern porous silicon in defined geometrical layouts.¹³ Patterned formation of porous silicon can be achieved by selective doping of the silicon substrates¹⁴ or by using appropriate masking materials against HF solutions. Unfortunately, this introduces additional processing steps (time consuming) and expensive materials.¹³ Thus, there are still a lot of challenges and problems to be addressed in the fabrication of porous silicon.

2.1.1 Aims of this work

The main objective of this part of the work is to investigate the formation of porous silicon samples using various aqueous electrolytes and by varying the conditions used for etching. It is very important to find a correlation between structure and morphology of porous silicon, and the nature of electrolyte and process parameters. This knowledge would allow us to produce porous silicon with control over structure and pore size. SEM and PL spectroscopy (for microporous silicon) served as the main tools for characterisation of porous silicon samples. BET (Brunauer-Emmet-Teller) surface area analysis by gas

desorption was also found to be useful for evaluation of the porosity of porous silicon samples.

2.2 Results and Discussion

2.2.1 Electrochemical etching of silicon with 7 vol% HF in H₂O

Porous silicon was formed by electrochemical etching of crystalline Si wafers in an HF solution. A schematic representation of the cell used for electrochemical etching in this study is presented in figure 2.1. Rubber O-rings, provided a tight seal and prevent HF leakage. The ohmic contact was made by applying a Ga-In (Gallium-Indium) eutectic on the backside of the wafer, when required. The etching was carried out under a constant current (galvanostatic) and the instrument provided a maximum of 2A (electrical current) and 150V (voltage). The sample enclosure of the cell had to be screwed tight to prevent the leakage of electrolyte solution. However, over tightening had to be avoided to prevent sample stressing and inhomogeneous etching. After etching, the samples were washed with deionised water and dried under dry nitrogen flow.

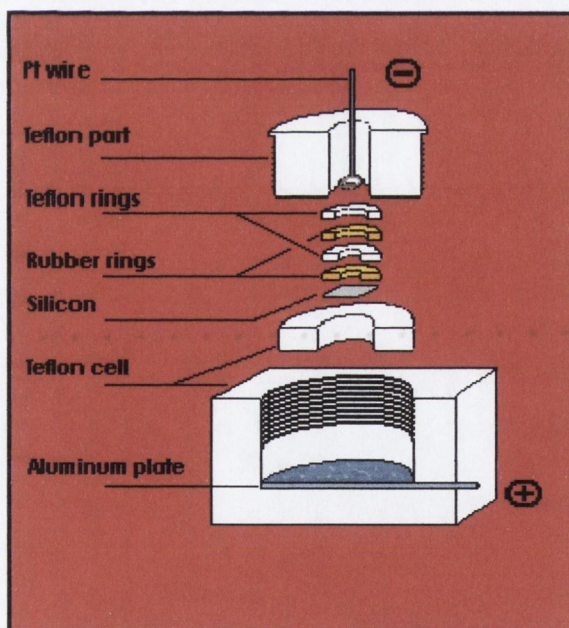
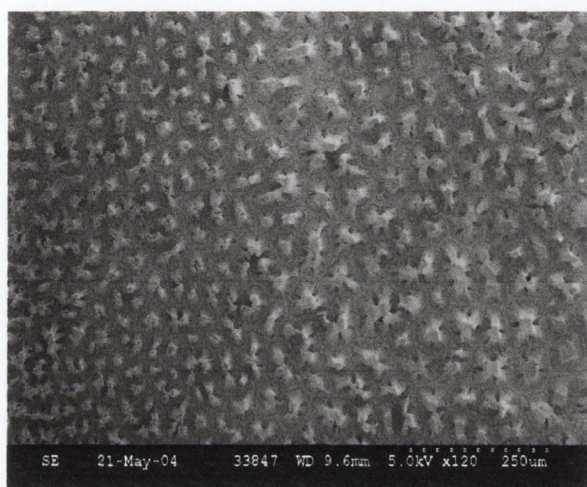
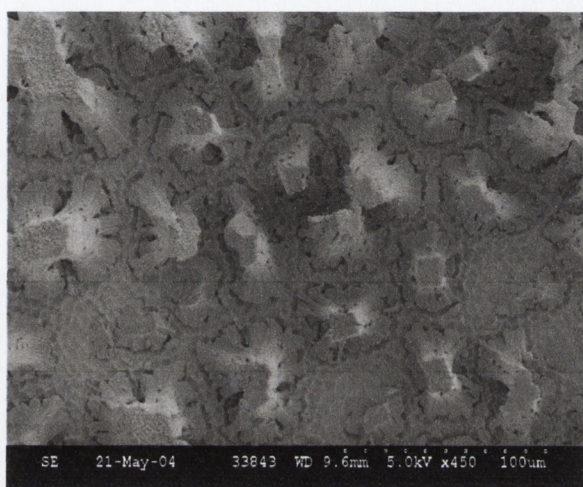


Figure 2.1 A schematic diagram of the electrochemical etching cell used for the fabrication of porous silicon.

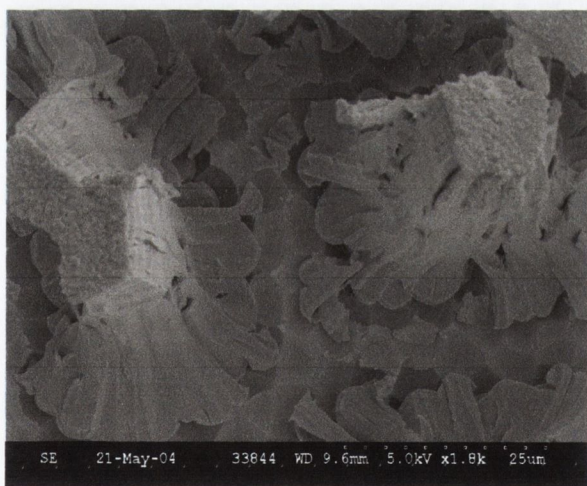
p-Type silicon(100) wafers of resistivity $\rho = 10 \Omega \text{ cm}$ were used in this experiment. Initially porous silicon samples were prepared by electrochemical etching using 7 vol% HF in H_2O electrolyte and applying a current density of 23.5 mA/cm^2 for 3 hours. The SEM images of the porous silicon samples are shown in figure 2.2.



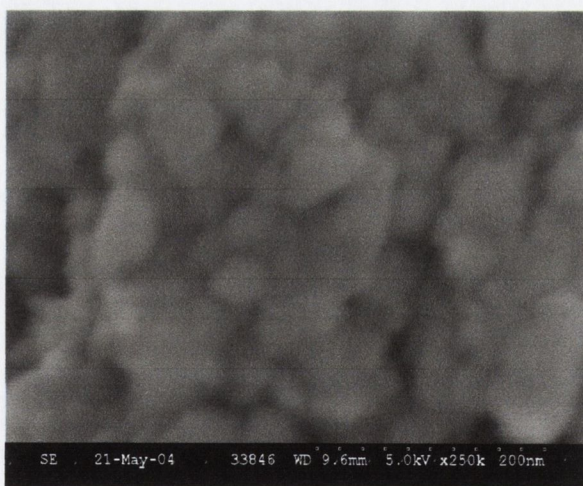
(a)



(b)



(c)



(d)

Figure 2.2 SEM images of the *island-like* structures on *p*-type silicon. (a) uniform distribution of *island-like* structures (b) magnified image of *island-like* structures (c) image showing individual *island-like* structure (d) image showing nano sized silicon crystallites on the upper part of the island like structure; [$\rho = 10 \Omega \text{ cm}$, $j = 23.5 \text{ mA/cm}^2$, 3 hours].

The surfaces of the samples contain *island-like* structures, which are uniformly distributed similarly to the patterning on the silicon surface. The average diameter of each island is around 13 μm . The magnified SEM images shown that each island has a distorted cube-like structure surrounded by petals forming a “flower-like” pattern. The enlarged image (figure 2.2c) shows that the island structures are composed of columnar structures, the top of which are formed from nano-sized crystallites.

The formation of *island-like* structures can be attributed to various factors.^{15,16} The most likely explanation for formation of these structures is a combination of the total charge [total charge(Q), $Q = J \times t$ where, J is current density and t is etching time] and the drying effects. It is established that the electrochemical etching starts at weak spots on the surface of the silicon substrate and the pores are formed mainly parallel to the current flow direction.⁷ The weak spots on the surface provide carriers more capable of sustaining the electrochemical reaction. When the etching proceeds, a few more weak spots will get etched out resulting in non-uniform etching rate and thereby creating interface roughness, which is related to current density. Therefore, larger current density results in a rougher interface and more non-uniformity of the pore size.¹⁶

It is also important to note that an increase in current density can result in the lateral etching of pores, thus increasing the diameter of pores which in turn results in large pores by coalescing of neighbouring pores. The residual silicon sponge-like structures are under tremendous stress because of the formation of these pores. This leads to shrinkage or cracking to minimize the total surface and reduce the total energy of the system when the stress exceeds a critical limit. Thus, cracks start at the weakest regions *i.e.*, in the regions between the pores. In the case of larger scale porosity, the residual silicon sponge would crack before it was taken out of the electrolyte and assemble to form islands. Thus the samples with higher porosity are more likely to forming island structures because the porosity increases with increasing total charge density flowing across sample surface.¹⁶

Secondly, as the sample undergoes drying the liquid escapes from the porous structure resulting in lateral stress causing it to collapse. A similar process has been described before by S. Buratto *et al.*¹⁵ As air replaces the liquid inside each pore, surface tension at the air-liquid interface strongly pulls the sides of the pores together which leads to the collapse of

the porous network. Thus the formation of the *island-like* structures can be attributed to both the total charge flowing across silicon and the drying effects on the sample.

The top part of the islands were found to be photoluminescent with a peak emission at 685 nm (figure 2.3). The photoluminescence is attributed to the presence of quantum-confined nano-sized silicon crystallites in these structures. The spectrum is broad and the width of the spectrum suggests a wide range of chromophore sizes.

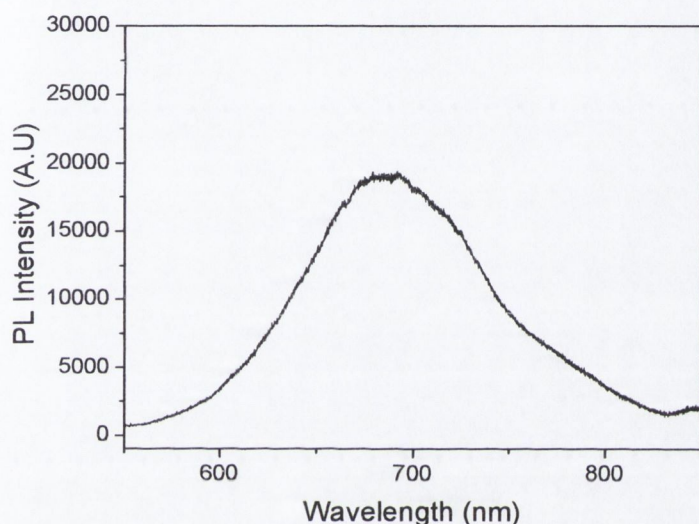


Figure 2.3 PL spectrum taken on the top part of the *island-like* structures.

The magnified SEM images (figure 2.4) show the region between two islands (marked with a red arrow), which are not photoluminescent while the cube-like core of the island is photoluminescent. The non-photoluminescent region between the islands must be the remains of the most active etching place before the islands are formed.¹⁶ These active etching regions were reported by other groups who have studied *island-like* structures on porous silicon.^{15,16}

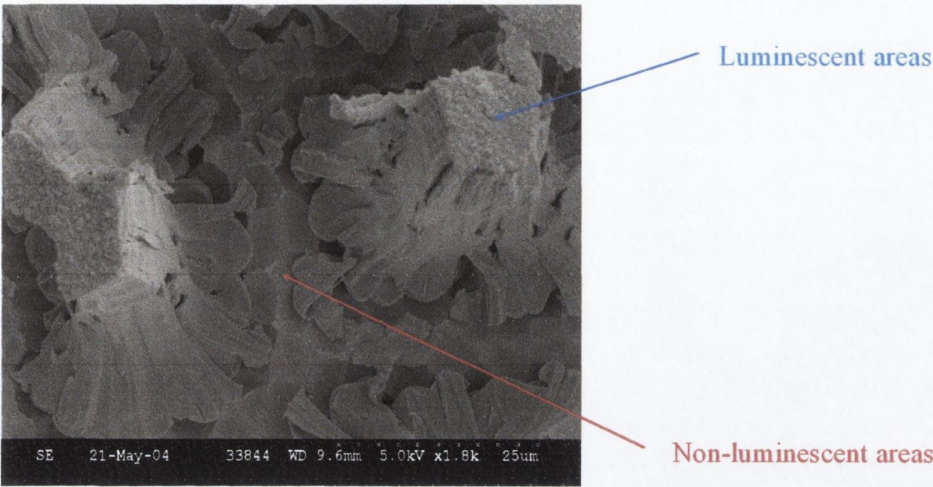


Figure 2.4 A magnified SEM image of the *island-like* structure showing the luminescent and non-luminescent regions; [$\rho = 10 \, \Omega \, \text{cm}$, $j = 23.5 \, \text{mA/cm}^2$, 3 hours].

Then the porous silicon samples of resistivity $10 \, \Omega \, \text{cm}$ were fabricated by the etching using the same electrolyte (7 vol% HF in H_2O) at the low current density of $0.39 \, \text{mA/cm}^2$ for 3 hours.

The SEM images of the resulting silicon samples are shown in figure 2.5.

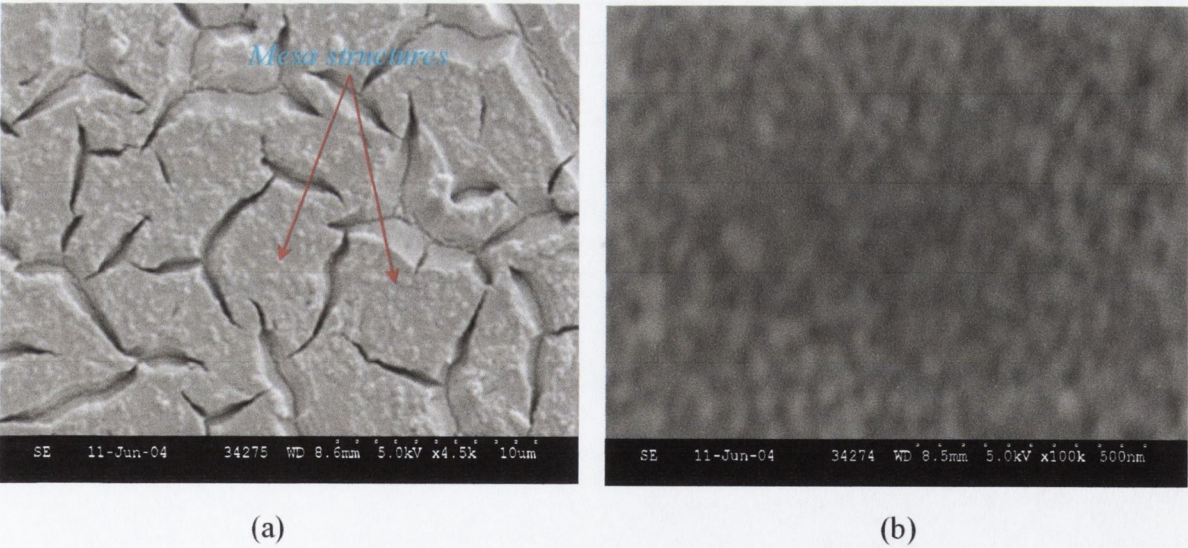


Figure 2.5 SEM images of porous silicon sample prepared under very low current density (a) Panoramic view (b) Magnified view on the top of *mesa* structures; [$\rho = 10 \, \Omega \, \text{cm}$, $j = 0.39 \, \text{mA/cm}^2$, 3 hours].

SEM images of the sample produced at low current density show a flat plateau like structures called '*mesa*' structure¹⁵ where the structures are not completely separated from each other. At the base of the *mesas*, the PS-Si interface remains intact and the PS network has not collapsed entirely. These structures could be premature forms of the *island-like* structures obtained for samples etched using high current density.

The top of these structures were also photoluminescent (figure 2.6) but a slight shift towards red region was observed in comparison with the PL spectrum observed for the *island-like* structures.

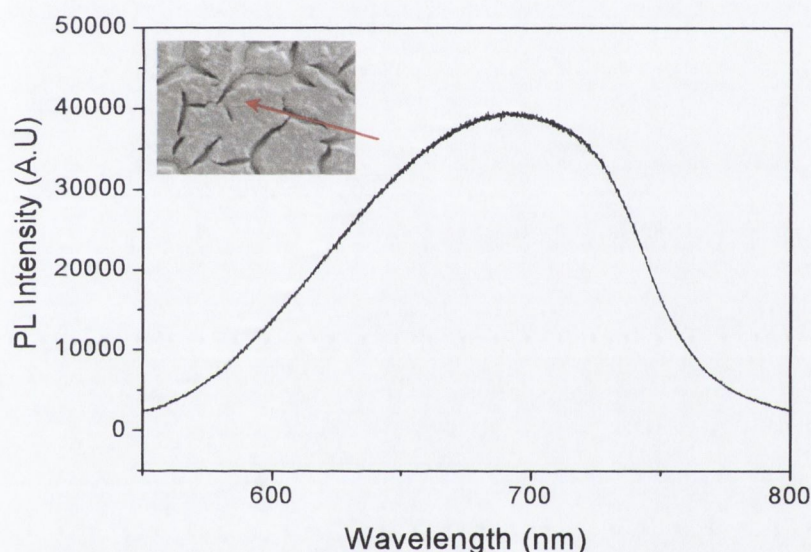


Figure 2.6 PL spectrum taken on top of the cracked surface (*mesa* structures).

The most likely explanation for the slight red shift in the *mesa* structures could be the oxidation of the structures during processing or the exposure of the sample to the air. Thus an oxide-related luminescence¹⁷ could be the possible mechanism, other than quantum size effects, as more oxygen is incorporated in the structures.

The morphology of porous silicon formed under the same current density as that used for forming the *island-like* structures (23.5 mA/cm^2), but using longer etching time (6 hours) has been investigated. In this case the total charge flowing across the silicon surface was much higher. The SEM images of the sample prepared under the above mentioned conditions are presented in figure 2.7. Gouges on the surface, that may have resulted either

from the complete collapse of the structures or from the pull out of the structures as a result of high total charge, are observed. These samples were not photoluminescent.

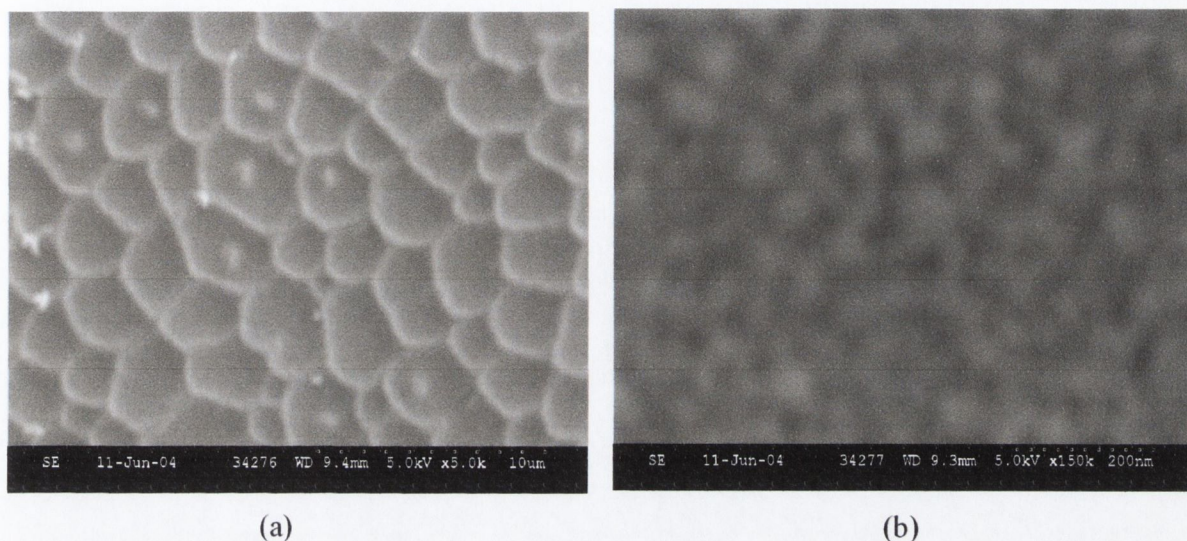
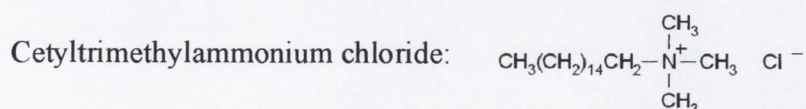


Figure 2.7 SEM images of porous silicon sample prepared under very high total charge on the silicon surface (a) Panoramic view (b) Magnified view; [$\rho = 10 \Omega \text{ cm}$, $j = 23.5 \text{ mA/cm}^2$, 6 hours].

Thus, these results indicated that the formation of *island-like* structures depends mainly on the total charge flowing across the silicon sample and the drying of the samples. In addition to these factors, the choice of electrolyte, resistivity and type of silicon samples can also influence the formation of the *island* and *mesa* structures.

2.2.2 Electrochemical etching of silicon with 1: 1: 1 HF: C₂H₅OH: H₂O with CTAC (Cetyltrimethylammonium chloride)



2.2.2.1 Preparation and characterisation of PS samples

The silicon samples with resistivity, $\rho = 17 \Omega \text{ cm}$ were used for the first part of the studies using 1: 1: 1 HF: C₂H₅OH: H₂O with CTAC electrolyte. The current density used for

etching was reduced at different time intervals (every hour), to prevent the lift off of the porous region from the bulk silicon. The cross-sectional SEM images of the sample etched with an initial current density, $j = 35 \text{ mA/cm}^2$ for one hour are presented in figure 2.8. The slightly curvy pore walls build of highly branched structures.

The SEM images of the sample etched with an initial current density, $j = 32 \text{ mA/cm}^2$ for 3.5 hours are presented in figure 2.9. In this case there is a formation of uniform smooth pores with a high aspect ratios. The formation of macropores with deep and thick pore walls suggest the role of CTAC as a pore wall modifier.¹⁸ It has been reported that during the anodization process, amphiphilic surfactants are adsorbed on the surface of the electrode, with their non-polar tails attached on the hydrophobic silicon surface.¹⁸ The density of adsorbed surfactant on the sidewall of macropores could be higher than that at the tip region due to geometric constraints. This may modify the wetting properties of the silicon surface as well as the electric field at the interface, which may, in turn, protect the sidewalls against dissolution.

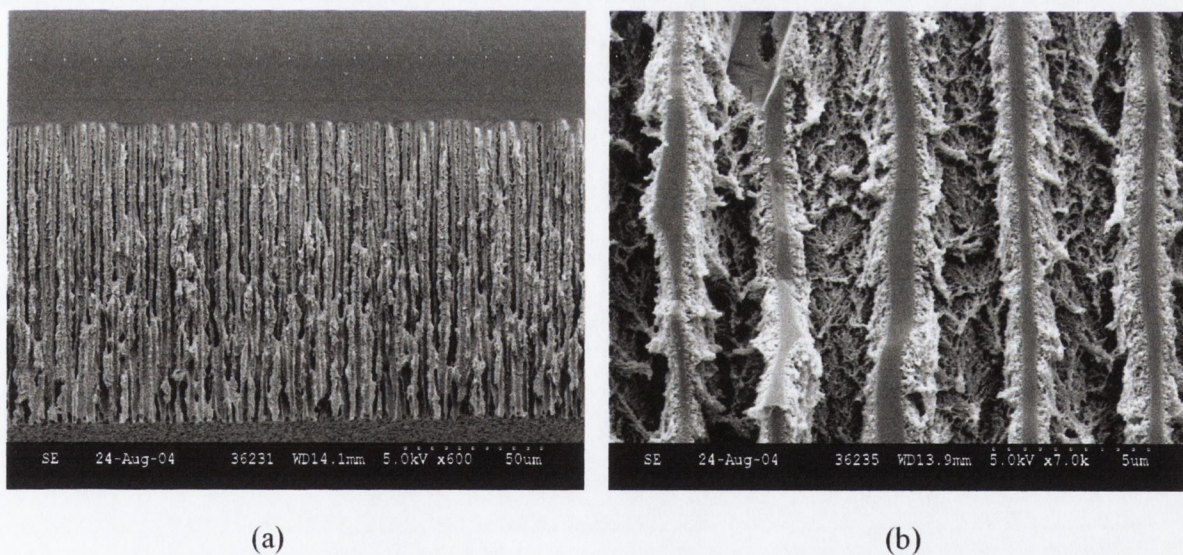


Figure 2.8 (a) Macroporous layer obtained on *p*-type (100) Si ($\rho = 17 \Omega \text{ cm}$) in 1: 1: 1 HF: $\text{C}_2\text{H}_5\text{OH}$: $\text{H}_2\text{O} + 10^{-3} \text{ M CTAC}$ solution, $j = 35 \text{ mA/cm}^2$ (etching time = 1 hour). **(b)** Higher magnification of (a).

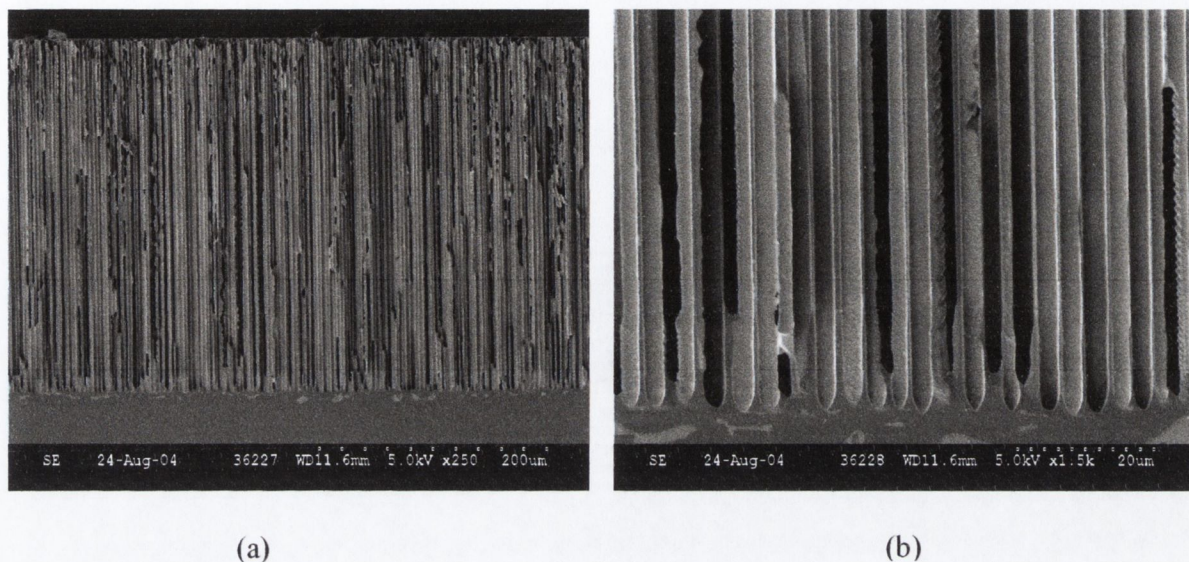


Figure 2.9 (a) Macroporous layer obtained on *p*-type (100) Si ($\rho = 17 \Omega \text{ cm}$) in 1: 1: 1 HF: $\text{C}_2\text{H}_5\text{OH}$: $\text{H}_2\text{O} + 10^{-3} \text{ M CTAC}$ solution, $j = 32 \text{ mA/cm}^2$ (3.5 hours) (b) Higher magnification of (a).

The SEM images of samples etched with slightly higher current density (40 mA/cm^2) and longer etching time (5 hours) are presented in figure 2.10. The images show broken pore walls, which may be due to the higher current density and long etching time. The broken pore walls and the non-uniformity of pore wall structures in figures 2.8 and 2.10 suggest that the optimal conditions for forming good quality macropores with high aspect ratio should be the use of a current density of 32 mA/cm^2 and etching hours of 3.5 hours. The growth rate was insensitive to CTAC concentration greater than 10^{-3} M and it has been reported that for electrolytes with concentration of CTAC of 10^{-2} to 10^{-3} M , it effectively promotes the unidirectional growth of macropores.¹⁸

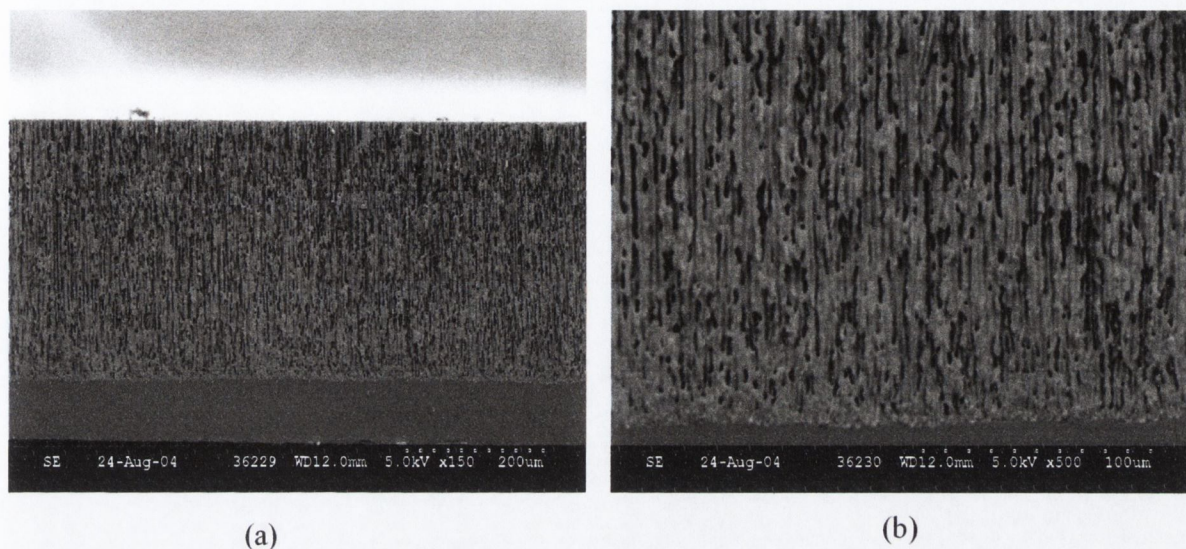


Figure 2.10 (a) Macroporous layer obtained on *p*-type (100) Si ($\rho = 17 \Omega \text{ cm}$) in 1: 1: 1 HF: $\text{C}_2\text{H}_5\text{OH}$: $\text{H}_2\text{O} + 10^{-3} \text{ M CTAC}$ solution, $j = 40.6 \text{ mA/cm}^2$ (5 hours). (b) Higher magnification of (a).

2.2.2.2 Influence of etching time on the porosity and pore depth of the sample

The electrochemical etching of the silicon using 1: 1: 1 HF: EtOH: $\text{H}_2\text{O} + 10^{-3} \text{ M CTAC}$ electrolyte was performed at different conditions in order to study the effect of etching time with respect to the porosity and pore depth of the sample.

Porosity is defined as the fraction of the total volume of the sample that is attributed to the pores. It is usually determined by using the equation:

$$P = \frac{\Delta m}{d \times A \times \rho_{\text{Si}}}$$

where, P is the porosity, Δm is the mass of the porous layer (determined by weighing the sample before and after etching), d is the layer thickness and A is the electrode area exposed to the electrolyte (A is 0.635 cm^2) Density of silicon, $\rho_{\text{Si}} = 2.3828 \text{ g/cm}^3$.

Table 2.1 shows the parameters that were used for the porous silicon preparation. The linear dependence of the pore depth with respect to the etching time (figure 2.11a) was observed. Similar effect also occurs for organic electrolytes (see Chapter III). The increase of porosity with respect to the etching time shows that the porosity depends not strictly only on the depth of the pores but also on the density of pores (figure 2.11b).

Table 2.1 Parameters used for electrochemical etching of silicon using 1: 1: 1 HF: C₂H₅OH: H₂O + 10⁻³ M CTAC solution.

Samples	LD1	LD2	LD3
Time (min)	30	120	180
Resistivity (Ω cm)	0.021	0.021	0.021
J (average) (mA.cm ⁻²)	34.47	34.53	34.46
Δm (g)	0.003498	0.019082	0.02968
d (μm)	50±2	220±2.5	295±2
Porosity (%)	46.23	57.32	66.49

Where, J is average current density and d is depth of the pores.

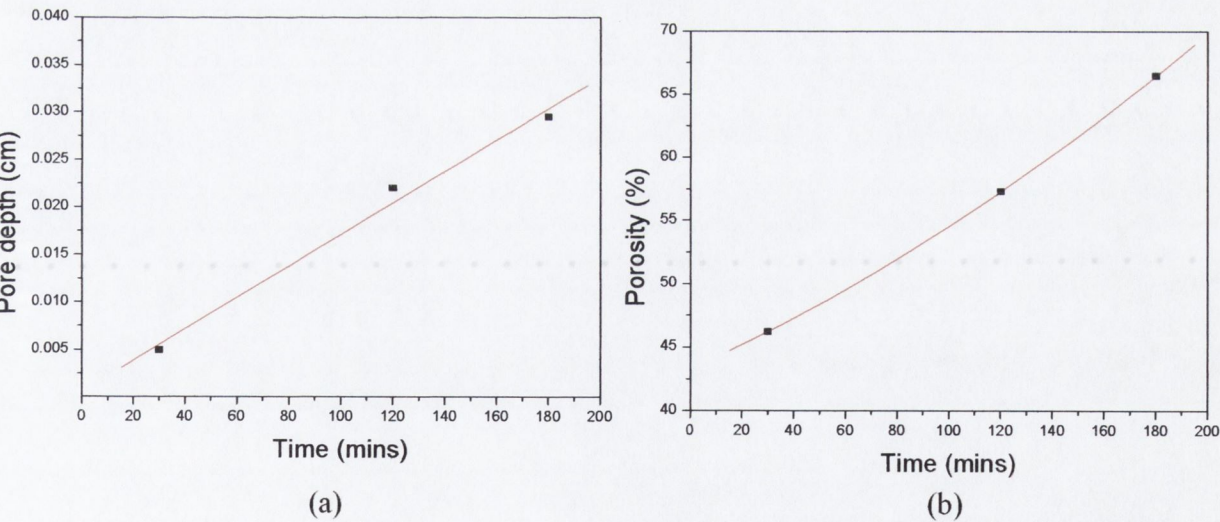
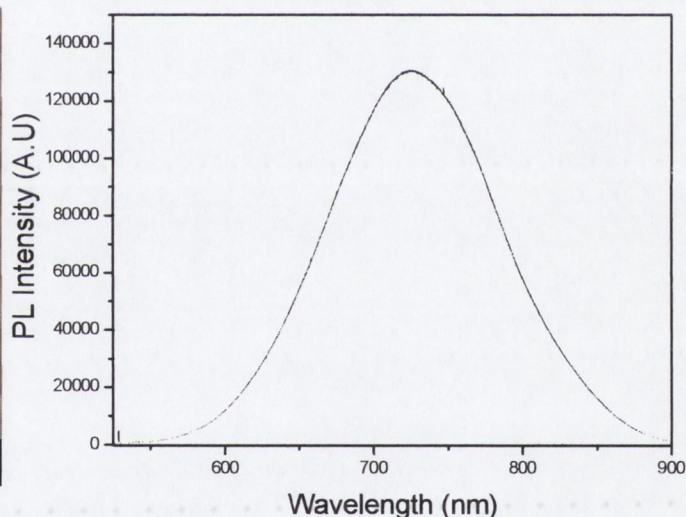


Figure 2.11 Graphs showing (a) the linear dependence of pore depth (in cm) with respect to etching time (b) dependence of porosity with respect to time. The graph 2.11(a) was fitted with the first-degree polynomial using $y = 6.44737E-4 + 1.65351E-4 x$ and graph 2.11(b) with second-degree polynomial.

The samples etched under the conditions given in table 2.1 showed luminescence properties. The SEM image of one of the samples (LD3) depicted in figure 2.12(a) showed the nanopores, in the range of <50 nm. This was also confirmed by BET (Brunauer-Emmet-Teller) pore size analysis based on adsorption-desorption data, which yielded an average pore diameter value of 16 nm. The BET finding of the nanopores is consistent with the results of SEM. Thus, the observation of visible luminescence from these samples can be attributed to quantum confinement (QC) effect,^{7,8} where the pores of nano dimensions are responsible for luminescence effects due to quantum confinement. In the QC model, the charge confinement within the nano silicon wires results in an increase of band gap of silicon, which pushes it in to the visible region, and more importantly increases the probability of a direct band-gap recombination.¹



(a)



(b)

Figure 2.12 (a) SEM image of microporous layer obtained on *p*-type (100) Si ($\rho = 0.021 \Omega \text{ cm}$) in 1: 1: 1 HF: EtOH: $\text{H}_2\text{O} + 10^{-3}$ M CTAC solution, $j = 34.46 \text{ mA/cm}^2$ (3 hours). (b) PL spectra of the sample.

It has to be noted that samples with the higher resistivity do not show any PL characteristics (figure 2.13a). The PL spectrum on the right side (figure 2.13b) shows the PL intensity which is negligible when compared to one for the highly doped sample. The

The SEM images of the higher resistivity samples showed that the pores diameters are in the μm range (see figures 2.8 – 2.10 and 2.15 - 2.16).

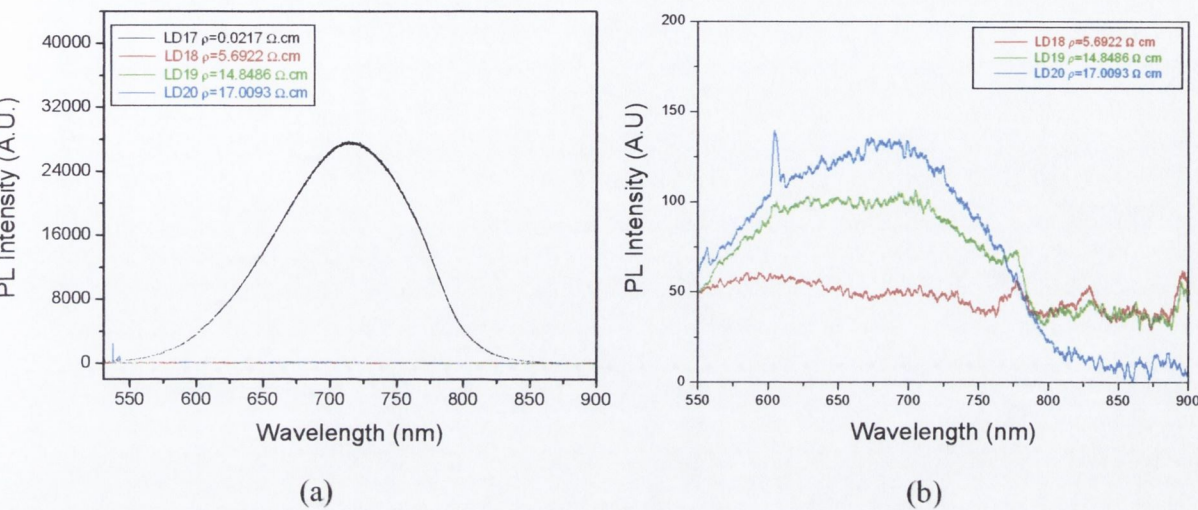


Figure 2.13 (a) and (b) Photoluminescence spectra of PS samples with different resistivities.

The PL dependence on the current density was also studied and presented in figure 2.14. The intensity of the PL emission increases with the current density used for PS preparation for a fixed electrolyte concentration. Obviously that higher current density allows preparing microporous silicon of high porosity with nanosized pores.

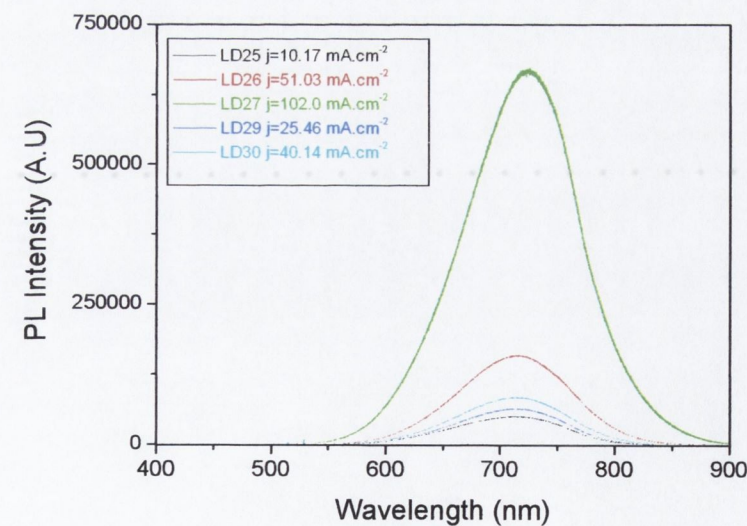


Figure 2.14 PL spectra of PS samples prepared at the different current densities.

2.2.2.3 Influence of silicon resistivity on the pore depth and morphology

The effect of silicon resistivity with respect to the pore depth was determined by using the same electrolyte, but keeping all other parameters constant. The resistivities of the samples studied were 0.021, 5.69, 14.85 and 17.01 Ω cm. The SEM images of the samples with higher resistivity are presented in the figures 2.15 and 2.16. The top view of the two samples are similar but the cross-section images have shown that the pore depth decreases (from 32 ± 1.3 μ m for $\rho = 14.85$ Ω cm to 10 ± 0.75 μ m for $\rho = 17.01$ Ω cm) with increasing the sample resistivity. This is also in agreement with the results that obtained for etching in organic electrolytes (see Chapter III).

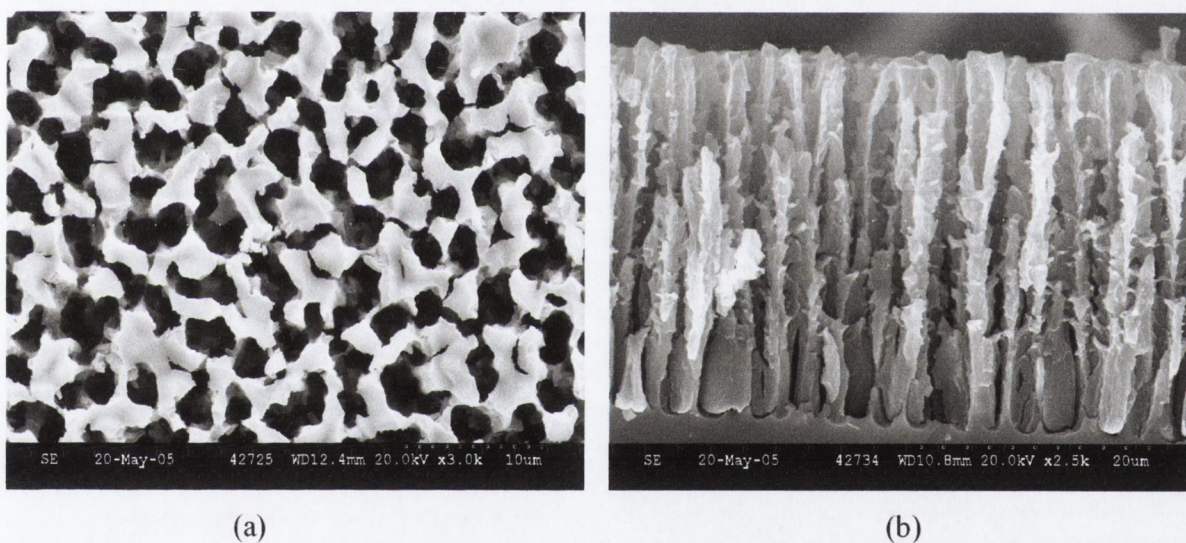


Figure 2.15 SEM image of sample etched in 1: 1: 1 HF: C₂H₅OH: H₂O + 10⁻³ M CTAC solution, (anodisation time: 60 min, $j = 10.01$ mA/cm², $\rho = 14.85$ Ω cm). **(a)** Top view **(b)** Cross-section (pore depth is 32 ± 1.3 μ m).

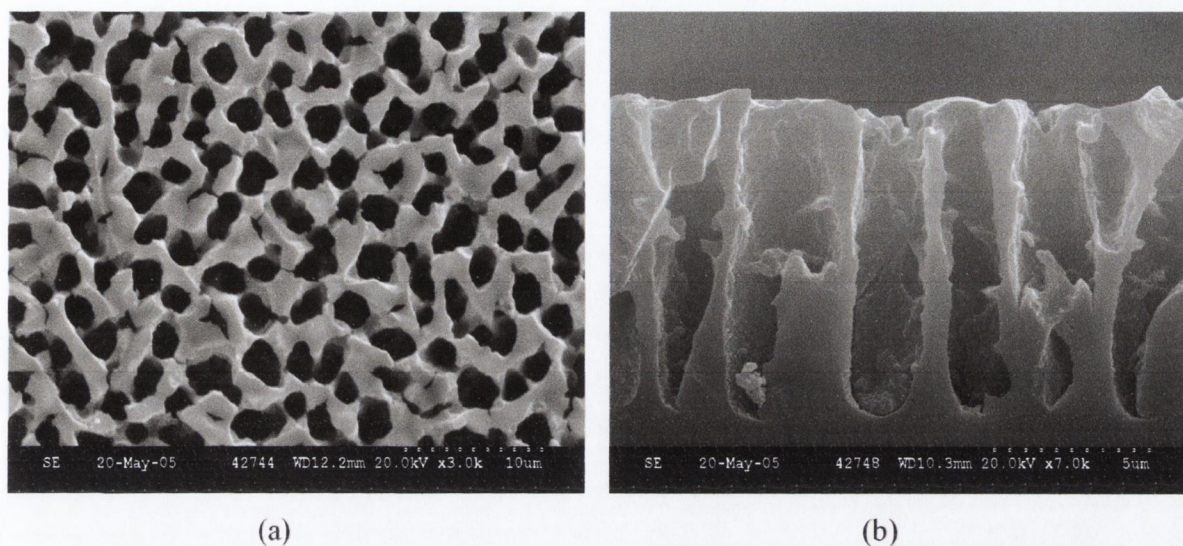


Figure 2.16 SEM image of sample etched in 1: 1: 1 HF: C₂H₅OH: H₂O + 10⁻³ M CTAC solution, (anodisation time: 60 min, $j = 10.03 \text{ mA/cm}^2$, $\rho = 17.01 \Omega \text{ cm}$ (a) Plan view (b) Cross-section (pore depth is $10 \pm 0.75 \mu\text{m}$).

Macropore samples with controlled pore structure can be formed using this electrolyte and high resistivity samples. The variation of porosity was studied by BET with respect to current density (figure 2.17).

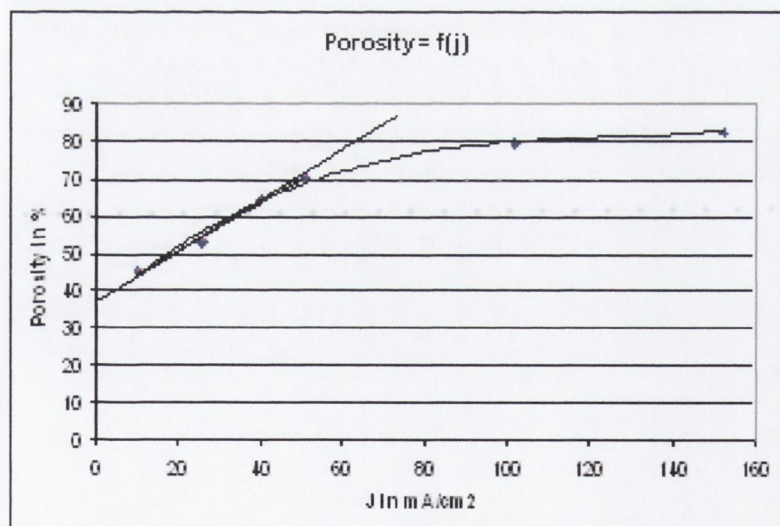


Figure 2.17 Graph showing the dependence of current density with respect to porosity.

It was found that the porosity increases linearly up to 60 mA/cm^2 and then it maintains more or less the same over a range of higher current density. An increase in the number of the pores, which is otherwise termed as branching of pores at high current density, may be one reason for more or less stable porosity at higher current density. So an increased current density leads to the formation of more branched pores. Another reason could be the formation of closed pores, but more detailed studies would be required to prove that.

2.2.3 Electrochemical etching of silicon with 1: 1 HF: $\text{C}_2\text{H}_5\text{OH}$

The electrochemical etching of three silicon samples with resistivities, $\rho = 0.021, 3.49$ and $17.01 \text{ } \Omega \text{ cm}$ was carried out for 1 hour using an average current density (20.02 mA/cm^2). The SEM images of the samples are presented in figures 2.18 and 2.19. The low resistivity sample etched with 1: 1 HF: $\text{C}_2\text{H}_5\text{OH}$ electrolyte and a current density of 20.025 mA/cm^2 showed spikes which have been reported for *n*-type mesoporous silicon.¹⁹ The spike-like structures are around 70 nm in diameter. The formation of spiking mesoporous silicon can be suppressed if low bias, low substrate doping density and high array porosity are used.²⁰

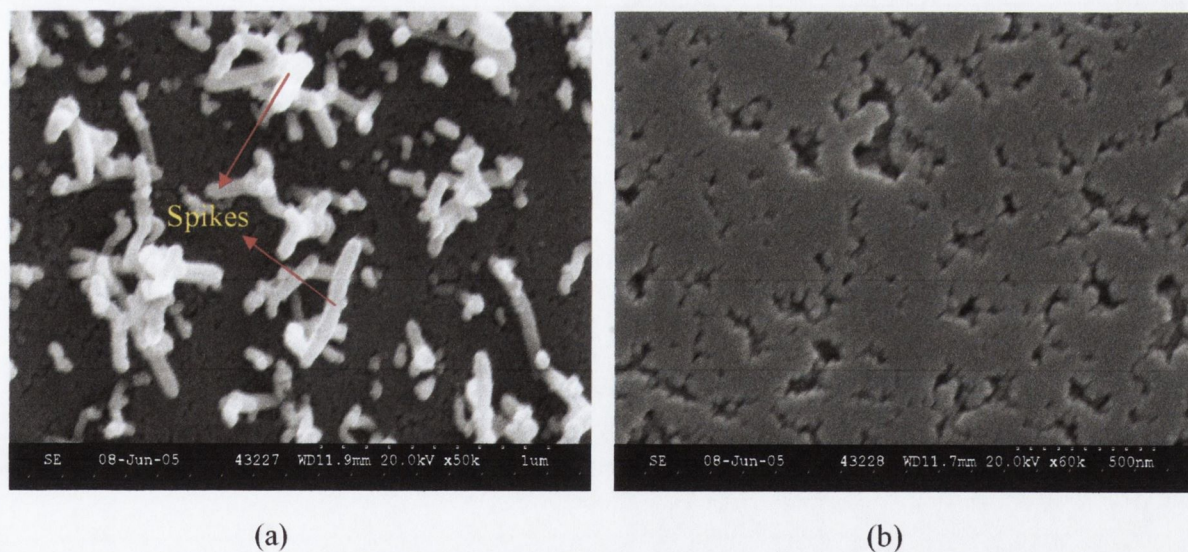


Figure 2.18 SEM image of sample etched in 1: 1 HF: $\text{C}_2\text{H}_5\text{OH}$ (anodisation time: 60 min, $j = 20.03 \text{ mA/cm}^2$, $\rho = 0.021 \text{ } \Omega \text{ cm}$): (a) spikes (b) mesopores.

The formation of macropores with pore diameters less than 1 μm were formed by etching a sample with resistivity 3.49 $\Omega\text{ cm}$. This result is presented in figure 2.19a. The pores showed small branching in the direction perpendicular to the main pore orientation. The figure 2.19b shows macropores, which consist of micropores demonstrating luminescence properties. The same behaviour has been reported for the etching of the silicon sample with resistivity 17.01 $\Omega\text{ cm}$ using an aqueous solution of HF.⁶

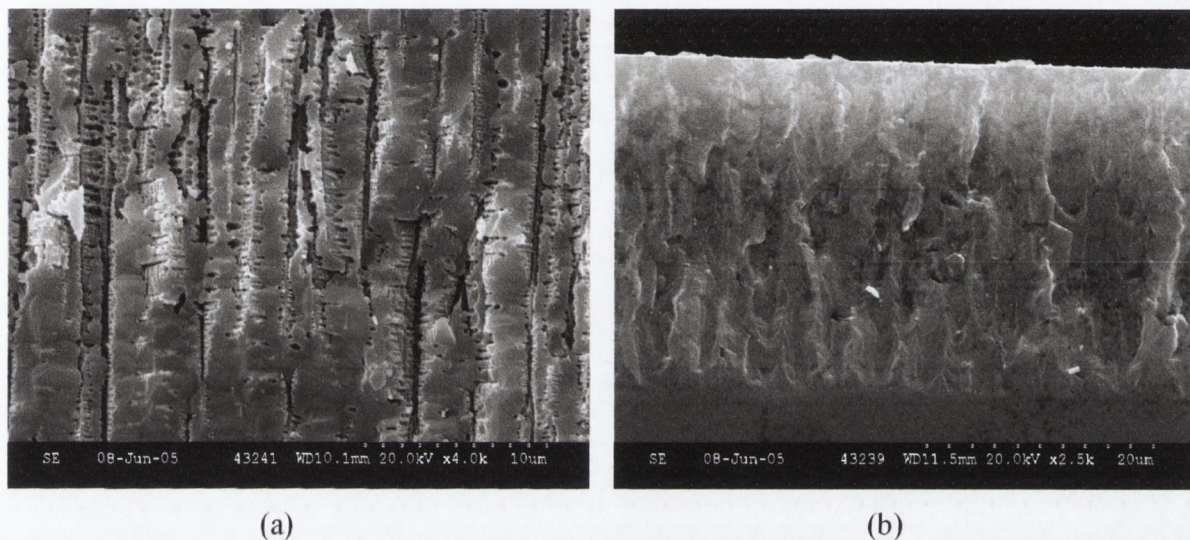


Figure 2.19 Cross-sectional SEM image of sample etched in 1: 1 HF: $\text{C}_2\text{H}_5\text{OH}$ (anodisation time: 60 min, $j = 20.14\text{ mA/cm}^2$): (a) $\rho = 3.49\text{ }\Omega\text{ cm}$ and (b) $\rho = 17.01\text{ }\Omega\text{ cm}$.

PL luminescence spectra of the samples with different resistivities are presented in figure 2.20. The luminescence intensity of the samples etched using 1: 1 HF: $\text{C}_2\text{H}_5\text{OH}$ increases with an increase in sample resistivity, by contrast to the results for the samples above etched using 1:1:1 HF: $\text{C}_2\text{H}_5\text{OH}$: $\text{H}_2\text{O} + 10^{-3}\text{ M CTAC}$ solution where the low resistivity sample showed an increase in luminescence compared to the high resistivity sample. Presumably, CTAC plays a role as a surfactant influencing the kinetic parameters of the etching process. In the CTAC added samples, the surfactant protects the wall of silicon from further dissolution. So etching of the highly doped samples is well compared to high resistivity samples. The formation of nanostructures in the highly doped samples might be the reason for PL whereas, etching in electrolyte solutions without CTAC, all samples showed PL with an increase in high resistivity samples.

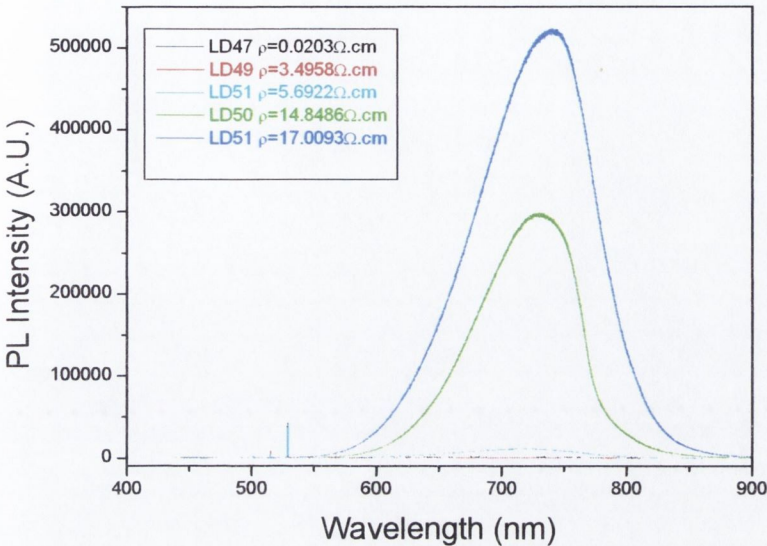


Figure 2.20 Photoluminescence spectra of PS samples with different resistivities.

2.2.4 Electrochemical etching of silicon with 5: 9: 26 HF: C₃H₈O: H₂O

The electrochemical etching of silicon samples with resistivity, $\rho = 10 \Omega \text{ cm}$ using 5: 9: 26 HF: C₃H₈O (iso-propanol): H₂O electrolyte at current density (31.5 mA/cm²) for 3 hours. The SEM images of the prepared PS samples (figure 2.21) revealed thin uniform pore walls with an average pore diameter of 3 μm and a pore depth of 83 μm . The sample tilted at an angle shows the density of pores (figure 2.21b).

The morphology of the pores obtained was studied for the samples with resistivity, $\rho = 5.69 \Omega \text{ cm}$ by keeping all parameters constant but using two different etching times. SEM images of the samples etched in HF: C₃H₈O: H₂O 5: 9: 26 having a resistivity, $\rho = 5.69 \Omega \text{ cm}$, etching current density $j = 11.19 \text{ mA/cm}^2$ and etched at two different anodisation periods of times, 90 min and 180 min are presented in figures 2.22 and 2.23 respectively.

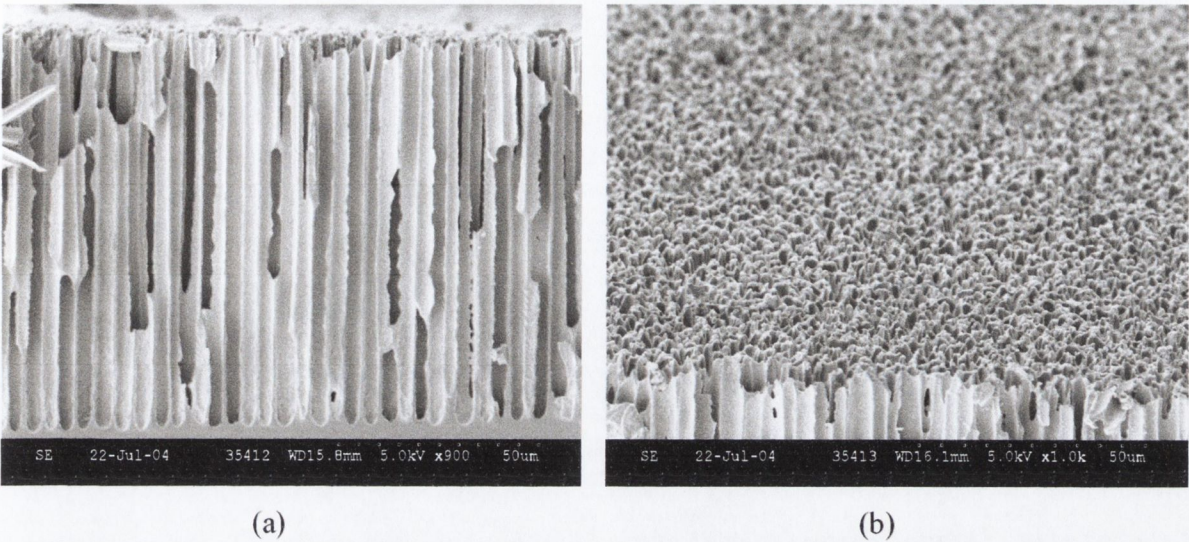


Figure 2.21 SEM image of sample etched in 5: 9: 26 HF: C₃H₈O: H₂O (anodisation time: 180 mins, $j = 31.5 \text{ mA/cm}^2$, $\rho = 10 \Omega \text{ cm}$) (a) Cross-sectional image (b) titled at angle of 30°.

The SEM images presented in figure 2.22 show the plan view of the pores formed.

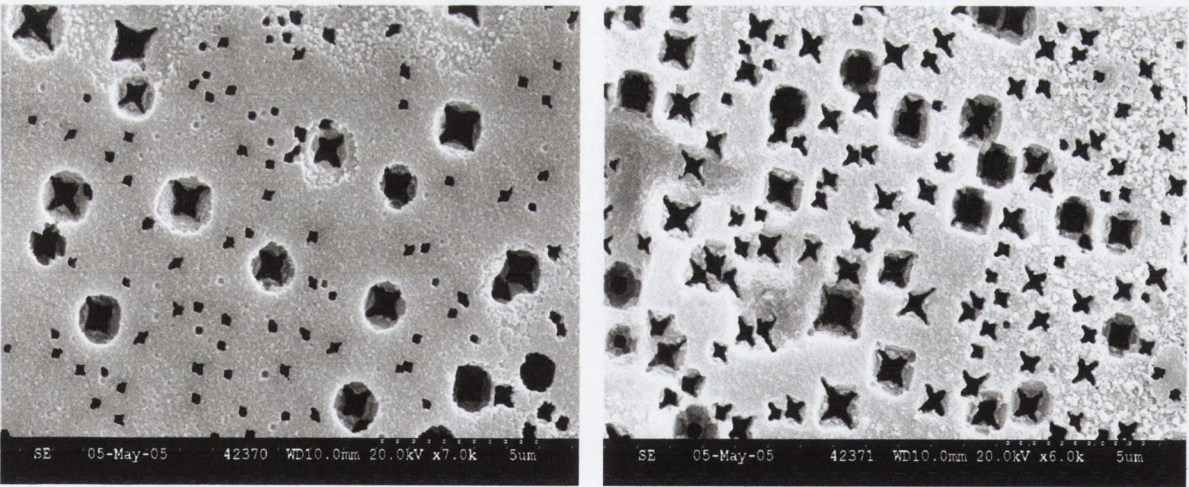


Figure 2.22 SEM image of sample etched in 5: 9: 26 HF: C₃H₈O: H₂O (anodisation time: 90 mins, $j = 11.19 \text{ mA/cm}^2$, $\rho = 5.69 \Omega \text{ cm}$). Size of the star shaped pores is 0.5 – 1.5 μm .

There are a number of star shaped pores with pore diameters in the range 0.5 – 1.5 μm on the surface. This type of porous structures was reported earlier for mesoporous silicon

structures.²¹ The possible explanation of these structures is the avalanche breakdown, but a clear understanding of this mechanism is still under discussion. The increase in etching time results in large etch pits as could be seen from figure 2.23.

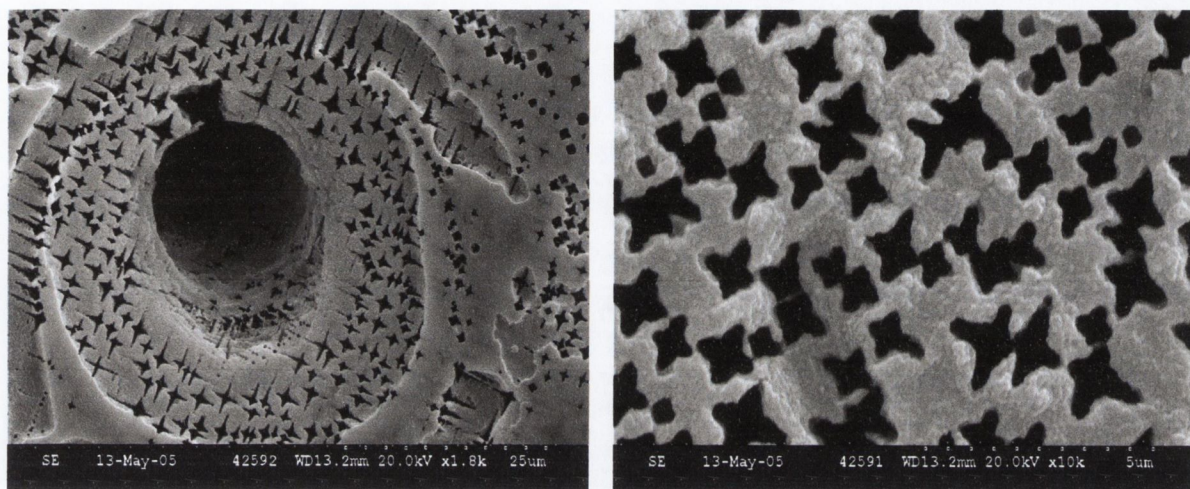


Figure 2.23 SEM image of sample etched in 5: 9: 26 HF: isopropanol: H₂O (anodisation time: 180 mins, $j = 11.19 \text{ mA/cm}^2$, $\rho = 5.69 \Omega \text{ cm}$).

The complex morphology contains large spherical etch pits with diameters in the order of tens of micrometers. The close inspection of such a large pit reveals that there are a number of star-shaped macropores (sizes of $1.3 - 3.7 \mu\text{m}$) in the outer perimeter of the pit, whereas the inner perimeter shows significant etching with a large central hole.

The pore depth decreases with increasing silicon resistivity, this effect which is also observed in other aqueous and organic electrolytes. The morphology of the sample with high resistivity showed the formation of pores having small pore diameters ($1.2 \pm 0.2 \mu\text{m}$) on the surface (bottleneck shape). This diameter is increased ($2.5 \pm 0.5 \mu\text{m}$) with pore depth (see figure 2.24b). The higher resistivity samples have lower pore densities than low resistivity samples (highly doped samples). The decrease in pore density causes an increase in pore tip current for the surviving pores, which leads to a bottleneck at the pore opening due to the dependence of pore diameter on current. Since less holes will be available for the enlargement of the pore diameter in high resistivity samples. After this initiation pore

growth becomes stable and a pattern of randomly distributed pores penetrates the electrode without a further change in the number of pores.²²

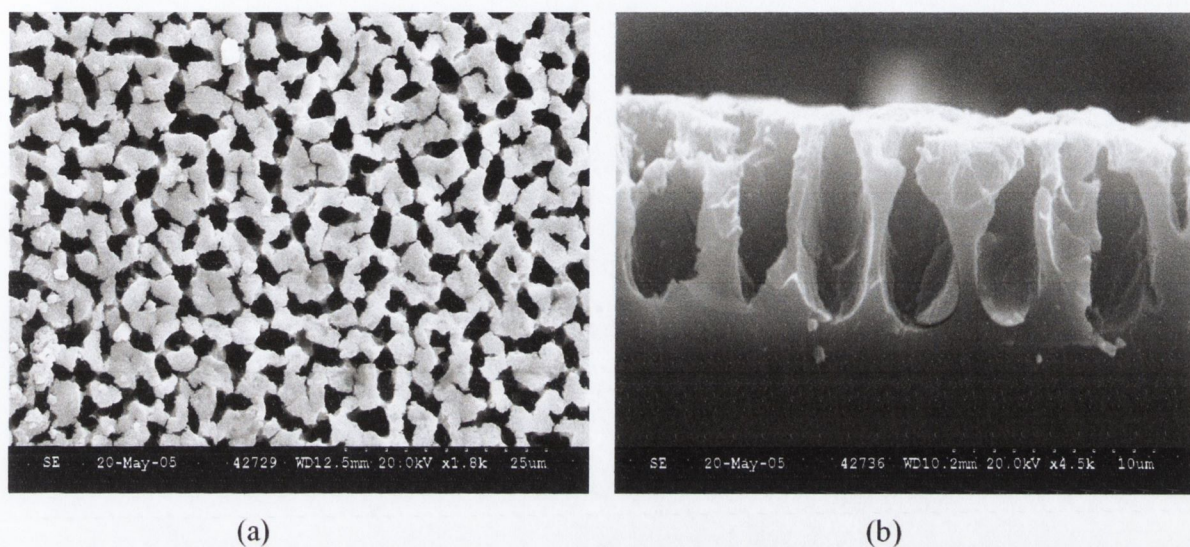


Figure 2.24 SEM image of sample etched in 5: 9: 26 HF: C_3H_8O : H_2O (anodisation time: 60 mins, $j = 10.01 \text{ mA/cm}^2$, $\rho=17.01 \text{ } \Omega \text{ cm}$). (a) Plan view (b) Cross-sectional view. The pore diameter increased with pore depth from $1.2 \pm 0.2 \text{ } \mu\text{m}$ to $2.5 \pm 0.5 \text{ } \mu\text{m}$.

2.2.5 Electrochemical etching of silicon with different percentages of HF in H_2O

In this section the effect of different HF percentage in H_2O and pH on the porosity of PS samples were investigated. The samples selected for the present study were named as LD32, LD34, LD36 and LD37. The table 2.2 (below) shows the parameters that have been used and the results obtained for these experiments. The SEM images of the samples etched in 4% HF in H_2O and 12% HF in H_2O for different resistivity samples are presented in figure 2.25. The samples etched in 4% HF in H_2O show more micropores compared to the silicon samples etched in 12% HF in H_2O electrolyte where both micropores and mesopores are present.

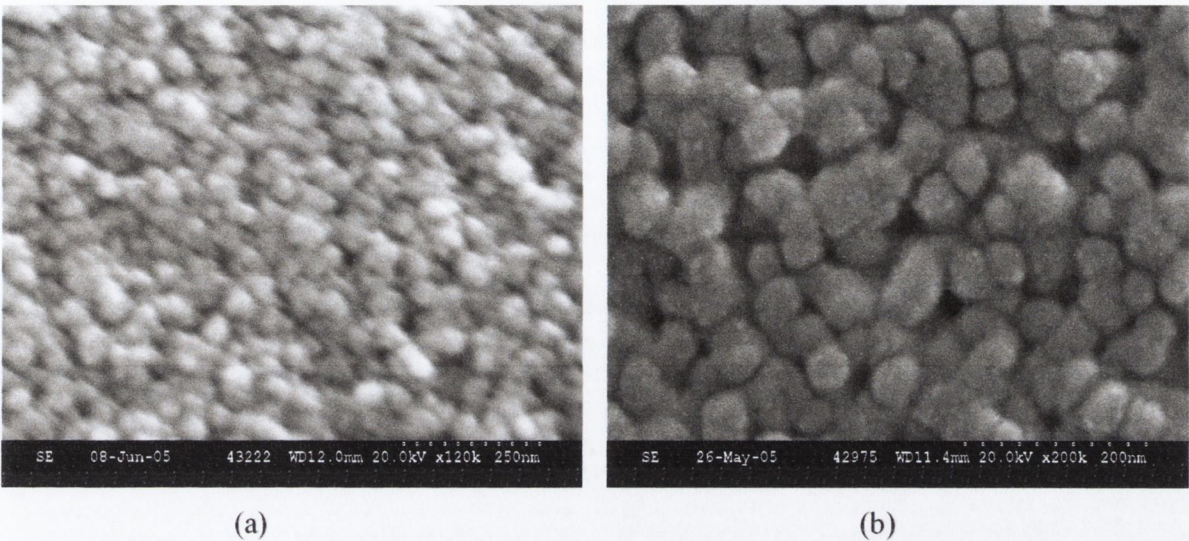


Figure 2.25 Plan view SEM image of the samples etched in (a) 4% HF in water (anodisation time: 120 mins, $j = 2.03\text{mA/cm}^2$, $\rho = 5.69\ \Omega\ \text{cm}$) (b) 12% HF in water (anodisation time: 60 mins, $j = 2.01\text{mA/cm}^2$, $\rho = 0.02\ \Omega\ \text{cm}$).

Table 2.2 Parameters used and results obtained for etching of silicon in HF-H₂O solutions.

Samples	LD32	LD34	LD36	LD37
Time (min)	60	60	60	60
% (HF)	4	8	12	16
pH	1.56	1.41	1.32	1.26
Resistivity ($\Omega\ \text{cm}$)	0.021	0.021	0.021	0.021
J (average) (mA.cm^{-2})	2.042	2.030	2.007	2.0055
Δm (g)	0.00091	0.00112	0.000792	0.00078
d (μm)	6	8	7.5	10
Porosity (%)	93.29	88.56	65.17	48.39
Where J is the average current density and d is depth of the pores.				

The results show that the porosity of the samples increase linearly with pH, from the lower pH values up to 1.45, it is then stabilised at higher pH values (figure 2.26a). According to

the graph in figure 2.26b the pore depth decreases in a linear manner with respect to the pH values.

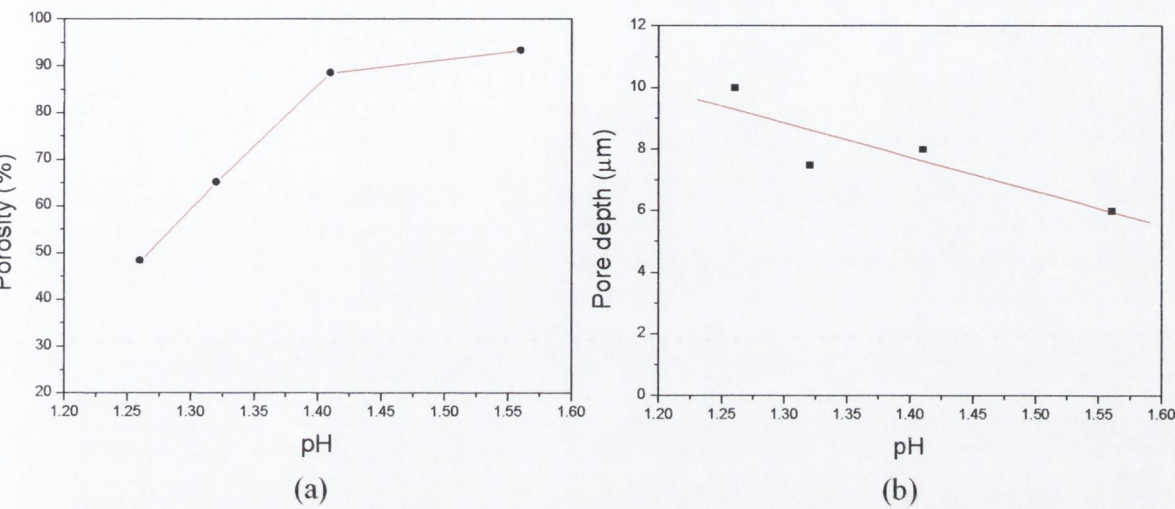


Figure 2.26 pH dependence with respect to (a) porosity and (b) pore depth.

The luminescence properties also depend on the concentration of HF in aqueous solution. The PL of PS samples prepared with different percentages of HF concentration is presented in figure 2.27.

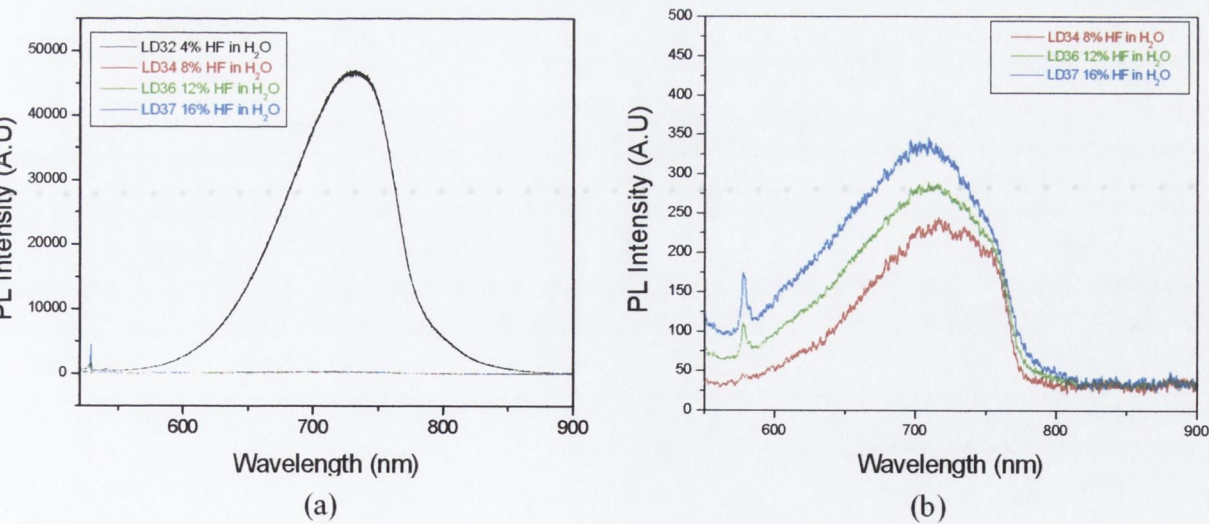


Figure 2.27 (a) and (b) Photoluminescence spectra of PS samples prepared with different percentages of HF concentration.

The figure 2.27a showed that the PS sample prepared using 4% HF in H₂O demonstrates very strong luminescence compared to the other PS prepared at higher % of HF in H₂O. Thus lower concentrations of HF and higher pH are favourable for the fabrication of luminescent microporous silicon samples. The PL spectrum on the right side (figure 2.27b) show the PL intensity of PS prepared with higher % HF is negligible when compared to 4% HF in H₂O electrolyte.

2.3 Conclusions

We have investigated etching of *p*-type silicon using different H₂O-HF electrolytes. The etching of *p*-type silicon in the H₂O-HF electrolyte under high current density resulted in the formation of unusual *island-like* structures on (100) silicon. These structures have been characterised by SEM and photoluminescence (PL) studies. The islands were uniformly arranged forming a regular structure. The structures also demonstrated a strong luminescence with the maximum at 685 nm. The formation of the *island-like* structures on PS is caused by the processing parameters: firstly the total charge flowing across silicon, secondly the drying effects on the sample.

The porous silicon samples have been prepared by using 1: 1: 1 HF: C₂H₅OH: H₂O + 10⁻³ M CTAC. It was found that porous silicon samples with high aspect ratios can be prepared with short etching time compared to the other electrolytes which need long etching hours for the same aspect ratios. The information from SEM images of the samples was in good agreement with the results obtained from BET analysis. The photoluminescence evolution with respect to the silicon resistivity and current density were determined. The intensity of the PL emission was increasing with the current density used for PS preparation for a fixed electrolyte concentration. Therefore a higher current density is necessary to prepare luminescent microporous silicon of high porosity. We have also found that for HF: C₂H₅OH: H₂O + 10⁻³ M CTAC electrolyte the increase in current density resulted in the formation of more branched pores. The etching of the samples in ethanol-HF electrolyte without CTAC resulted in the formation of spikes in the silicon matrix. It was observed that the luminescence intensity of the samples etched using ethanol-HF electrolyte was increasing with an increase in a sample resistivity. By contrast the low resistivity silicon samples etched using similar electrolyte with an addition of CTAC showed an increase in the luminescence compared to the high resistivity sample. Most likely CTAC plays a role as a surfactant influencing the kinetics of the etching process.

The etching of the samples using 5:9:26 HF: isopropanol: H₂O demonstrated the formation of etch pits and star-shaped pores in *p*-type porous silicon samples. The pore depth decreased with increasing silicon resistivity, which is also observed in other aqueous electrolytes such as HF in ethanol.

The investigation of different HF percentage and pH in aqueous electrolytes showed that the porosity of the PS samples increased linearly with pH values up to 1.45, it is then stabilised at higher pH values. It was also found that lower concentrations of HF and higher pH are favourable for the formation of luminescent microporous silicon samples.

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III

Preparation of *p*-type Porous Silicon using Organic Electrolytes and its Characterisation

3.1 Introduction

The formation of porous silicon (PS) by anodisation of silicon in HF^1 is very important for modern technology and has been widely investigated.² The morphology of pores in silicon can be controlled by the pre-patterning of the silicon before etching. This is normally done using photolithographic techniques.³ Etching on patterned silicon surfaces deals with the controlled removal of silicon. The process is normally performed by masking the silicon surface initially. For thin film etching, the mask acts as a photoresist. When silicon is etched with considerable depth, the resist may not be stable enough. In these cases, a structured thin film is used as mask.⁴ The main steps for etching are:

- i. Preparation of the lithographic mask: This is a plate of glass with a thin structured film of chromium on it. The chromium is structured either by a pattern generator or by electron beam lithography.
- ii. Deposition of the masking layer (silicon nitride) on the wafer.
- iii. Deposition of photosensitive resist by spin on coating.
- iv. Pattern transfer from the mask into the resist by exposure to UV-light (optical lithography).
- v. Development of the resist: The exposed parts of the resist are removed (positive resist).
- vi. Structuring of the masking layer (e.g. by plasma etching).
- vii. Removing of the resist: (wet chemical etching by acetone or dry etching in an oxygen plasma).
- viii. Etching plasma.

The process of making patterns in silicon is most commonly done by anisotropic etching or in other words, anisotropic etching is the most commonly used method for the micromachining of silicon.⁵ The common etching solution used for anisotropic etching is a KOH solution. In our present study also we have used a KOH solution for forming the prepatterned silicon surfaces.

Macropore formation on *n*-type silicon is well documented and understood in terms of the space-charge region effect, which results in a collection of the charge carriers at the tip of the macropores.⁶ In the case of *p*-type silicon, the formation of nanoporous (micro- and

mesoporous) Si is generally observed.⁷ As an extended space-charge region is not expected in the anodic regime, macropore formation in *p*-type silicon appears to be a “curiosity” which is still poorly understood.⁸ Thus the mechanism of macropore formation in *p*-type silicon is highly controversial.⁹ Among the various models to be developed to explain the formation of macropores on *p*-type silicon, only four models are logical. The first model by Lehmann and Rönnebeck, based on charge-transfer mechanism in a Schottky diode with a nonplanar interface.¹⁰ As a result the macropore formation on *p*-type silicon can be understood as a consequence of the charge-transfer mechanisms in a Schottky diode if applied to a non-planar interface. The model predicts that macropore formation on *p*-type silicon electrodes in HF solution is caused by the increase of the diffusion current density at the pore tips, when compared to the flat electrode areas. But the model was having disadvantages when the thermionic emission process dominates charge transfer, which is sensitive only to barrier height and not to barrier width.

The second model concentrated more at the early stages of porous silicon formation and was first proposed by Valance¹¹ and by Kang and Jorne¹² and was developed by Ozanam *et al.*¹³ The model based on linear stability analysis incorporates the transport phenomena of holes in the semiconductor and ions in the electrolyte. The model, as was shown by Ozanam *et al.*, predicts the characteristic structure sizes is comparable with the SCR width; however the model cannot be used to describe the pore growth process in a proper way.

The third model, Current Burst Model (CBM), which accounts for most of the processes of the reactive Si-liquid interface, including the current oscillations on the current voltage characteristics, which causes the formation of micro-, meso-, and macropores with their specific dependence on crystal orientation which has been recently proposed by Föll *et al.*¹⁴ This model can predict some of the experimental results like frequency dependence of macropore parameter formation on external experimental parameters¹⁵ but it is too general to be practically useful for many applications. For example, the model cannot predict pore diameter, pore wall thickness, pore formation rate, and other parameters, which are of primary importance for practical applications. The fourth model is a pure chemical model¹⁶ which has been developed for *n*-type silicon, but can be applied to *p*-type silicon as well. In this kinetic model, unoxidized silicon surface atoms are represented by Si(0). At the first step of the anodic dissolution, Si(0) atoms capture a valence band hole. It is assumed that

the hole is captured in a Si-Si bond and the Si(I) intermediate state corresponds to a one-electron-deficient Si-Si back bond. This intermediate state is very mobile and can act as a catalyst for the dissolution reaction. Along with the models discussed briefly above, many other mechanisms of the macropore formation in *p*-type silicon have been proposed. At the present time, existing models and mechanisms of the macropore formation in silicon cannot explain all experimental data.⁹

Propst and Kohl prepared *p*-type silicon with macropores using organic electrolytes for the first time.¹⁷ The authors studied the dissolution of silicon in the absence of water in hydrofluoric acetonitrile and obtained for the first time macropores (rather poor) in *p*-type silicon. They also predicted that the simple space charge region model cannot be the only reason for macropore formation. While it first appeared that *p*-macropores (org) were limited to silicon with a rather high resistivity of $\geq 100 \Omega \text{ cm}$. The idea was soon invalidated as Ponomarev and Levy-Clement¹⁸ successfully etched macropores on $1 \Omega \text{ cm}$ (100) and (111) oriented *p*-type silicon substrates using different organic electrolytes.

A very stable growth condition for *p*-type silicon with macropores using organic electrolytes with a depth of 400 μm attracted attention because of its possible application.¹⁹ Christophersen's article was followed by Ohji *et al.*, who were able to build free standing silicon structures based on electrochemically etched pre-structured *p*-type porous silicon using organic electrolytes.²⁰ A recent article by Lévy-Clément *et al.*, suggested the formation of nanopores and macropores on *p*-type silicon is dependent on the composition of electrolyte and silicon resistivity.²¹ The authors studied the dependence of the electrochemical process at the silicon-electrolyte interface on structural dimensionality by using in-situ pulsed surface photovoltage (SPV) and photoluminescence measurements. The authors concluded that the chemistry of the electrolyte plays a major role in the formation of macroporous and microporous silicon but these processes are still very poorly understood and should be studied in more details.

3.1.1 Aims of this work

The main aim of this part of our work is to develop the preparation of porous silicon samples using various organic electrolytes. We also plan to investigate and understand the factors influencing the structure and size of the pores in PS prepared in organic electrolytes

at different conditions. Anodic oxidation of both prepatterned and non-prepatterned silicon (100) samples with different substrate resistivities are also to be studied. The dependence of various etching parameters on the porous silicon morphology is another focus on this chapter. The organic electrolytes used for the present studies were containing formamide (FA), dimethyl formamide (DMF), acetonitrile (MeCN) and dimethyl sulfoxide (DMSO). SEM was used as a major tool for determining the structure and morphology of porous silicon samples. The PL spectroscopy was applied to study characteristic optical and light emitting features of microporous silicon samples.

3.2 Results and Discussion

3.2.1 Electrochemical etching of non-prepatterned silicon samples

3.2.1.1 Electrochemical etching of silicon samples with HF in DMF

Initially electrochemical etching was performed for silicon (100) samples with resistivity, $\rho = 10 \Omega \text{ cm}$ using 4 % HF in DMF electrolyte for 4 hours at low current density (0.4 mA/cm^2). The SEM images of the prepared PS samples (figure 3.1 a and b) revealed a relatively uniform pore distribution with an average pore diameter of $1.5 \pm 0.2 \mu\text{m}$, and a pore depth of $12 \mu\text{m}$.

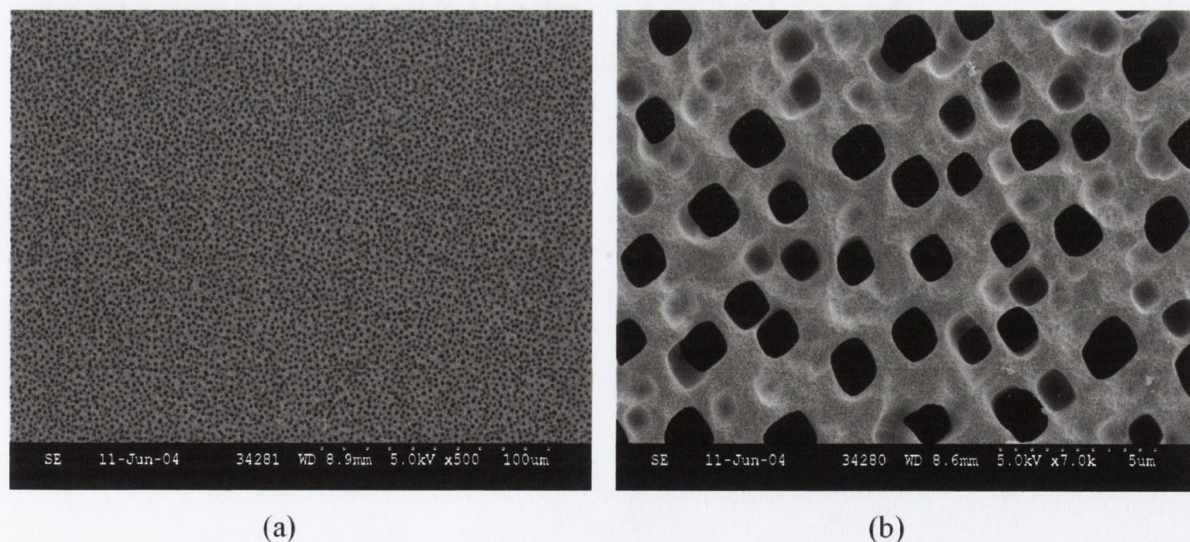


Figure 3.1 SEM images of (a) macroporous silicon layer obtained on *p*-type (100) Si ($\rho = 10 \Omega \text{ cm}$) in 4% HF in DMF solution (b) Higher magnification of (a). Pore wall thickness in the range $0.77 \mu\text{m} - 0.42 \mu\text{m}$.

The formation of square pores (figure 3.1b) has been observed before during etching in DMF electrolyte solution.⁸ The mechanism of formation of square pores is not very well understood. The silicon resistivity is one of the factors having an influence on pore shapes. By comparing the figures in 3.1, 3.8 and 3.9 it can be seen that the higher resistivity samples tend to form square pores whereas low resistivity samples have rounder pores (figures 3.2 and 3.7).

The electrochemical etching of a silicon sample using relatively high current density (10 mA/cm²) was performed for 2 hours in 4% HF - DMF electrolyte.

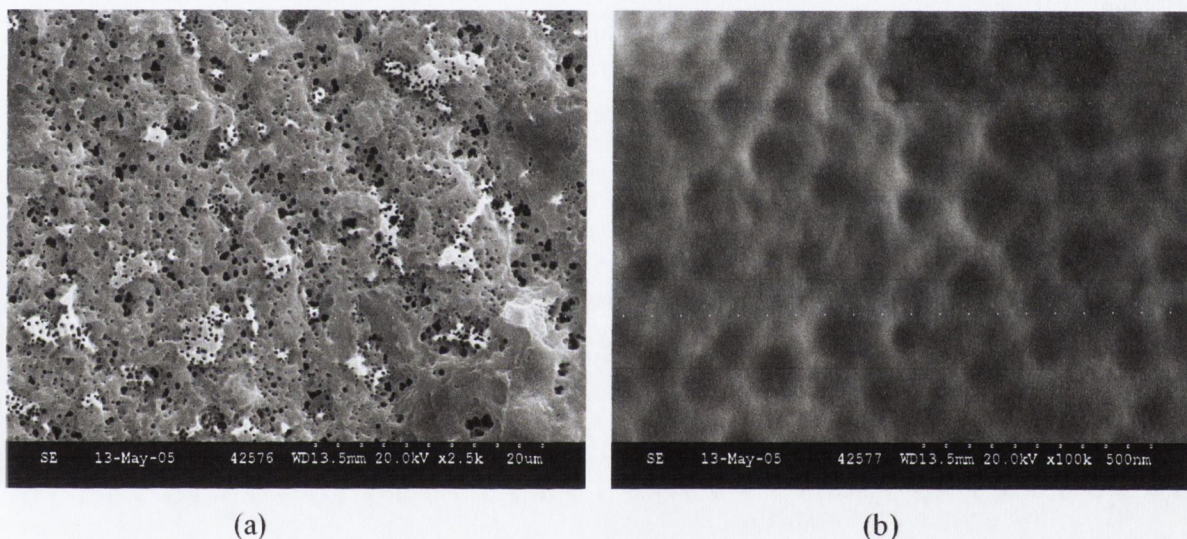


Figure 3.2 SEM images of (a) porous layer obtained on *p*-type (100) Si ($\rho = 5.69 \Omega \text{ cm}$) in 4% HF in DMF solution (b) Higher magnification of (a). Pore wall thickness in the range 100 nm – 300 nm.

Generally the etching using high current density leads to higher porosity and electropolishing of the sample. The SEM image presented in figure 3.2(a) show porous layer formed on silicon, which are a combination of macro and mesopores. The SEM image presented in figure 3.2(b), which is a higher magnification of 3.2(a) shows, the formation of mesopores. The pore wall thickness (0.77 μm - 0.42 μm) in the low-doped sample ($\rho = 10$

$\Omega\text{ cm}$) is larger when compared to the high-doped sample ($\rho = 5.69\ \Omega\text{ cm}$) $0.1\ \mu\text{m} - 0.3\ \mu\text{m}$.

The influence of etching time on the porous layer formation was studied using 0.4 mA/cm^2 current density as the lower current density should result in the formation of “good” macropores in this electrolyte solution. The investigation of the influence of the etching time on loss of mass of the sample, on the porous layer thickness was one of the aims of our research. The results revealed that the porosity and growth rate changed in proportion with the etch time (Table 3.1). The SEM images of macroporous layers obtained on *p*-type (100) Si ($\rho = 10\ \Omega\text{ cm}$) in 4% HF in DMF solution at different etching time with a current density of 0.4 mA/cm^2 are shown in figure 3.3 (a-e).

As explained before (in Chapter II) porosity was calculated using the formula:

$$P = \frac{\Delta m}{d \times A \times \rho_{Si}}$$

Table 3.1 Porosity and pore growth rate dependence of the etch time in 4% HF in DMF with a current density of 0.4 mA/cm^2 .

Etching Time	Loss of mass (mg) Δm	Porous layer Thickness (μm), d	Width of the pores (μm)	Porosity (%)	Growth rate (depth) (nm.s^{-1})
1h	0.25	2.8 ± 0.5	1.1	47.7 ± 8	0.8
1h 30mins	0.41	6.6 ± 0.4	1.3	33.2 ± 2	1.2
2h	0.58	7.3 ± 0.6	1.3	42.5 ± 3.5	1.0
3h	0.77	11.3 ± 0.6	1.77	36.4 ± 2	1.0
4h	1.15	18.1 ± 0.3	1.4	33.9 ± 0.5	0.8
5h	1.40	20.3 ± 0.4	1.5	36.9 ± 1	1.1
6h	1.58	24.5 ± 0.7	1.6	34.43 ± 1	1.2

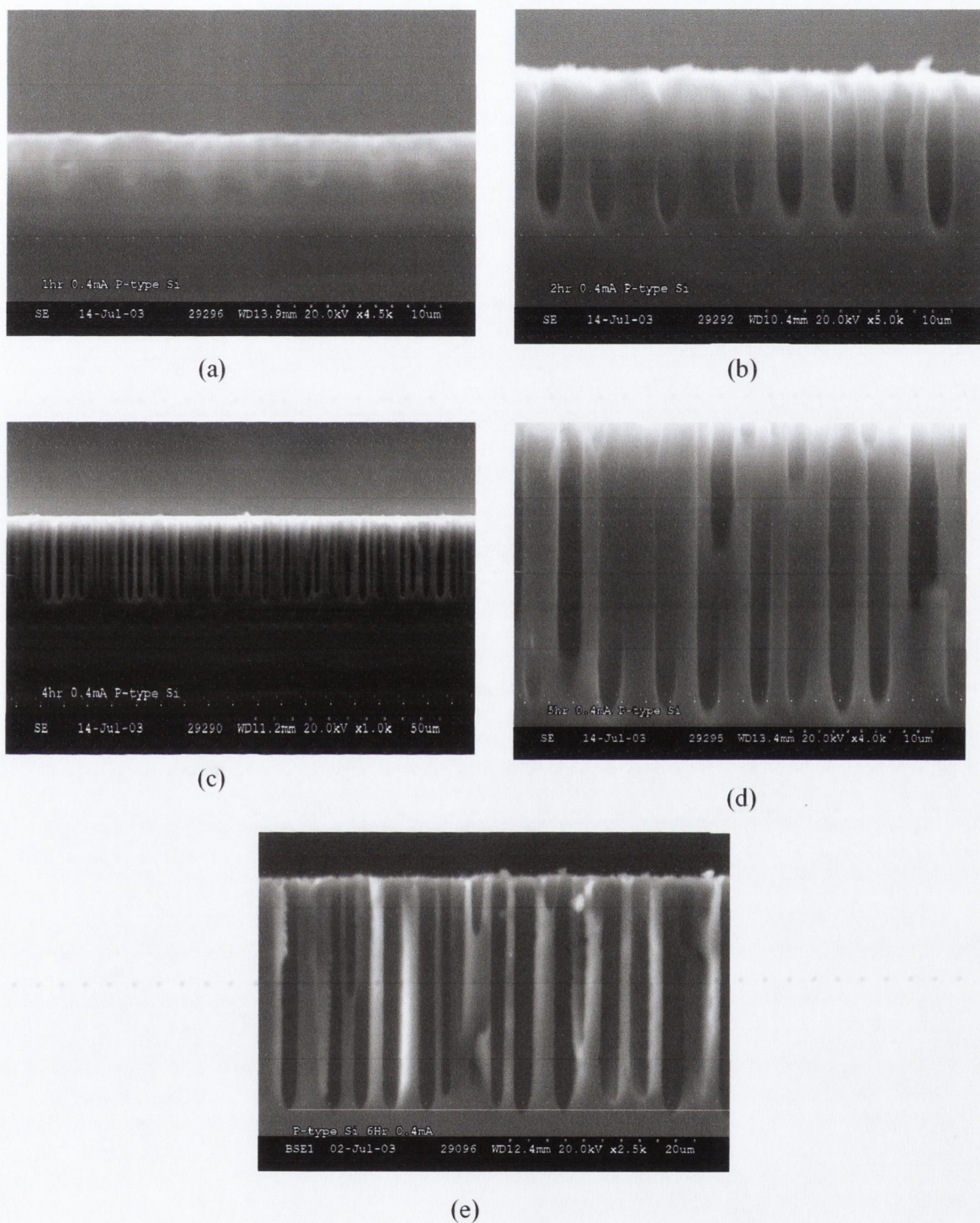


Figure 3.3 (a –e) SEM images of macroporous silicon layer obtained on *p*-type (100) Si ($\rho = 10 \Omega \text{ cm}$) in 4% HF in DMF solution at different etching time with a current density of 0.4 mA/cm^2 . Time corresponds to each sample, a = 1 hr, b = 2 hrs, c = 4 hrs, d = 5 hrs and e = 6 hrs.

The graph presented in figure 3.4 show the linear dependence of mass loss with etching time. It is clear from the graph that loss of mass linearly increases with increasing etching times. The low current density as in this case is significant, because it leads to the uniform pore growth.

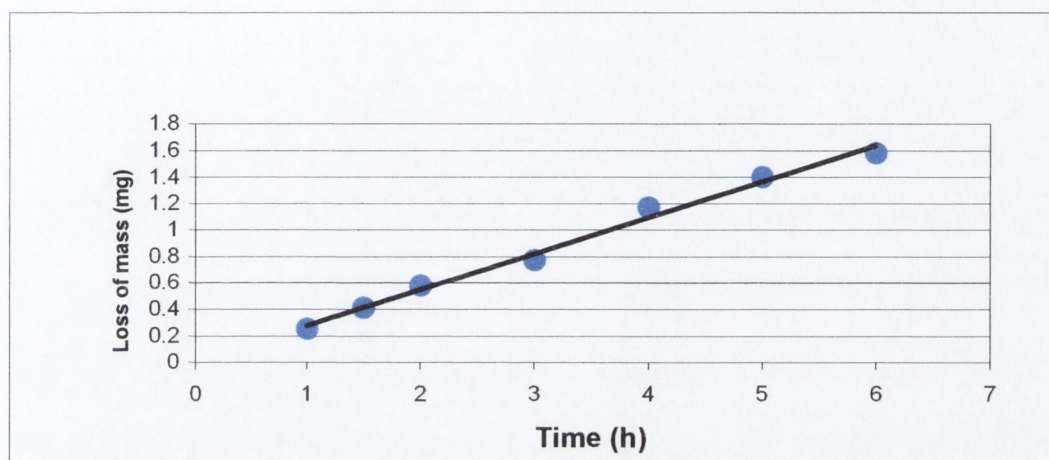


Figure 3.4 Graph showing the linear dependence of loss of mass with respect to etching time at 0.4 mA/cm^2 etching current density.

The SEM images [figure 3(a-e)] revealed the morphology of pore growth. The pores grew very rapidly (in less than 1 hour) and keep roughly the same width. The pore depth increases linearly with the etching time. For example in 6 hours etching, the depth of pores was almost increased by a factor of 10 compared to one hour etched sample. Therefore it is possible to etch pores with large depths (like $100 \text{ }\mu\text{m}$ or more) using this process. The formation mechanism of macropores using this electrolyte (4% HF in DMF) can be explained on the basis of Current Burst Model (CBM).¹⁴

The effect of etching current density on the porous silicon layer formation was studied using two different etching times (1 hour and 3 hours) with four different current densities (3.2 mA/cm^2 , 2.17 mA/cm^2 , 1.28 mA/cm^2 and 0.51 mA/cm^2). The results obtained after 1 hour etching are presented in table 3.2. The samples where the electropolishing occur were

difficult to calculate the growth rate. The results obtained after 3 hours etching are presented in table 3.3.

Table 3.2 Results of etching silicon sample in 4% HF in DMF after one hour.

Current density (mA/cm ²)	Loss of mass (mg) Δm	Porous layer Thickness (μm) d	Width of the pores (μm)	Porosity (%)	Growth rate (depth) (nm.s ⁻¹)	Remarks
3.20	1.17	12.2 $\pm$ 2	1.3	51	-	Mostly electro polishing
2.17	0.73	13 $\pm$ 1.5	1.3	30	-	Partially electro polishing
1.28	0.52	13.56 $\pm$ 0.9	1.3	20.50	3.76	-
0.51	0.25	2.8 $\pm$ 2.4	1.1	47.7	0.8	-

Table 3.3 Results of etching silicon sample in 4% HF in DMF after three hours.

Current density (mA/cm ²)	Loss of mass (mg) Δm	Porous layer Thickness (μm) d	Width of the pores (μm)	Porosity (%)	Growth rate (depth) (nm.s ⁻¹)	Remarks
3.20	2.52	9.5 $\pm$ 1.5	1.3	Unable to determine	-	Mostly electro-polishing
2.17	1.76	13.2 $\pm$ 1.2	1.3	71.3	-	Partially electro-polishing
1.28	1.35	18 $\pm$ 0.8	1.17	40.1	1.7	-
0.51	0.77	11.3 $\pm$ 1	1.77	36.4	1.0	-

According to data in the tables 3.2 and 3.3, the current density increases, mass loss also increases for the two etching times (1 hour and 3 hours). This can be further seen from the graph in figure 3.5, which shows a linear dependence of mass loss with current density, additionally the loss of mass is always greater for 3 hours etching than for 1 hour etching. A combination of a high current density with a long etching time (for example, a five hours

etching at 3.2 mA/cm^2) causes a very high loss of mass (5.12 mg for this case), but it would result in electropolishing, consequently the obtained pores may not be very regular.

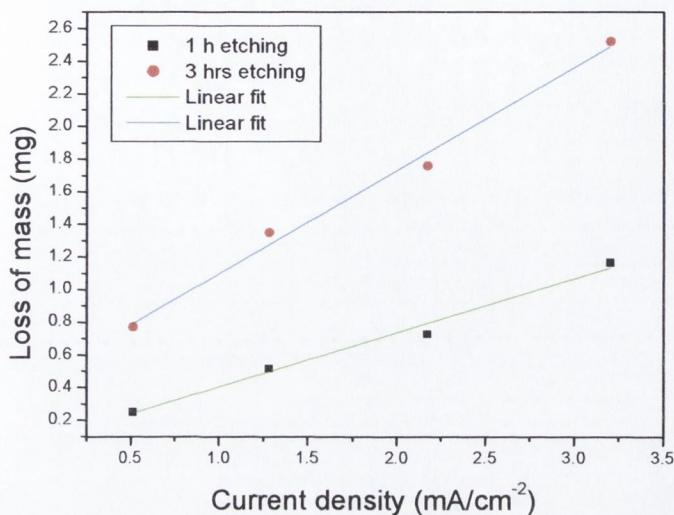


Figure 3.5 Graph showing the linear dependence of loss of mass with current density at 1 hour and 3 hours etching.

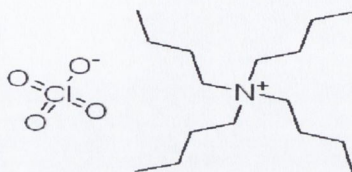
It is known that, if the etching current is too high, then an electrochemical reaction may result in electropolishing.²² Thus the loss of mass increases with increasing the etching current; but this loss of mass is not always dependent on pores depth, and can be a result of electropolishing.

The present investigations on the formation of macroporous silicon using 4% HF in DMF solution allows to conclude that it is possible to etch macro porous silicon with low etching current (in this case, sample's mass loss is only due to pores size). However, if a higher etching current density is used (greater than 1.28 mA/cm^2), this results in extensive electropolishing and a large loss of mass on the sample.

It is also a fact that pore depth increases with the increase of current density, but only if low etching current density is used. In the case of higher current density, electropolishing interrupts pore formation, and can result in a smaller irregular pores as presented in figure 3.2. The photoluminescence measurements on macroporous silicon which are prepared by using 4% HF in DMF showed that the samples are not luminescent.

3.2.1.2 Electrochemical etching of silicon samples with 15% HF in DMF + 0.11M TBAP (Tetrabutylammonium perchlorate)

Tetrabutylammonium perchlorate:



TBAP was used as a supporting electrolyte for the electrochemical etching of silicon samples with 15% HF in DMF. TBAP is normally used in organic reactions as an oxidising agent. In the present investigation we used a dilute concentration of TBAP (0.11M) solution. With TBAP the conductivity of the electrolyte is driven up, thus the conditions for electropolishing are not reached as easily as in the case of pure organic electrolytes.²³ The role of TBAP as pore modifier is not well established but the conducting salt helps to avoid the electropolishing regime. This is probably due to the adsorption of cationic part of TBAP to the walls of the pore and thereby passivating it from further electrochemical dissolution. It is reported that the possible adsorption of organic molecules on silicon electrodes can locally change the rate of silicon dissolution during anodisation in non-aqueous HF solution.¹⁸

The electrochemical etching of the silicon sample using 15% HF in DMF + 0.11M TBAP was performed with a current density of 40 mA/cm² using 1 hour etching time. The effect of resistivity with respect to the porosity was determined. Table 3.4 shows the parameters that have been used for the preparation.

Table 3.4 Parameters used for electrochemical etching of silicon using 15 % HF in DMF + 0.11M TBAP.

Samples code	LD21	LD22	LD23	LD24
Time (min)	60	60	60	60
Resistivity (Ω cm)	0.0217	5.6922	14.8486	17.0093
J (average) (mA.cm^{-2})	40.01	40.01	40.04	39.96
Δm (g)	0.00604	0.011212	0.012256	0.006838
d (μm)	47.5 ± 1.5	87.5 ± 2.5	23.5 ± 0.75	20 ± 1
Porosity (%)	78.47	70.97	52.77	46.63
Pore diameter (μm) in the range	-	0.7 – 0.9	1 - 2	1.4 –1.8
Where J is the average current density and d is depth of the pores.				

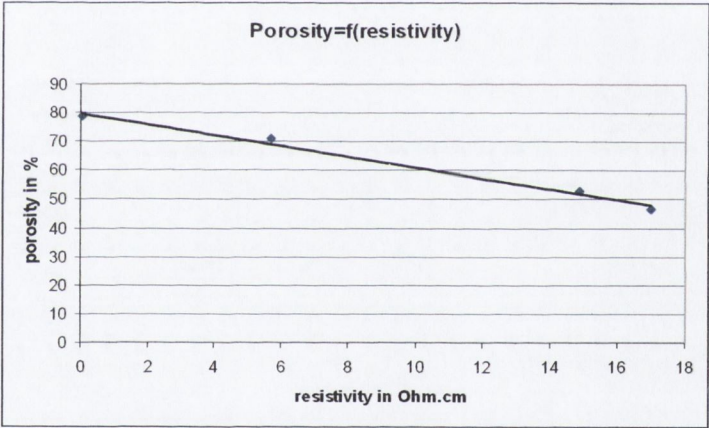


Figure 3.6 Graph showing the linear decrease of porosity with respect to resistivity.

Figure 3.6 shows a linear decrease of porosity with respect to silicon resistivity, this is caused by an increase in the number of holes. When the resistivity decreases (for example in high conductive sample), the density of pores increases. Fewer holes are available for increasing the depth of pores (results showed a decreasing of pore depth except in LD 22 sample). The increase of pore diameter might be due to the fact that the trajectory of charge carriers will become non-linear if we decrease their concentration and thereby not concentrating onto the tip of the pores rather they are involving in the widening of the pores.

Generally organic electrolytes have a weak oxidation power,²³ compared to the aqueous electrolytes, therefore they are highly desirable candidates. A higher HF concentration (C_{HF}) is chosen to allow for the quicker dissolution of the oxide, which is increasing linearly with the HF concentration. In conventional macropore growth this doesn't lead too far because the stability of the pore walls decreases rapidly as soon as C_{HF} is increased.²⁴ So for a better macropore growth with higher C_{HF} the addition of supporting electrolytes will be useful.

The electrochemical etching is done with a high current density of 40 mA/cm^2 for all the samples. SEM images of the etched sample having resistivity, $\rho = 5.69 \text{ } \Omega \text{ cm}$ (figure 3.7a & b) show that the pore walls formed are thin and the pore diameter is in the range $0.7 - 0.9 \text{ } \mu\text{m}$.

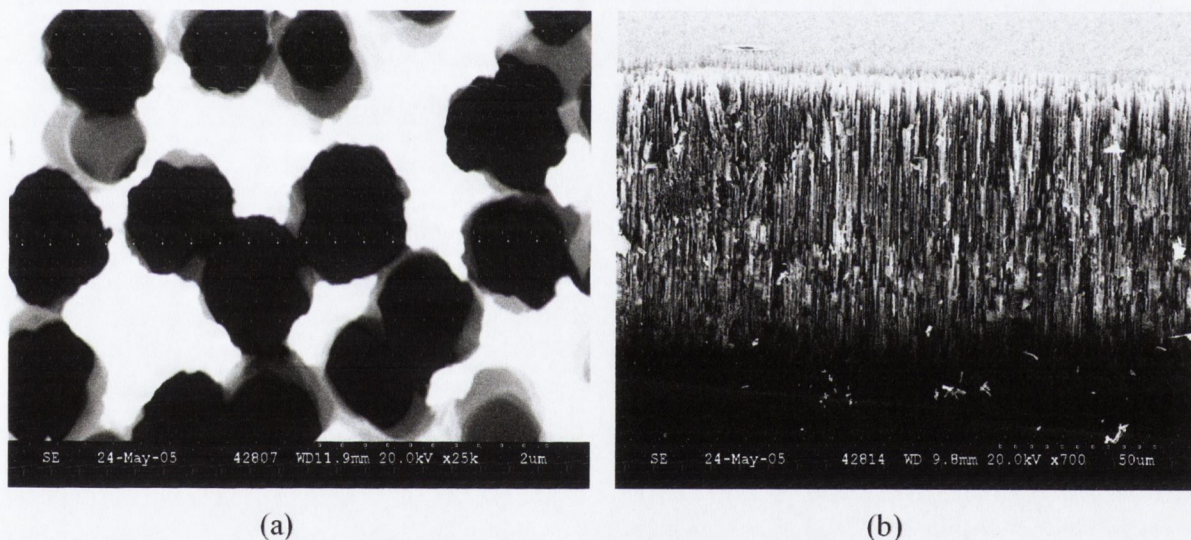


Figure 3.7 SEM images of sample etched (one hour) in 15% HF in DMF + 0.11M TBAP ($j = 40.01 \text{ mA/cm}^2$, $\rho = 5.69 \text{ } \Omega \text{ cm}$).

The formation of uniform macropores is observed with silicon samples of resistivity, $\rho = 14.84 \text{ } \Omega \text{ cm}$. Figure 3.8 (a) shows SEM image of the plan view of the sample, it can be seen that pore diameters are in the range $1 - 2 \text{ } \mu\text{m}$ and the cross-sectional SEM image (figure 3.8b) revealed uniform pores with depth of $23.5 \pm 0.75 \text{ } \mu\text{m}$. The increase of silicon resistivity leads to the formation of the porous silicon membrane as shown in figure 3.9 (a & b). Figure 3.9a showed the plan view of the membrane while figure 3.9b presents the

cross-sectional view of the membrane. The pore diameter was found to be in the range 1.4 – 1.8 μm and the pore depth of $20 \pm 1 \mu\text{m}$.

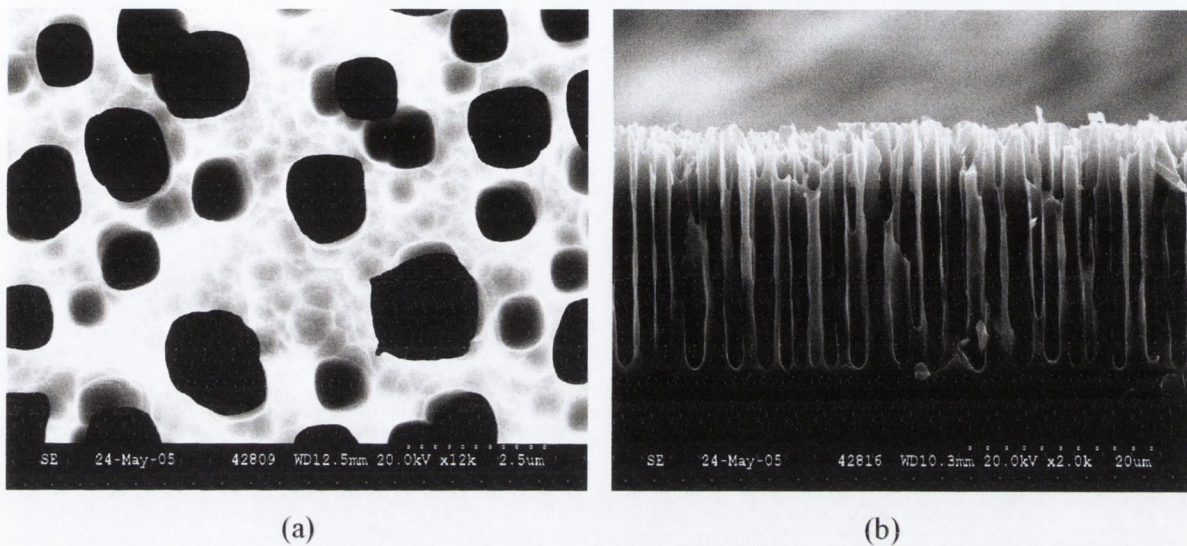


Figure 3.8 SEM images of sample etched in 15%HF in DMF + 0.11M TBAP ($j = 40.04 \text{ mA/cm}^2$, $\rho = 14.84 \Omega \text{ cm}$). (a) Plan view. (b) Cross-sectional view. Pore diameter in the range 1 – 2 μm and pore depth = $23.5 \pm 0.75 \mu\text{m}$.

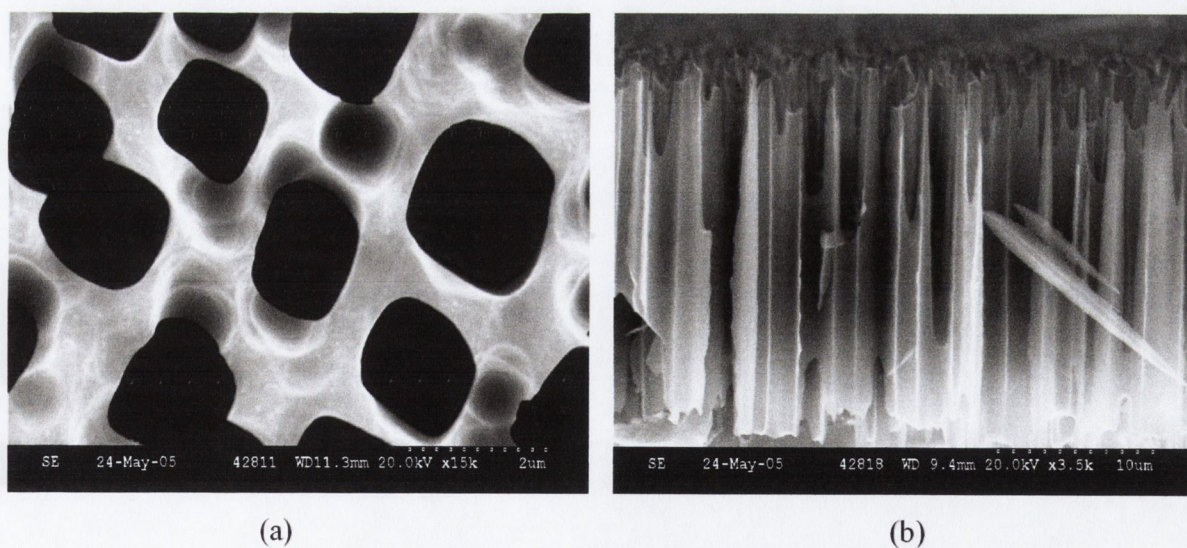


Figure 3.9 SEM images of sample etched in 15%HF in DMF + 0.11M TBAP ($j = 39.96 \text{ mA/cm}^2$, $\rho = 17.01 \Omega \text{ cm}$). (a) Plan view. (b) Cross-sectional view. Pore diameter in the range 1.4 – 1.8 μm and pore depth = $20 \pm 1 \mu\text{m}$.

The experiment using different resistivity samples using 15% HF in DMF + 0.11M TBAP enables us to conclude that the sample with resistivity 14.84 Ω cm is the most suitable for the preparation of good macropores compared to high and low resistivity samples. The former leads to membrane while latter leads to thin and broken silicon walls. The reports on electrochemical etching of *n*-type silicon using organic electrolyte (high current density, $j = 80$ mA/cm²) without conducting salt resulted in high oscillatory structures resembling puff pastry.²⁵ Thus the electrochemical etching with a current density of $j = 40$ mA/cm² is suitable for preparing good macropores as well as membranes using these electrolytic conditions. The formation mechanism for the macropore formation using this electrolyte can also be explained on the basis of CBM.

3.2.1.3 Electrochemical etching of silicon samples with HF in FA

The electrochemical etching of a silicon (100) sample of resistivity, $\rho = 10$ Ω cm using the current density of 25.19 mA/cm² and etching time of 6 hours was performed in the electrolyte solution of formamide. The SEM images of the samples etched with 4% HF in formamide are presented in figure 3.10. The top view of the samples revealed “sponge” like structures. A detailed look into one of the pores showed that it consists of a layered structure on the walls (figure 3.10b). The silicon electrochemically etched with 4% HF in formamide form a structure which according to SEM to consist of large macropores with possible smaller microporous structures of the wall. PL spectroscopy (figure 3.11) have shown that the sample is luminescent that confirmed the formation of micropores.

The ability of the solvent to act as H⁺ donor and polarity of the electrolyte is important when considering the morphology of porous silicon.²⁶ Most of the articles dealing with macropores in silicon agree with the opinion that two basic dissolution reactions take place at the pore tip. The first reaction path is the direct silicon dissolution and the second path is the silicon dissolution *via* an anodic oxide.²³ The H-termination of the silicon surface acts as the main passivation mechanism of the pore walls.²⁶ The better the wall passivation the higher the dissolution rate at the pore tip. If oxide is formed, no $\{hkl\}$ dependent H-passivation of surfaces is possible. This leads to smooth silicon surfaces, if oxide formation and dissolution is the dominant chemical process (*e.g.* at high anodic potentials) and electropolishing occurs.¹⁴

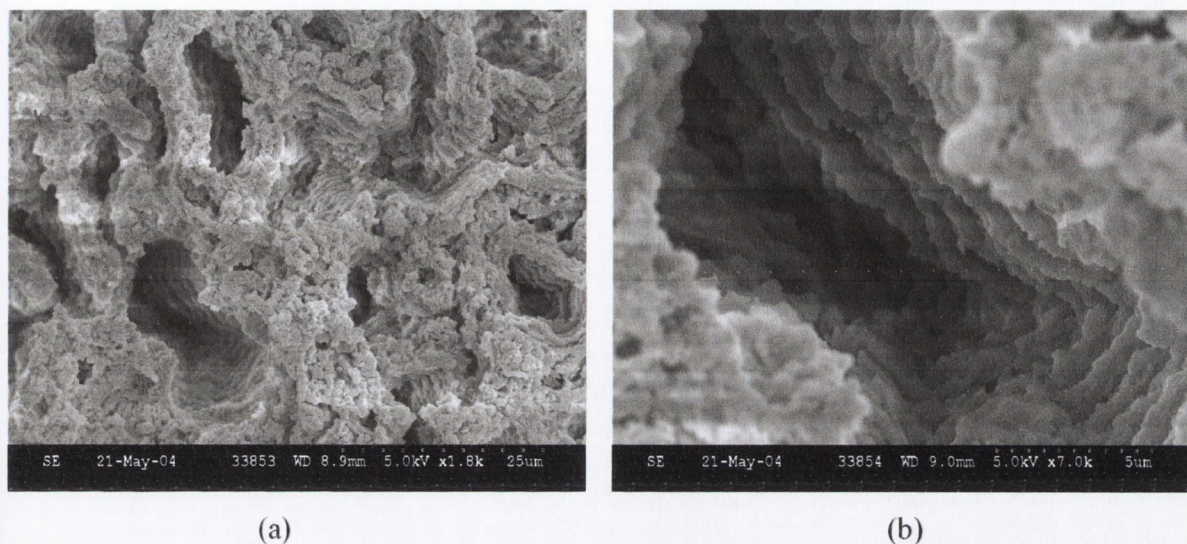


Figure 3.10 (a) SEM images of plan view of the sample showing the layered structures (b) Higher magnification of (a) showing the micropores in the layered structures.

Our results suggest that the formation of oxide might have lead to the layered structures without $\{hkl\}$ dependency. Also, it has been reported that formamide (FA) with an oxidizing power exceeding that of water forms *p*-micropores rather than *p*-macropores.²⁵ This is also evident from the photoluminescent studies as it shows very strong luminescence (figure 3.11) which is having a shift towards the blue region confirming the presence of oxide formation.²⁷

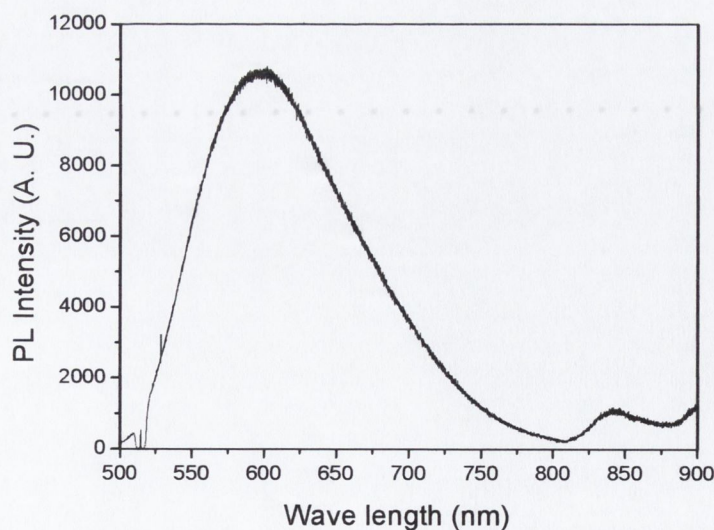


Figure 3.11 PL spectrum of porous silicon sample prepared using 4% HF in formamide.

3.2.1.4 Electrochemical etching of silicon samples with HF in MeCN

The effect of etching current density on the porosity of the samples was studied by using silicon samples with resistivity of $\rho = 0.02 \text{ }\Omega \text{ cm}$ and average current densities of 2.03, 10.86, 20.01 and 40.08 mA/cm^2 and an etching time of 60 minutes. The dependence of pore depth with respect to the current density was also determined. The effect of silicon resistivity on the porosity was investigated by using 10% HF in MeCN electrolyte solution by the silicon samples of resistivities, $\rho = 0.021, 3.49, 5.69, 14.84$ and $17.01 \text{ }\Omega \text{ cm}$.

The table 3.5 (below) shows the parameters, which have been used for the preparation.

Table 3.5 Parameters used for electrochemical etching of silicon using 10% HF in MeCN.

Samples	LD53	LD54	LD55	LD56
Time in min	60	60	60	60
Resistivity in $\Omega \text{ cm}$	0.021	0.021	0.021	0.021
J (average) in mA.cm^{-2}	2.026	10.865	20.004	40.080
Δm in g	0.000736	0.003056	0.005380	0.010124
d in μm	20	50	70	75
Porosity in %	22.71	37.72	47.43	83.31

Where J is the average current density and d is depth of the pores.

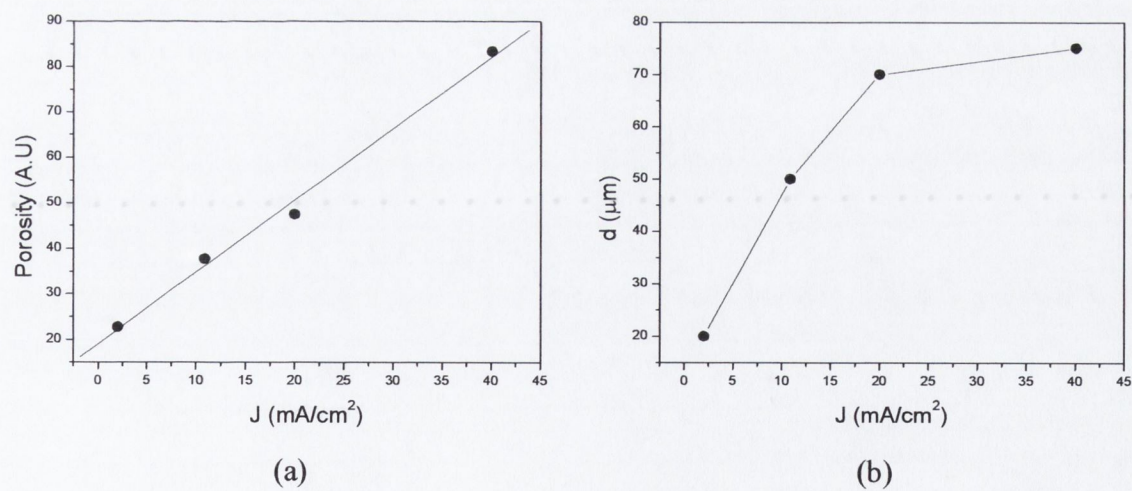


Figure 3.12 Graphs showing (a) the linear dependence of current density with respect to porosity. (b) Pore depth as a function of current density.

The results revealed that the porosity of the samples has a linear dependence with respect to the current density as presented in figure 3.12a.

Figure 3.12(b) shows a monotonic increase of pore depth with current density for the same anodization time. The non-linear saturation at higher current density can be explained by the thinning of the wall as current density increases.²⁸

The effect of silicon resistivity with respect to the porosity was determined by using the same electrolyte. The table 3.6 (below) shows the parameters that have been used for the electrochemical etching.

Table 3.6 Parameters used for electrochemical etching of silicon using 10% HF in MeCN for different resistivity samples.

Samples	LD55	LD57	LD58	LD59	LD60
Time in min	60	60	60	60	60
Resistivity in $\Omega\cdot\text{cm}$	0.0209	5.6922	14.8486	17.0093	3.4958
J (average) in $\text{mA}\cdot\text{cm}^{-2}$	20.004	19.998	20.044	20.108	20.081
Δm in g	0.005380	0.004932	0.005996	0.006326	0.005028
d in μm	70	125	97.5	80	112.5
Porosity in %	47.43	24.35	37.95	48.80	27.58
Where J is the average current density and d is depth of the pores.					

The results showed that the porosity of the samples (figure 3.13a) and depth of the pores (figure 3.13b) have a non-linear dependence with respect to the resistivity of the sample. If the doping density, the current density, the HF concentration or the temperature are fluctuating over the sample surface or over anodization time, the porosity also does accordingly.²

The porosity of the samples showed an initial decrease in the low resistivity samples and then a gradual increase for the high resistivity samples. The possible explanation of this is the formation of different pore morphologies in different resistivity samples. The same effect was reported by Lehmann *et al.*,²⁹ after their observation of porous silicon etching in ethanoic HF. It can be seen from the graph relating pore depth and resistivity of the sample

(figure 3.13b) that as the resistivity increases a gradual increase and then a decrease in pore depth are observed.

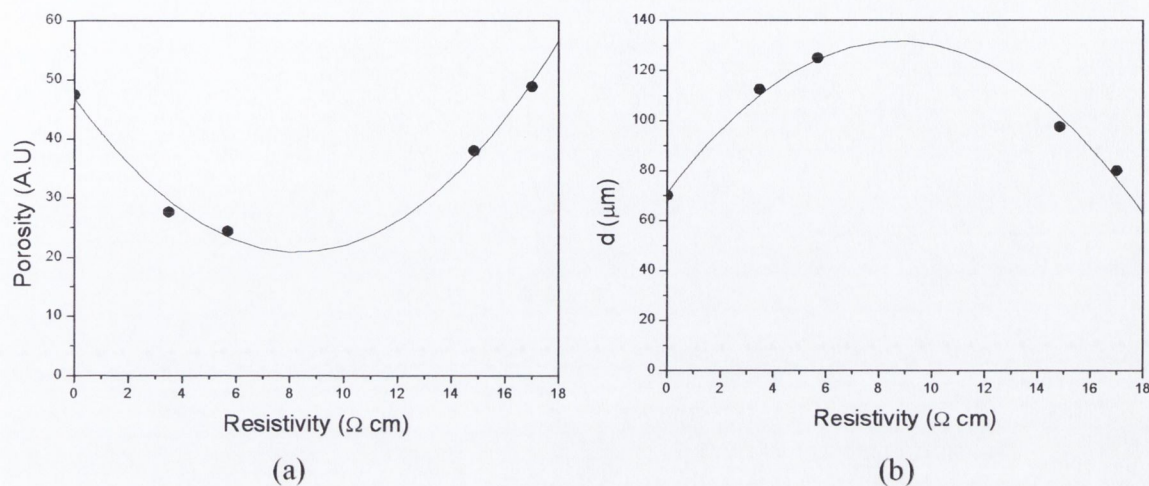


Figure 3.13 Graphs showing (a) the non-linear dependence of porosity with respect to silicon resistivity. (b) Pore depth as a function of resistivity.

The SEM images of the samples etched with 10% HF in acetonitrile are presented in figures 3.14 and 3.15.

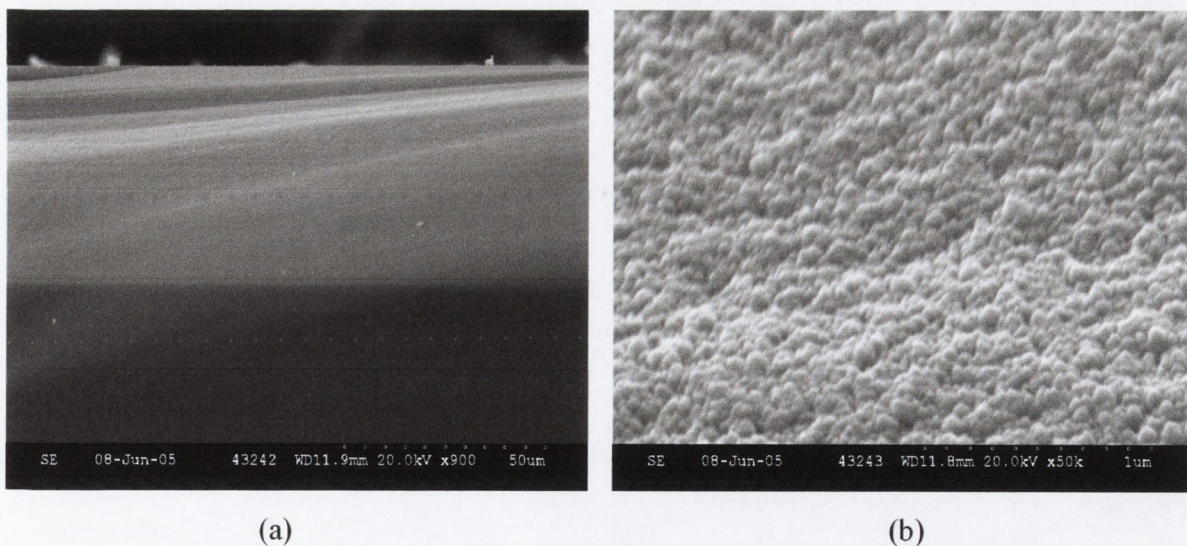


Figure 3.14 SEM images of sample etched in 10% HF in acetonitrile with ($j = 10.86$ mA/cm², $t = 1$ hr, $\rho = 0.021$ Ω cm). (a) overview image, (b) higher magnification.

The cross-sectional view of the sample prepared with $j = 10.86 \text{ mA/cm}^2$ (figure 3.14 a & b) show pores having rough surface morphology and suggests that the dimension of the pores are in nanometer range which suggested the formation of micropores in highly doped samples. The highly branching of the pores might be the reason for the rough surface morphology.

A SEM image presented in figure 3.15 show the formation of micropores in the samples etched with 10% HF in MeCN but with thin walled structures compared to the sample with low current density where the pores are highly branched out. This was also clear from the graph showing the non-linearity dependence of pore depth with respect to the current density.

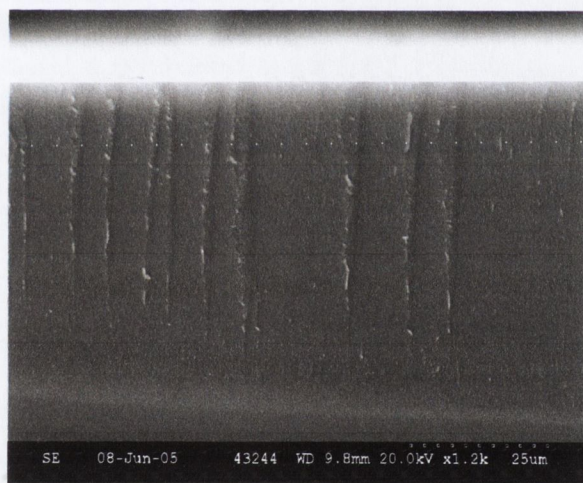


Figure 3.15 SEM image of the sample etched in 10% HF in acetonitrile with current density, $j = 20.004 \text{ mA/cm}^2$, $t = 1 \text{ hr}$, $\rho = 0.021 \Omega \text{ cm}$).

The cross-sectional SEM image of the sample having resistivity of $5.69 \Omega \text{ cm}$ etched with a current density of 19.99 mA/cm^2 is presented in figure 3.16.

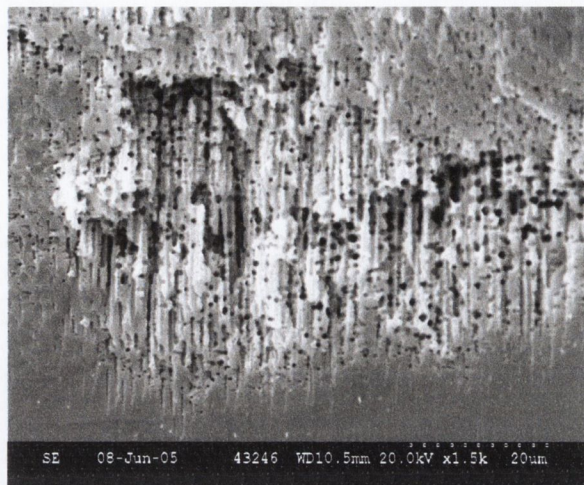


Figure 3.16 SEM image of the sample etched in 10%HF in acetonitrile ($j = 19.99 \text{ mA/cm}^2$, $t = 1 \text{ hr}$, $\rho = 5.69 \Omega \text{ cm}$).

These etching conditions resulted in a sample usually have thick pore walls (approximately $0.5 \mu\text{m}$) compared to the previous samples etched with the same electrolyte. The pore walls in the sample having pores which are formed perpendicular to the original pores, that suggests branching out from the “mother” pore.

3.2.2 A comparison of the etching parameters of aqueous and organic electrolytes

The variation of porosity with respect to the etching time is plotted in figure 3.17a. The graphs show a linear dependence for the organic electrolyte and a non-linear dependence for aqueous electrolytes. The porosity graphs demonstrate a linear relationship with respect to current density for organic and aqueous electrolytes as presented in figure 3.17b. A monotonic increase in porosity is observed in HF: EtOH: H_2O 1: 1: 1 + 10^{-3} M CTAC electrolyte solution. Thus the use of low current density leads to higher porosity samples. The longer etching time can also increase porosity in organic electrolytes.

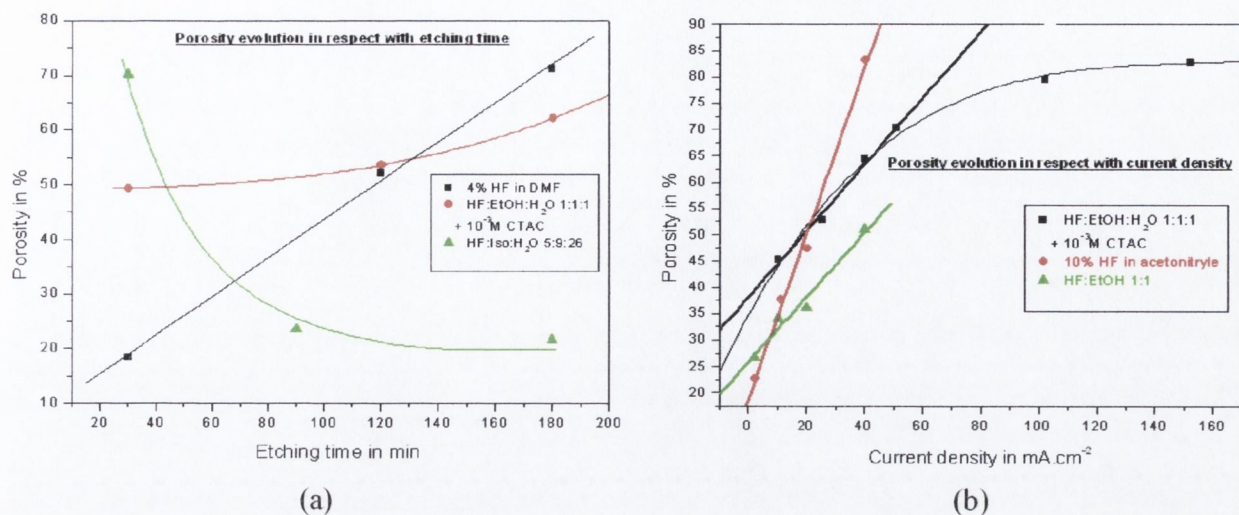


Figure 3.17 Graphs showing the porosity dependence of different electrolytes with respect to (a) Etching time and (b) Current density.

An increase in current density results in an increase in pore depth as presented in figure 3.18. It can be seen that current density around 20 mA/cm² is suitable to obtain a good pore depth although the CTAC added sample showed a steep increase in pore depth with current density.

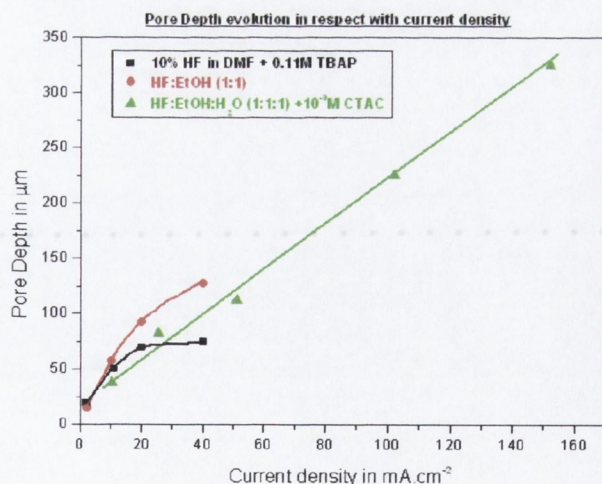


Figure 3.18 Graph showing the pore depth dependence of different electrolytes with respect to current density.

The factors influencing the pore depth and the porosity of a sample and the variation of these parameters with respect to the silicon etching conditions are summarised in table 3.7.

Table 3.7 Porosity and pore depth evolution summary with respect to different etching parameters.

Parameters	Electrolyte	Porosity	Pore depth
HF concentration increases	HF in H ₂ O	Decreases	Increases
Anodization time increases	HF: C ₂ H ₅ OH: H ₂ O (1:1:1)+10 ⁻³ M CTAC	Increases	Increases
	4% HF in DMF	Increases	Increases
	HF:C ₃ H ₈ O: H ₂ O (5: 9: 26)	Decreases	Constant
Current density increases	HF: C ₂ H ₅ OH: H ₂ O (1: 1: 1)+10 ⁻³ M CTAC	Increases	Increases
	HF:C ₂ H ₅ OH (1: 1)	Increases	Increases
	10% HF in MeCN	Increases	Increases

3.2.3 Electrochemical etching of silicon on pre-patterned silicon samples

3.2.3.1 Electrochemical etching of silicon on pre-patterned samples with HF in DMF

To form the nucleation pits two photo-masks were used. The masks had round holes arranged in a triangular ‘lattice’. One of them had a period of 12 μm , and another had a period of 4 μm . The silicon samples with resistivities $\rho = 7.5 \, \Omega \, \text{cm}$ and 20 $\Omega \, \text{cm}$ prepatterned with pits of lattice period (a), the distance between the centre of one pore to the centre of the adjacent pore, $a = 12 \, \mu\text{m}$ were used for the present study. The etching of this sample has been performed in 4% HF in DMF for 25 hours, at the current density of 1.6 mA/cm^2 at an ambient temperature (20°C). The SEM images of etched silicon samples having resistivity $\rho = 7.5 \, \Omega \, \text{cm}$ are shown in figures 3.19(a)–(c).

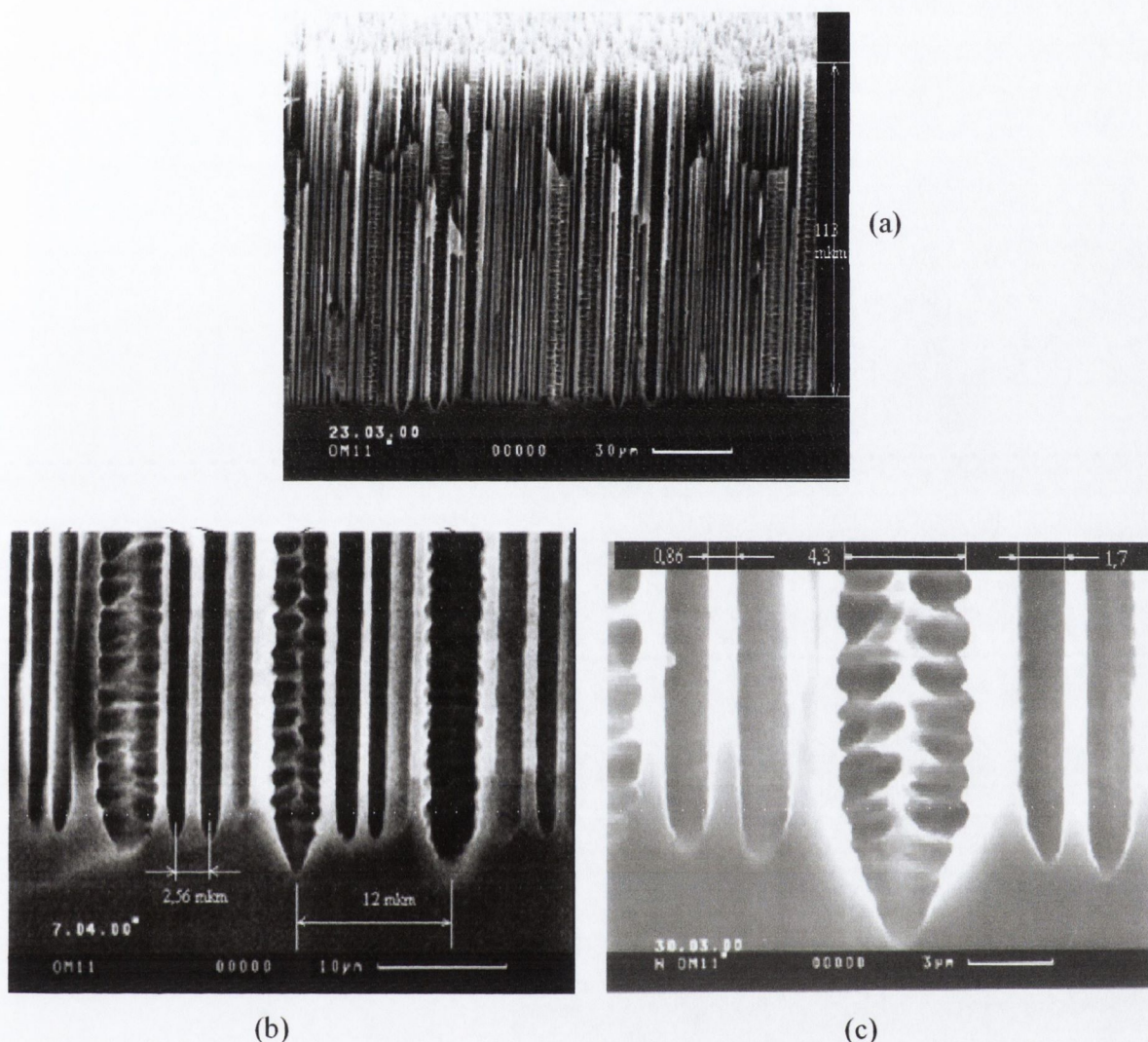


Figure 3.19 SEM images of the macroporous layer obtained on *p*-type (100) Si ($\rho = 7.5 \Omega \text{ cm}$) with pits of period 12 μm . (a) general view, (b) relative position of two pore types and (c) morphology and diameter of ‘pit-formed’ and ‘additional’ macropores.

The obtained macroporous layer is $113 \pm 3 \mu\text{m}$ deep and contains two types of pores. One of the pore types formed from the pits has a larger diameter ($4.3 \pm 0.3 \mu\text{m}$) and depth ($116 \pm 0.5 \mu\text{m}$). The pores formed from pits showed characteristic features of periodic cellular structure and strong wall roughness. The second type of pores we call it self-formed pores has a smaller diameter (approximately 2.5 times) and a slightly smaller depth ($113 \pm 0.4 \mu\text{m}$)

and also possess smooth walls. The average distance between the self-formed pores is approximately 2.7 μm .

The SEM images of etched silicon samples having resistivity $\rho = 20 \Omega \text{ cm}$ (4 hours, at the current density $j = 2 \text{ mA/cm}^2$) are shown in figure 3.20. By comparing SEM images of figures 3.19 and 3.20 it can be seen that the density of 'additional' pores does not depend greatly on the resistivity of silicon. The pore diameter is 6 μm and depth of the pore is found to be 25 μm (see table 3.8 for comparison of etching process).

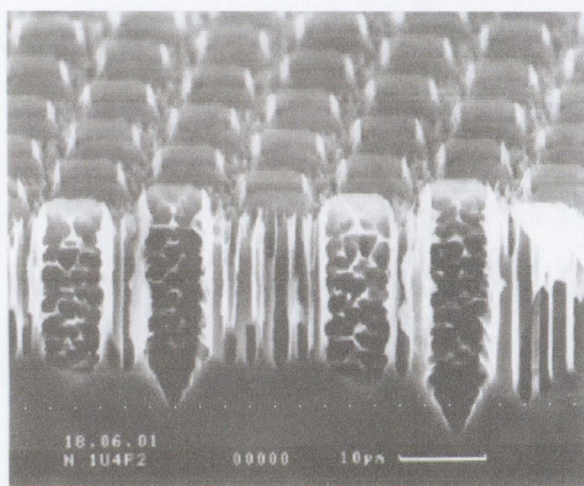


Figure 3.20 SEM image of the macroporous layer obtained on *p*-type (100) Si ($\rho = 20 \Omega \text{ cm}$) with pits of period 12 μm in 4% HF in DMF electrolyte solution.

3.2.3.2 Electrochemical etching of silicon on pre-patterned samples with HF in DMSO

The silicon samples with resistivities, $\rho = 20$ and $7.5 \Omega \text{ cm}$ prepatterned with pits, of lattice period $a = 12 \mu\text{m}$ and $a = 4 \mu\text{m}$ respectively, were used for the present study. The etching of this sample has been performed in 4% HF in DMSO for 3 hours at the current density of $j = 2 \text{ mA/cm}^2$. The SEM images of etched silicon samples having resistivity $\rho = 20 \Omega \text{ cm}$ with lattice period of 12 μm is presented in figure 3.21. The diameter of the pore is $6 \pm 3 \mu\text{m}$ and its depth is $13 \pm 3.5 \mu\text{m}$.

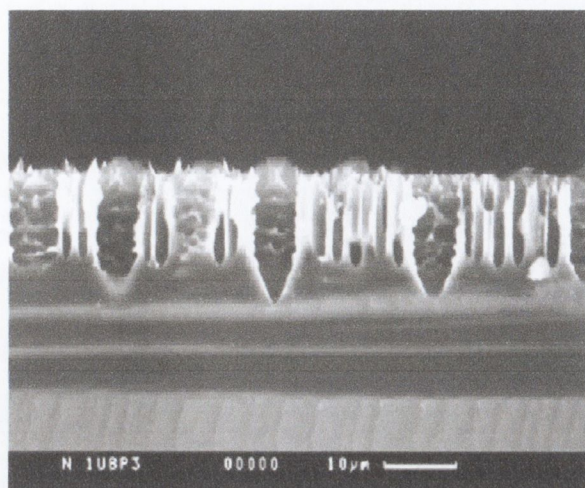


Figure 3.21 SEM image of the macroporous layer obtained on *p*-type (100) Si ($\rho = 20 \, \Omega \, \text{cm}$) with pits of period $12 \, \mu\text{m}$ in 4% HF in DMSO electrolyte solution.

Exactly the same phenomenon of two different types of pores (pit-initiated and self-formed pores) were observed for the Si (100) etched in DMSO based electrolyte. The average distance between self-formed pores is $2.7 \, \mu\text{m}$.

The SEM images of etched silicon samples having resistivity $\rho = 7.5 \, \Omega \, \text{cm}$ with lattice period of $4 \, \mu\text{m}$ is presented in figure 3.22. The SEM images showed that there is no formation of additional pores when the pit lattice period was decreased up to $a = 4 \, \mu\text{m}$. This was observed for the silicon samples of resistivities 20 and $7.5 \, \Omega \, \text{cm}$. The macropores formed (pore diameter $= 2.5 \pm 0.1 \, \mu\text{m}$) in organic electrolytes have pronounced faces on the walls, which show up as terraces (figure 3.22a) or wave-like edges (figure 3.22b) depending on the view angle. This type of wall structure on macropores obtained in organic electrolytes was first reported by Föll *et al.*¹⁹

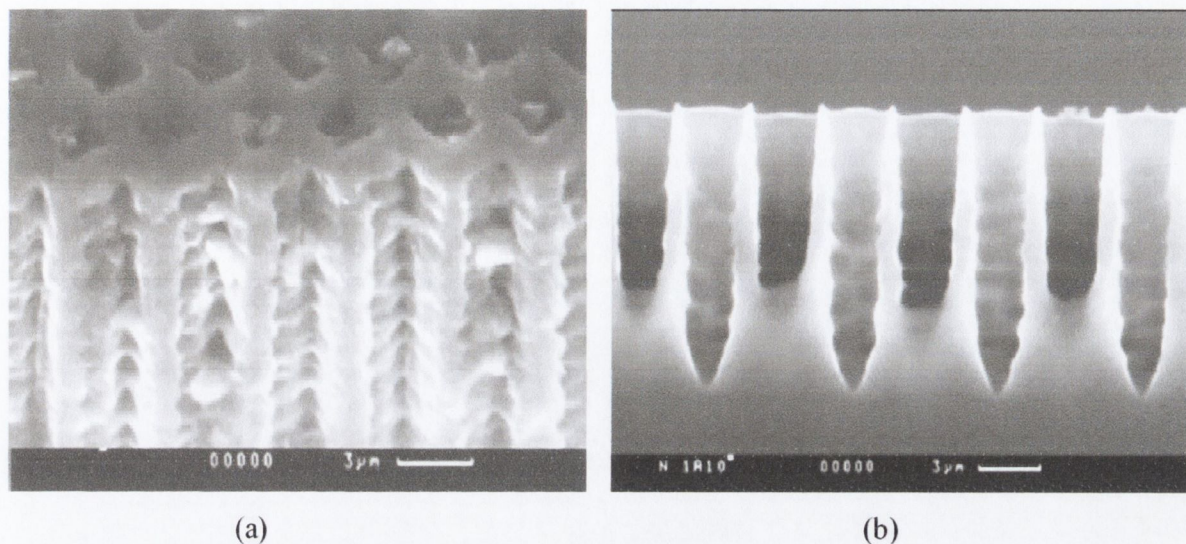


Figure 3.22 SEM images of the macroporous layer obtained on *p*-type (100) Si ($\rho = 7.5 \Omega \text{ cm}$) with pits of period, $a = 4 \mu\text{m}$, in 4% HF in DMSO electrolyte solution. **(a)** terraces on the pore walls (the sample tilted to 45°); **(b)** sharp tips and rough pore edges (cross-sectional view).

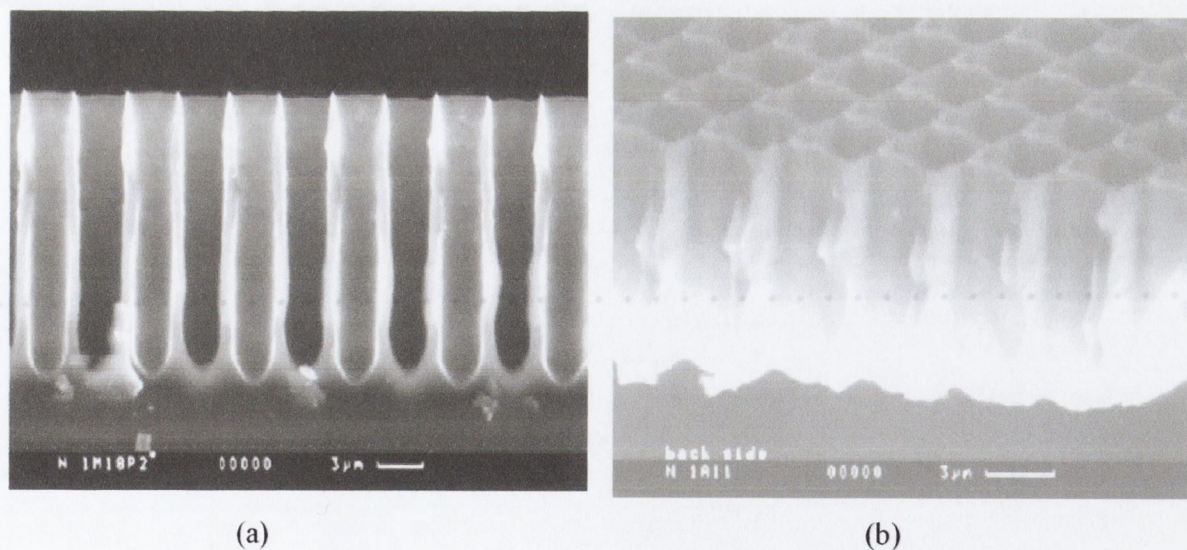


Figure 3.23 **(a)** SEM image of the macroporous layer obtained on *p*-type (100) Si ($\rho = 7.5 \Omega \text{ cm}$) with pits of period, $a = 4 \mu\text{m}$, in 4% HF in DMSO + H_2O electrolyte solution. **(b)** SEM image of the silicon membrane with pore-channels formed by etching in DMSO electrolyte.

The role of oxidants in the wall roughness is demonstrated by etching in 4% HF in DMSO and H₂O electrolyte solution (DMSO: H₂O = 4: 1). The figure 3.23a shows that the addition of water, playing the role of the oxidant, results in smoothing of pore walls. It can be seen that the increase in the current density itself does not make the walls smoother rather as shown in figure 3.23b, the increase in current density results in the removal of porous layer from the substrate. The membrane is 9 μm in thickness and has a diameter of 20 μm.

The parameters used for the etching of patterned silicon samples are presented in table 3.8.

Table 3.8 Parameters of the etching process (patterned silicon samples).

SEM Figure	Substrate resistivity (Ω cm)	Period of pits (μm)	Electrolyte 4% HF in	Current density, <i>j</i> (mA/cm ²)	Comments
3.19	7.5	12	DMF	1.6	Dependent on the density of pores
3.20	20	12	DMF	2	
3.21	20	12	DMSO	2	Formation of self-formed pores and pores initiated by pits
3.22a	7.5	4	DMSO	1.6	
3.22b	7.5	4	DMSO	1.77	
3.23a	7.5	4	DMSO + H ₂ O	2	Role of oxidants
3.23b	7.5	4	DMSO	3	

3.3 Conclusions

Thus our research on the preparation of PS using organic electrolytes demonstrated following. The presence of pits, which act as nucleation sites, plays a crucial role in the mechanism of macropore formation in *p*-type (100) Si. In order to obtain regular macropores, the pattern of pits should fit the average distance between the random pores. In the absence of such a correspondence, the two types of pores can form. The morphology of these types of pores differs drastically. The macropores obtained in organic electrolytes have strongly pronounced etch features, which characterize the etching process as anisotropic. It has been confirmed that increasing the electrolyte water content leads to a decrease in this anisotropy. Electrochemical etching of *p*-type Si allows formation of macroporous layers with higher porosity than for *n*-type Si. However, the stable growth of macropores is restricted by the narrow range of possible lattice periods.

The preparation of porous silicon using 4% HF in DMF suggests that the best parameters for the formation of regular *p*-type macropores involve a solution of 4% HF in DMF, with a low etching current (in order to avoid electropolishing). It has also been demonstrated that the etching current density is crucial in determining the pores depth.

We have demonstrated that using conductive salt (here TBAP) in HF in DMF solution allows to etch silicon samples with higher current density. A similar process, but without conductive salt would result in electropolishing. The electrochemical etching in formamide solution resulted in sponge-like macroporous silicon structures, which composed of micropores. The photoluminescence properties of these porous structures have been studied. The electrochemical etching in acetonitrile electrolyte solution showed the dependence of porosity of the samples on various parameters such as current density and the sample resistivity. Thus by the right combination of electrolytes it is possible to prepare macroporous silicon of good quality with controlled pore morphology. We believe that this research could be useful in preparing porous silicon samples with controlled dimensions.

3.4 References

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IV

Preparation and Characterisation of Porous Silicon–Magnetic Iron Oxide Composites

4.1 Introduction

Porous silicon may serve as an important substrate or matrix for incorporating various types of nanoparticles such as magnetic and semiconducting (quantum dots) nanoparticles. The unique properties of the nanoparticles combined with those of the porous silicon might result in new composite materials with various applications. The great advantage of porous silicon is that it has a large surface area, which can be easily functionalised using chemical methods. There are various reports on the modification of silicon, both flat (non-porous) and porous, using different chemical precursors.^{1,2} The silicon surface especially porous silicon modified using amorphous iron oxide nanoparticles has recently proved to possess very interesting properties.¹ There are a few publications on the incorporation of Fe_2O_3 nanoparticles onto flat silicon wafer and further heat treatment leading to multiple functionality (magnetic, metallic, semiconducting, insulating and optical),² in which the authors describe about a “plug and play” approach where externally synthesized nanoparticles of desired size and functions are incorporated onto the semiconductor surface. Magnetic nanoparticles are intensively studied for their application in various fields such as information storage,³ colour imaging,⁴ bioprocessing⁵ and controlled drug delivery.⁶ Magnetic particles when reduced to their nanometers size exhibit a number of physical properties such as giant magnetoresistance, large coercivities, superparamagnetism and high Curie temperature.⁷

Another important property of nanoparticles is their ability for self-organisation and formation of the structured assemblies.⁸ Self-assembly of nanoparticles have been studied extensively and the preparation of novel nanostructured material is one of the interesting topics in the field of advanced materials.⁹ The formation of self-assembled nanomaterials strongly depends on inter-particle interactions,^{10,11} particle size distribution and particle shape.¹²⁻¹⁴ The self-assembly of nanoparticles can take different shapes – as a ring, rod or needles *etc.*⁸ It is known that the fundamental forces responsible for the self-assembly process can be both intra- and inter-molecular.⁹ It is important to note that the interaction of nanoparticles with a substrate can lead to different shapes which has its contribution from the attraction or repulsion of individual particles with the substrate and also on the interfacial chemistry between the nanoparticles and the substrate. Thus by varying the

experimental conditions of nanocrystals deposition on substrates, a variety of organised structures can be formed.

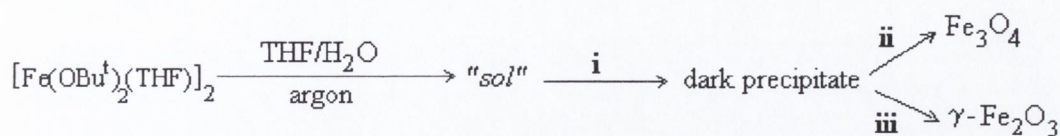
4.1.1 Aims of this work

Magnetite nanoparticles (Fe_3O_4) have been intensively studied due to their potential applications in information technology and bio technology.¹⁵ Main objective of the present work is to prepare and characterise porous silicon-magnetite composites by introducing magnetite nanoparticles to porous silicon substrate. We plan to use different approaches to prepare magnetite nanoparticles on silicon substrates, including sol-gel processing of an organometallic precursor and co-precipitation of magnetite nanoparticles from the aqueous solution of Fe(II) and Fe(III) salts. The effect of a thermal treatment on the magnetite-PS composites is also to be investigated. Magnetite–porous silicon composite materials are going to be studied by various instrumental methods such as Raman Spectroscopy, Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) (for phase analysis), powder X-ray diffraction technique (XRD) (Structural analysis), Mössbauer spectroscopy and Magnetisation measurements, Magnetoresistance (MR) and SIMS (Secondary Mass Ion Spectroscopy).

4.2 Results and discussion

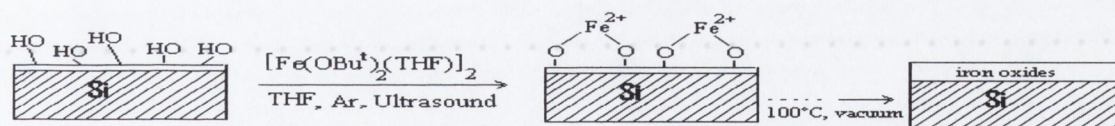
4.2.1 Preparation and characterisation of iron oxide on porous Si layers using a metallorganic precursor

In the present study, we have used a metallorganic precursor and a sol-gel approach to prepare iron oxide-porous silicon composite materials. First, we have carried out experiments using metallorganic $[\text{Fe}(\text{O}^t\text{Bu})_2(\text{THF})]_2$ precursor, which has been previously reported by Y.K. Gun'ko *et al.*, as single source precursor for the preparation of magnetite and maghemite nanoparticles.¹⁶ A schematic illustration for the preparation of magnetic nanoparticles from $[\text{Fe}(\text{O}^t\text{Bu})_2(\text{THF})]_2$ is presented in scheme 4.1. The resulting precipitate can be Fe_3O_4 or $\gamma\text{-Fe}_2\text{O}_3$ depending on thermal treatment conditions used.¹⁶



Scheme 4.1 Schematic representation of the preparation of magnetic iron oxide nanoparticles where, i = ultrasound, 1 h; ii = vacuum, 3 h, *ca.* 20 °C; iii = heat, *ca.* 200 °C, in air, 30 min.

The preparation of iron oxide layers on porous silicon samples were performed according to scheme 4.2. Hydroxylated porous silicon samples were treated with $[\text{Fe}(\text{OBU}^t)_2(\text{THF})]_2$ precursor solution in dry THF. After the ultrasonic treatment, the PS samples were washed with dry diethyl ether, twice with wet diethyl ether followed by drying under vacuum. Then porous silicon samples were heated up to 100°C under vacuum for 12 hours. The mechanism of formation of iron oxide involves an oxidation of Fe(II) into Fe(III) by ultrasonically generated radical and peroxide species from THF. A similar type of process has been recently reported by A. Gedanken et al.¹⁷ The thermal treatment at 100°C allows the completion of conversion from the precursor into iron oxide coating. The as-prepared layers have been studied by FTIR and micro-Raman spectroscopy. The IR spectrum (figure 4.1) exhibited a shoulder at 1027 cm^{-1} which was assigned to Fe-O-Si stretching vibrations.¹⁸ Broad bands at 1097 cm^{-1} and 825 cm^{-1} were attributed to Si-O and Fe-O bonds respectively.^{19,20} A band at 1625 cm^{-1} is characteristic for bending mode of Fe-OH groups, which are present at the surface of iron oxides.



Scheme 4.2 Schematic representation of the preparation of iron oxide layers on porous silicon surface.

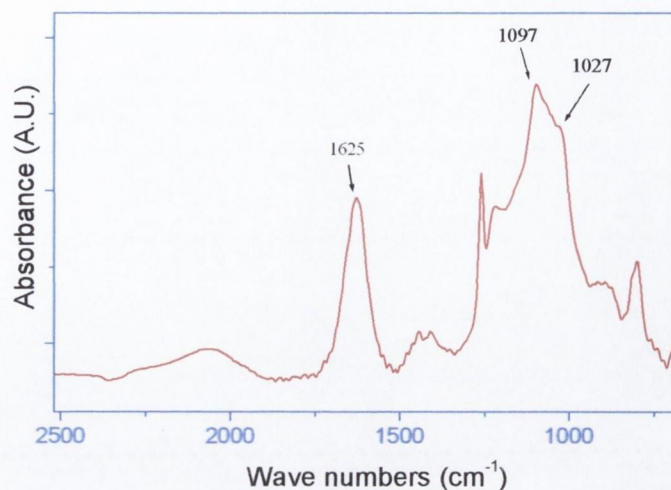
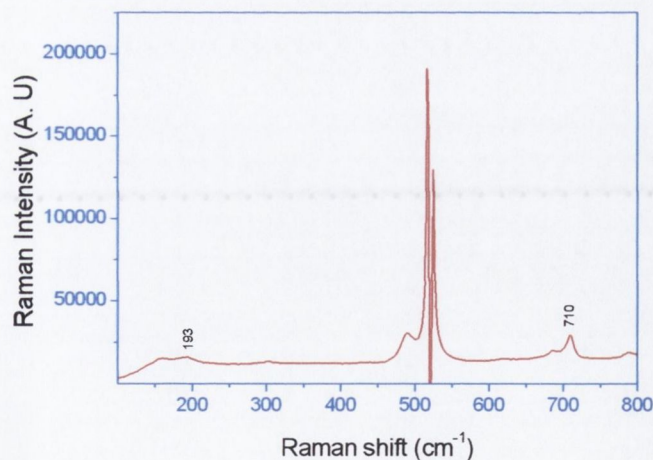
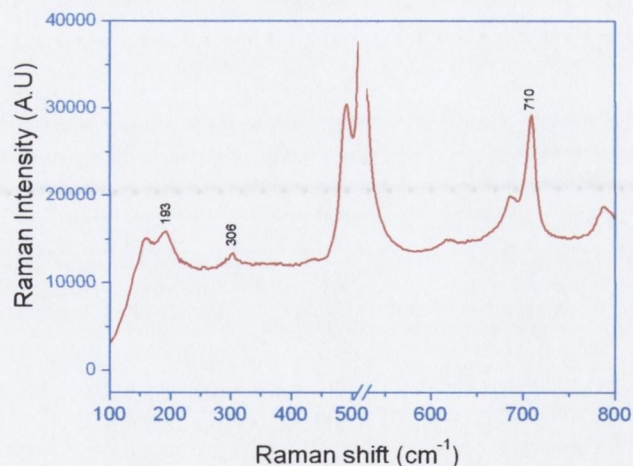


Figure 4.1 FTIR spectrum of iron oxide layers on porous silicon.

Raman spectrum [figure 4.2a and 4.2b (which is an enlarged spectrum of 4.2a)] of the sample clearly shows peaks belonging to a mixture of magnetite and maghemite.²¹ The peaks at 193, 306 and around 680 cm^{-1} are attributed to magnetite, whereas the peaks at 161, 617 and 710 cm^{-1} are attributed to maghemite.²¹ The strong peak around 520 cm^{-1} is attributed to silicon substrate.²²



(a)



(b)

Figure 4.2 (a) Raman spectra showing presence of iron oxides on porous silicon. (b) Enlarged Raman spectrum of 4.2a showing the smaller peaks.

SEM microscopy of both the top and cross-section areas of the sample does not show any changes. We presume that a very thin layer of iron oxide formed can not be detected by SEM, due to the SEM resolution limitations.

Thus the results from FTIR and Raman spectroscopy confirm the presence of mixed iron oxide layers, prepared from the metallorganic precursors and formed on porous silicon. It also gave an insight into the various types of bonding of the iron oxide layers to the porous silicon substrate. The magnetisation studies on the iron oxide–porous silicon composite sample (figure 4.3) showed a weak magnetic response of the iron oxide layer on porous silicon. This can be attributed to the presence of very thin layer of magnetic iron oxide. Magnetisation (m) is defined as the property of a material to generate a magnetic field, either in the presence of an external magnetic field or spontaneously. In other words, magnetisation is defined as the amount of magnetic moment per unit volume.

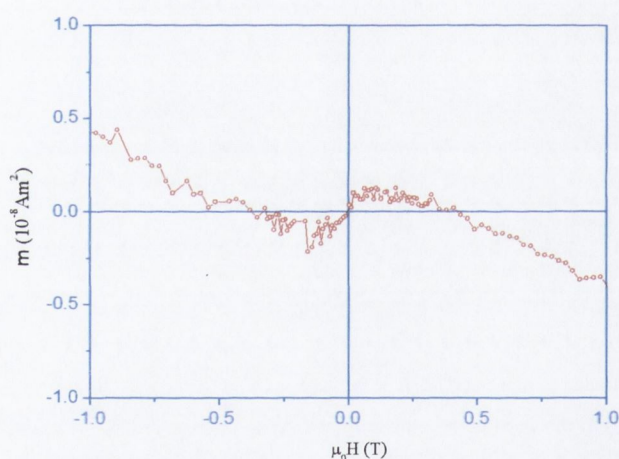


Figure 4.3 Magnetisation measurements of the iron oxide–porous silicon composite.

4.2.2 Preparation of magnetite–porous silicon composite materials

4.2.2.1 Preparation of magnetite – porous silicon composite

In this experiment, the hydroxylated porous silicon samples were treated with magnetic nanoparticles prepared by in situ co-precipitation of the mixture of iron ($\text{Fe}^{3+}/\text{Fe}^{2+}$) salts taken in the stoichiometric ratio ($\text{Fe}^{3+}/\text{Fe}^{2+} = 2$) with ammonia solution.²³ The porous silicon samples used were of both n -type (pore diameter of 3 - 4.5 μm with round pores)

and *p*-type (pore diameter in the range 0.5 – 1.5 μm). SEM images of the *p*-type PS samples are presented in figure 4.4.

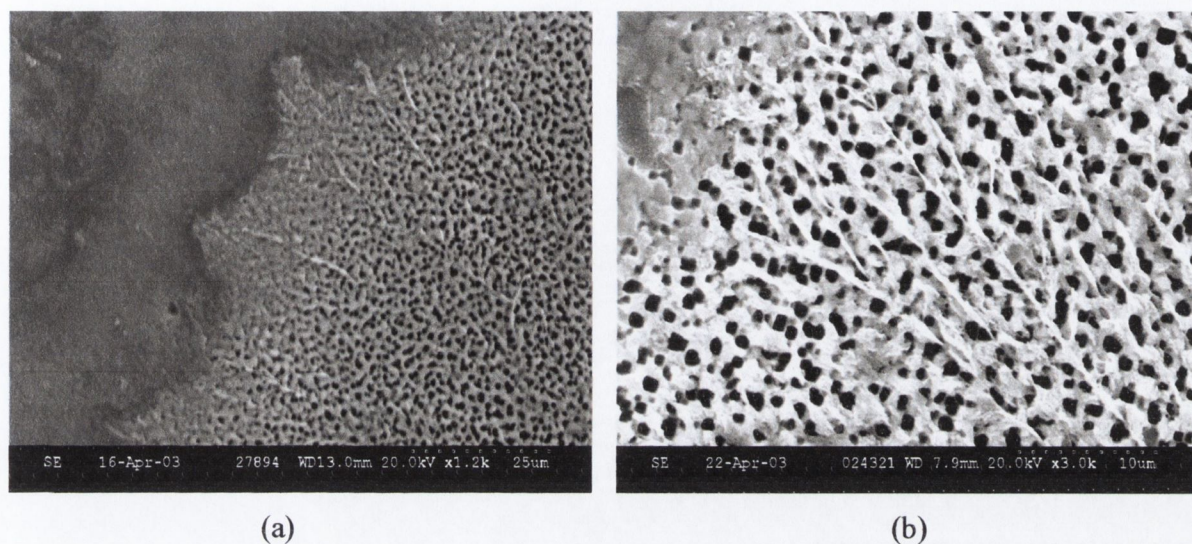
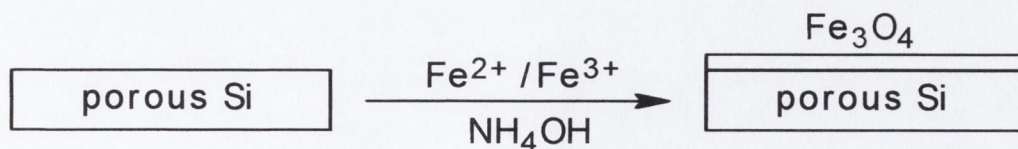


Figure 4.4 SEM images of *p*-type porous silicon sample used in present studies (a) Plan view (b) Magnified plan view of (a).

From the images it is quite clear that the pore distribution in the macroporous silicon sample has fractal-like morphology. This porous silicon sample with the hydroxyl-terminated surface was then used as a substrate for deposition of magnetic nanoparticles. Porous silicon samples were placed into a degassed water solution containing a mixture of ferrous chloride and ferric chloride solutions prepared in 2:1 ratio under argon gas to prevent oxidation. The black precipitate together with porous silicon samples were washed with organic solvents and dried under vacuum. A schematic representation of the process is given in scheme 4.3



Scheme 4.3 Schematic representation of the preparation of PS–magnetite composites.

The black product prepared in this experiment was investigated initially by X-ray powder diffraction. The reflections in the XRD pattern show d spacing values and relative peak intensities, which correspond to the spinel structure (JCPDS No. 851436). All reflections are identified on the basic cubic unit cell, with an isometric crystal system and cell parameter of 8.39Å , as shown in figure 4.5.

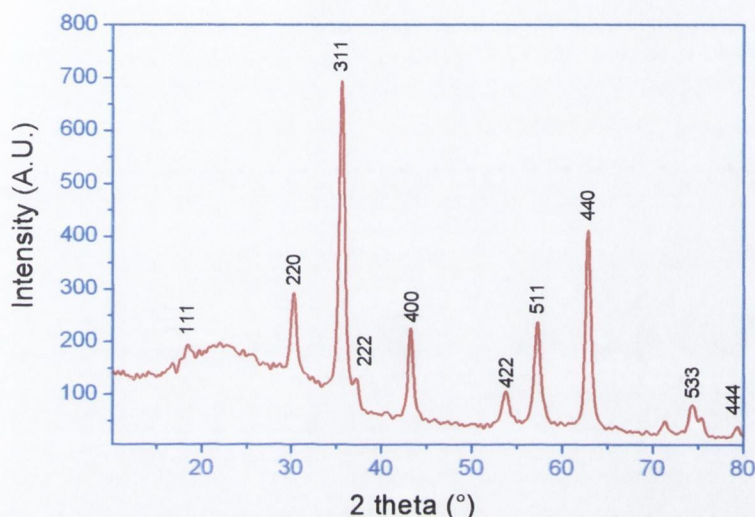


Figure 4.5 X-ray diffraction patterns of the magnetite nanoparticles.

A further identification has been made by comparing the magnetite samples with the commercial magnetite powder samples. Figure 4.6 compares the XRD patterns of as-prepared magnetite nanoparticles with the patterns obtained on commercially available (Sigma Aldrich, 99.99% purity) micron-sized magnetite powder. The pattern shows that the positions of the as-prepared samples are in good agreement with that of commercial magnetite powder. It can be noted that the reflections are quite broad in the magnetite sample under investigation revealing the small size of the particles. The crystallite size of particles was calculated by using the Debye-Scherrer equation below.²⁴

$$\text{Crystallite size} = \frac{0.9 \lambda}{\beta \cos \theta}$$

Where, λ is X-ray wavelength (1.54 Å), θ is Bragg angle and β is the FWHM of the peak in radians (theoretically corrected from the instrumental broadening).

The crystallite size of the particles was found to be approximately 7 nm.

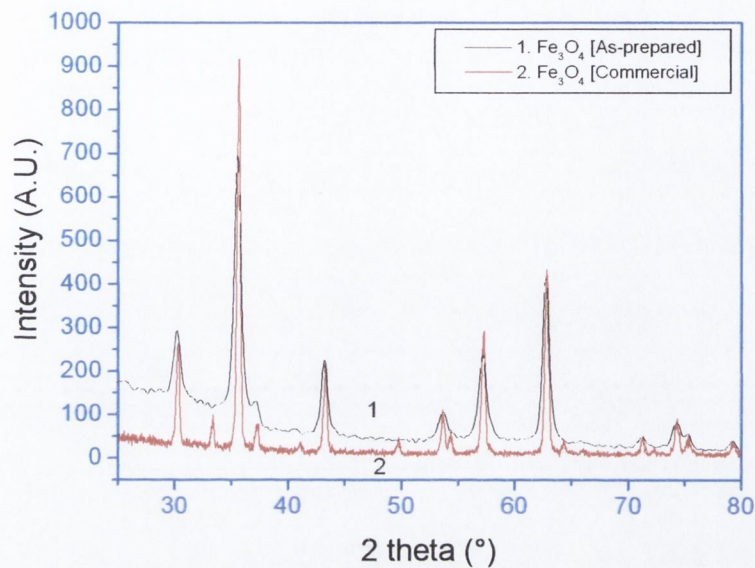


Figure 4.6 XRD patterns of the magnetite samples (1) as-prepared (2) commercial.

X-ray diffraction pattern of the blank porous silicon sample were compared with porous silicon–magnetite in figure 4.7.

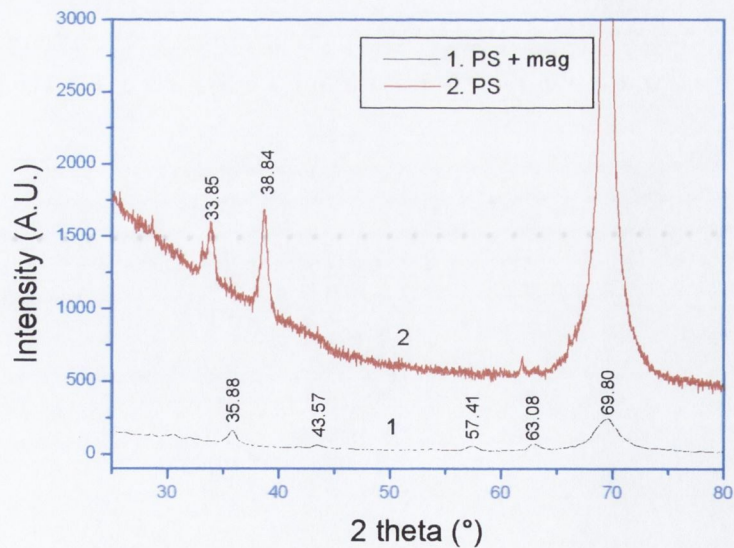


Figure 4.7 XRD patterns of porous silicon–magnetite composite (room temperature).

The patterns showed reflections corresponding to porous silicon and that of magnetite ($2\theta = 35.8^\circ$). Some of the reflections for magnetite overlap with a reflection pattern of porous silicon. In addition, the intensity of reflections from porous silicon dominate the patterns compared to that from magnetite. The reflection at 69.8° in the porous silicon-magnetite composite sample corresponds to silicon [Si (100)] plane.

Then the PS-magnetite samples were characterised using Raman spectroscopy, which is a very convenient tool for characterisation of magnetic iron oxide materials. The Raman spectrum of the PS-magnetite sample (figure 4.8a) shows a peak position at 520 cm^{-1} which is characteristic for the silicon²² and a peak at 667 cm^{-1} , a characteristic peak for magnetite.²⁵ The Raman spectrum of the magnetite powder sample alone shows a peak at 667 cm^{-1} in figure 4.8b.

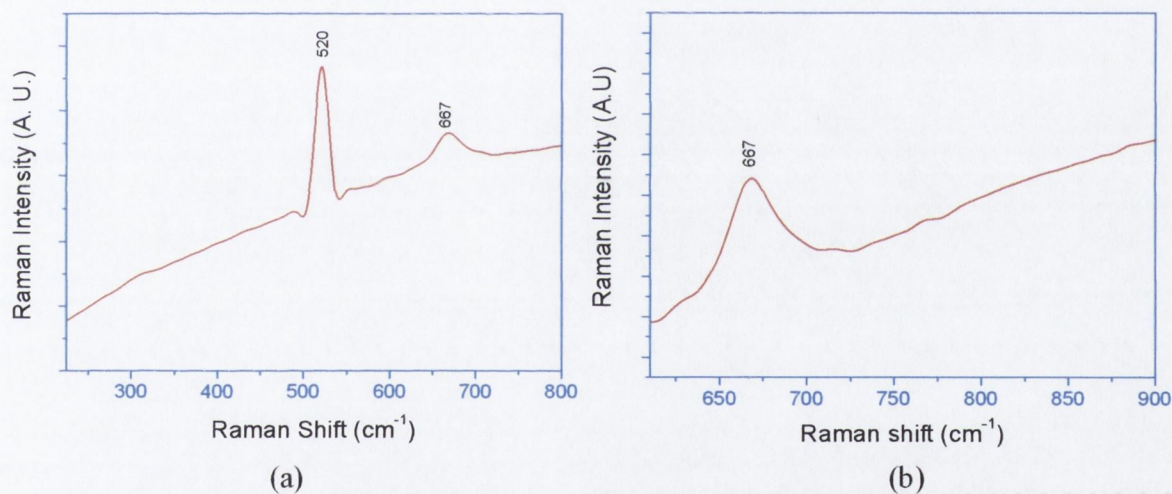


Figure 4.8 Raman spectra of (a) PS-magnetite composite (b) magnetite nanoparticles.

Thus the Raman spectroscopy confirmed the presence of magnetite particles on porous silicon.

Mössbauer spectra (MS) recorded at 300 K, 150 K, and 77 K for both the magnetite on PS and for nanoparticles samples are compared in figure 4.9. Initially comparing the spectral shape of the two samples at same temperatures it can be seen that they look very similar. At

all temperatures, in particular at 300 K, the spectral lines for both samples are quite broad and asymmetric. Consequently, four sextets are required to describe the magnetite hyperfine structure.

The isomer shift (IS) is a measure of the energy difference between the source (E_s) and the absorber (E_a) transition. The corresponding samples when measured in the Mössbauer at 300 K and 150 K, the IS values for all components are quite close to each other and the weighted average lies in the range of 0.40 mms^{-1} – 0.42 mms^{-1} . The corresponding hyperfine field (B_{hf}) values range between 27.0 T - 52.0 T for both samples. The difference in the B_{hf} values between the four components reflects the distribution of particle sizes. The reduction in B_{hf} values corresponds to particle size effects. The thermal fluctuation influences more significantly the shape of the Mössbauer spectrum.²⁶⁻²⁸ At 77 K three components have similar IS values with weighted average around 0.45 mms^{-1} and increased B_{hf} values between 49.0 T - 53.2 T. The fourth component, which has the lower absorption area, possess higher IS value around 0.63 mms^{-1} while its B_{hf} value remains of 45.0 T for both samples. The more divalent character for this fourth component reflects the onset of some charge ordering in the magnetite particles below the characteristic Verwey transition.²⁷

The line broadening and asymmetry is a striking feature of magnetite particles with distribution of particles sizes, which are in the range of a few tenths of nanometers.²⁶⁻²⁹ The temperature independent paramagnetic component indicates that the particle sizes exceeds the limit to produce super-paramagnetic behaviour. The upper size limit for the appearance of super-paramagnetism in magnetite nanoparticles is about 6 nm.^{26,27,30} The major contribution probably arises from particles with sizes of a few tenths of nanometers. On the other hand, the observed line broadening also indicates very small contributions from micron-sized particles. This is confirmed by the absence of symmetric and narrower lines in the mössbauer spectrum at room temperature. These results agree well with the results of the SEM analysis (discussed later in the chapter), which yield particle size distribution in the range 6 to 10 nm.

From the analysis of Mössbauer data, it is evident that both the porous silicon-magnetite composite and magnetite nanoparticles show no major differences on their particle size distribution. This is confirmed further by other characterisation techniques *viz.*, scanning

electron microscopy, x-ray diffraction. This is expected as the two samples were prepared by a similar procedure. The striking difference lies in the arrangement of these particles – ordered dendrite-like structures on the PS sample and random orientation of magnetite nanoparticles.

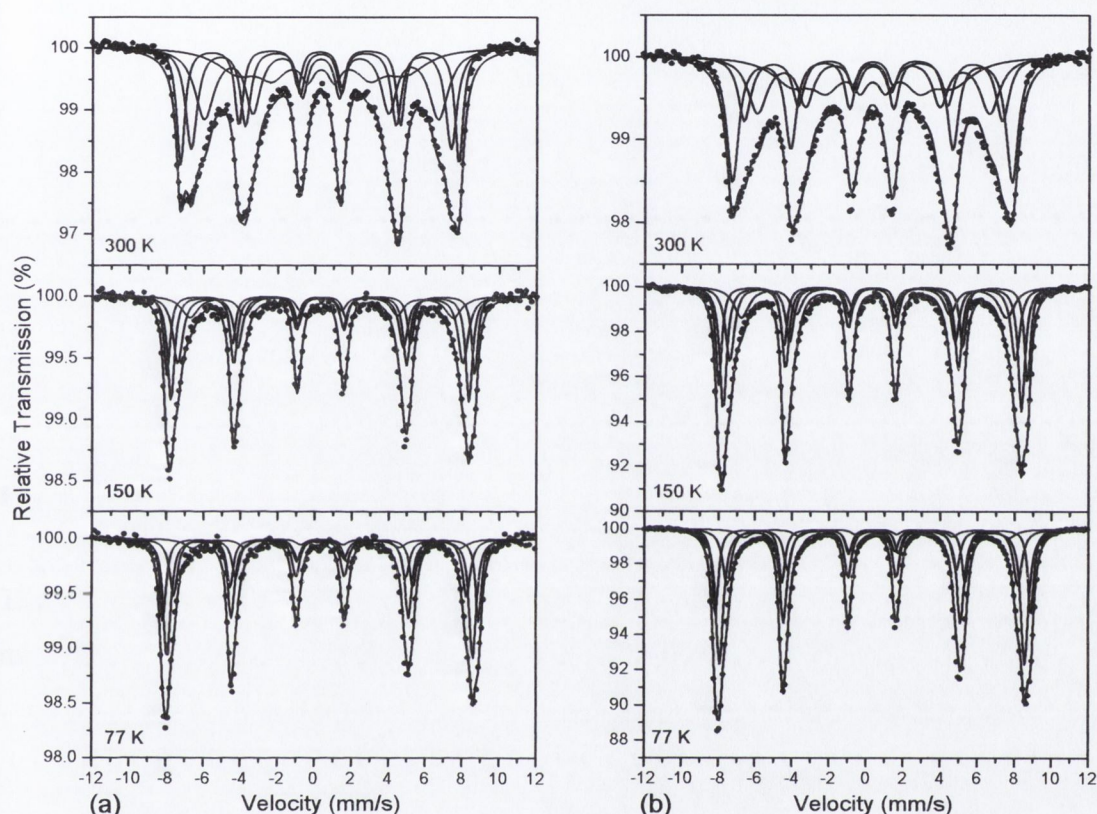


Figure 4.9 Mössbauer spectra of magnetite particles (a) grown on porous Si, and (b) grown free, recorded at different temperatures.

The magnetisation versus field (M-H) curves for magnetite powder measured at 300 K and 5 K is presented in figure 4.10. The magnetisation is unsaturated even at 5 T. The magnetisation at 5 K is $56 \text{ Am}^2\text{Kg}^{-1}$, much less than the value of $90 \text{ Am}^2\text{Kg}^{-1}$ experimentally calculated for a half-metallic ferrimagnetic configuration of Fe^{3+} and Fe^{2+} ions. The reduction and lack of saturation could be attributed to the particle size effect. If a specimen consists of small particles, its total magnetisation decreases with decreasing particle size due to the increased dispersion in the exchange integral³¹ and finally reaches the

superparamagnetic state, when each particle acts as a big ‘spin’ with suppressed exchange interaction between particles. Thus the magnetisation results revealed the superparamagnetic behaviour of these particles.

Figure 4.10 Magnetisation curves of magnetite nanoparticles measured at 300K and 5K.

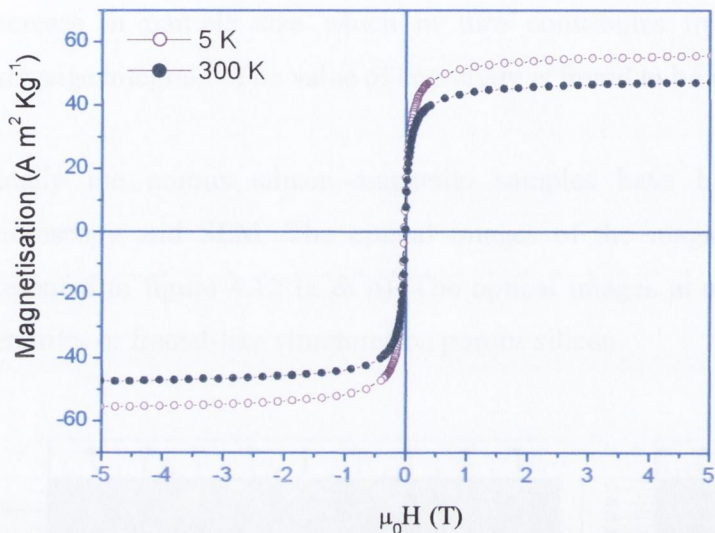


Figure 4.10 Magnetisation curves of magnetite nanoparticles measured at 300K and 5K.

The room temperature magnetisation curve for porous silicon–magnetite composite material is presented in figure 4.11.

Figure 4.11 Magnetisation curves of magnetite–porous silicon composite measured at RT.

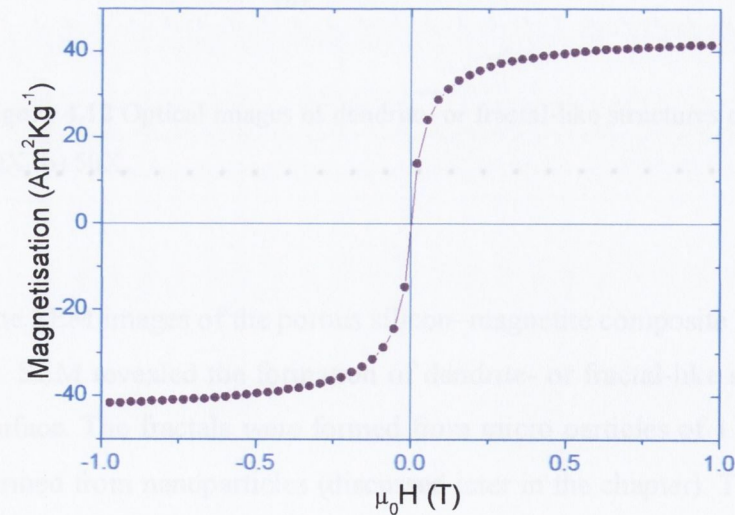


Figure 4.11 Magnetisation curves of magnetite–porous silicon composite measured at RT.

The room temperature magnetisation (σ) is $43 \text{ Am}^2\text{Kg}^{-1}$ in a field of 1 T, which is considerably less than the room temperature saturation magnetisation (*ca.* $90 \text{ Am}^2\text{Kg}^{-1}$) of bulk Fe_3O_4 .³² Similar to the magnetite nanoparticles behaviour, a decrease in saturation magnetisation with particle size is observed. The decrease in total magnetisation due to the decrease in particle size which in turn contributes from the increased dispersion in exchange integral.³¹ The value of coercivity is found to be around 5 mT.

Finally the porous silicon–magnetite samples have been investigated using optical microscopy and SEM. The optical images of the magnetite-porous silicon sample are presented in figure 4.12 (a & b). The optical images at objectives 20X and 50X showed dendrite- or fractal-like structures on porous silicon.

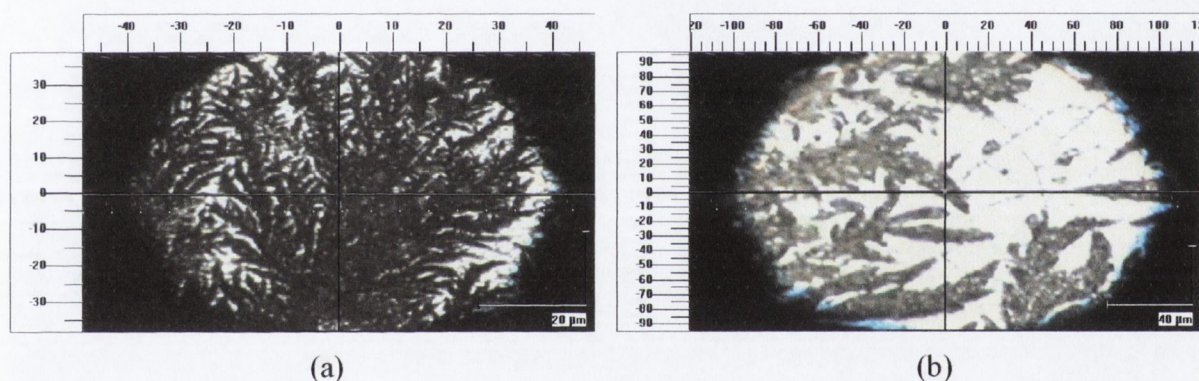


Figure 4.12 Optical images of dendrite- or fractal-like structures on porous silicon. (a) Objective at 20X (b) 50X.

The SEM images of the porous silicon–magnetite composite are presented in figure 4.13 (a–d). SEM revealed the formation of dendrite- or fractal-like structures on the top of silicon surface. The fractals were formed from micro particles of $1.5 \pm 0.5 \text{ μm}$, which in-turn were formed from nanoparticles (discussed later in the chapter). The cross-sectional SEM image of the magnetite-porous silicon sample is presented in figure 4.14. The images showed the partial filling of pores with magnetite powder. The cross-section images also revealed that the filling of pores is not complete down the pores but to a certain depth of 10–15 microns.

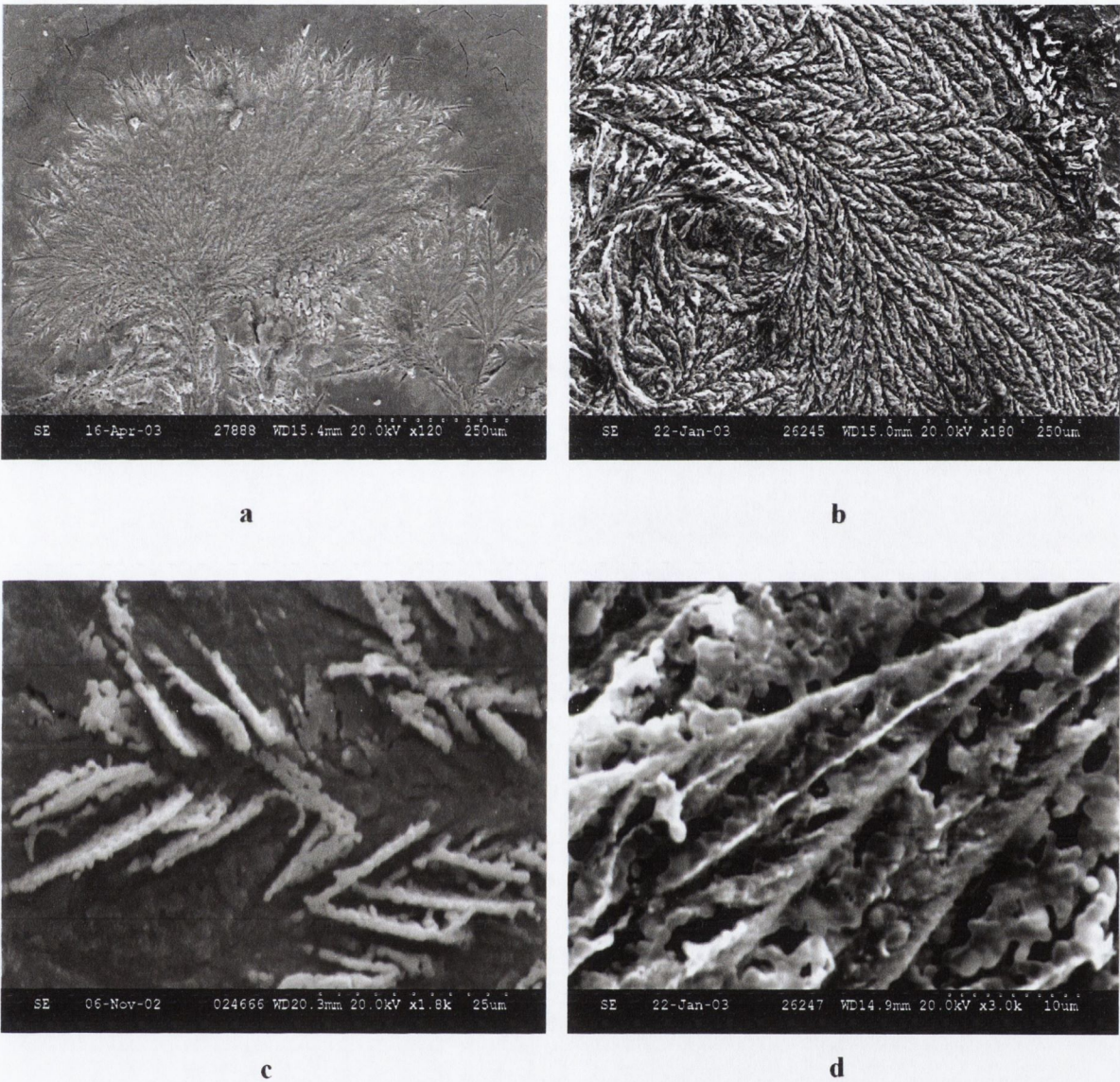


Figure 4.13 (a–d) SEM scans on PS–magnetite sample at different magnifications.

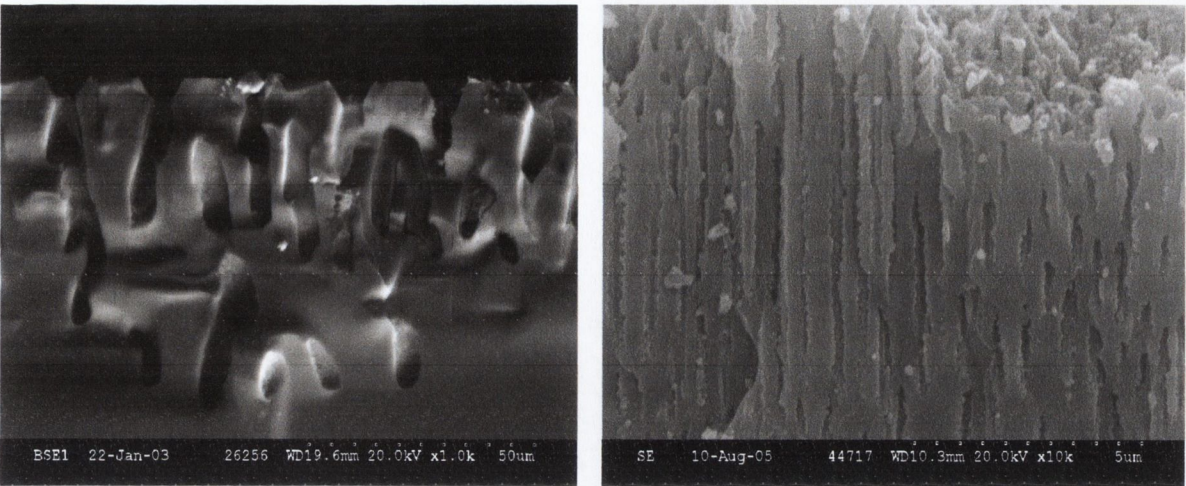


Figure 4.14 Cross-sectional SEM images of PS–magnetite sample.

EDX, which was taken on these fractals, confirmed the presence of iron and silicon (figure 4.15). The inset shows the sample area, where EDX was taken.

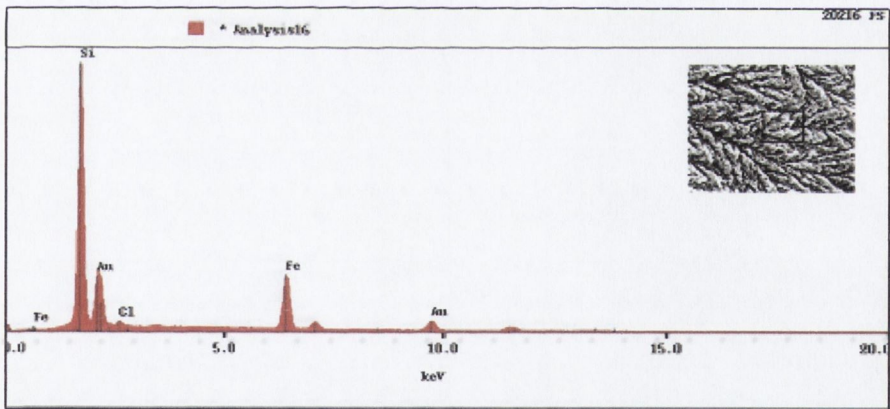


Figure 4.15 EDX of the magnetite fractal on the surface of porous silicon.

Magnified SEM images have clearly shown that the fractal consists of nano-sized particles assembled in the branched arrays. The TEM image (figure 4.16) of the magnetite scratched off from porous silicon surface has clearly shown the presence of nanoparticles with the size distribution in the range of 6-12 nm. The magnetite nanoparticles are self-assembled in peculiar dendrite- or fractal- like structures of microns in size forming branches. The term

“fractal” has been used a large number of times in literature. There are a few reports on fractal structures formed by metal nanoparticles, for example a report on forming fractal silver nanocrystallites by using γ -radiation in presence of solvents.³³ The formation of fractal structures on solid substrates depends on the roughness of the surface of the substrate as proved theoretically.³⁴ To add with the mathematical basis for the formation of fractals has been studied quite well.³⁵

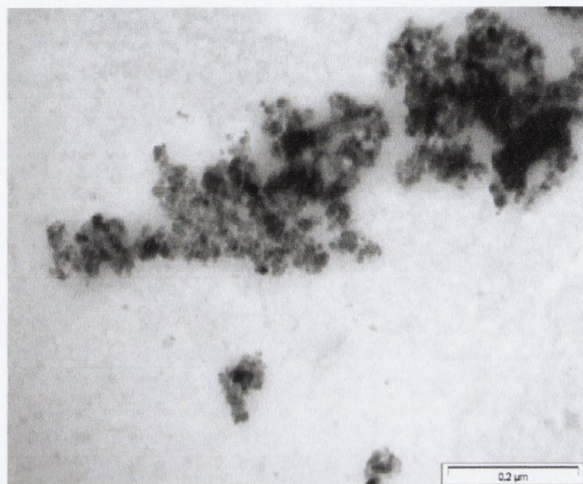


Figure 4.16 TEM image of the magnetite nanoparticles, scratched off the PS surface.

Regarding the reasons and mechanism of the formation of the fractal-like structures, we can propose the following explanation. The fractal formation and side branching depends on the nanocrystal anisotropy and the growth mechanism. We believe that the growth mechanism of magnetite dendrites should be considered within the framework of a Diffusion Limited Aggregation (DLA) model,³⁶ which involves cluster formation by the adhesion of a particle with a random path on contact with a selected seed, thus allowing the particle to diffuse and stick to the growing structure. A fractal-like pre-patterned porous silicon surface serves as a template initiating and facilitating the formation of dendritic structures at the solid-liquid interface. The substrate–nanoparticles interaction is also important in determining the morphology of nanoparticles assembly. The substrate effect on the fractal geometry was studied using two different experiments. In one set of experiments, we used a flat silicon substrate and in the other set of experiment we have used a glass substrate to see the effect of nanoparticles on substrates other than silicon. None of these experiments showed the fractal or dendrite like formations of magnetite nanoparticles.

It was reported that magnetite nanoparticles prepared by co-precipitation method have a number of hydroxyl groups on the surface of precipitates from contacting the aqueous phase.³⁷ The formation mechanism of magnetite fractals on porous silicon is also attributed to the dipole-dipole interactions of magnetite particles after their treatment with diethyl ether. We have hypothesised that the diethyl ether facilitated the partial destruction of OH groups and water shells around the nanoparticles, polarizing them and facilitating the self-organisation into fractal-like structures. Our experiments with ethanol also demonstrated similar type of behaviour in the magnetite nanoparticles but this did not work for other solvents such as chloroform.

The magnetite-porous silicon composite samples were then analysed by secondary ion mass spectroscopy (SIMS). The secondary positive ion spectrum taken on the composite surface is shown in figure 4.17. The value quoted in brackets represent the atomic mass of the isotope. The measurement on the surface of porous silicon sample shows the presence of Fe ions. The sample also shows the presence of Na^+ ions, this is from the solution used for the SIMS process.

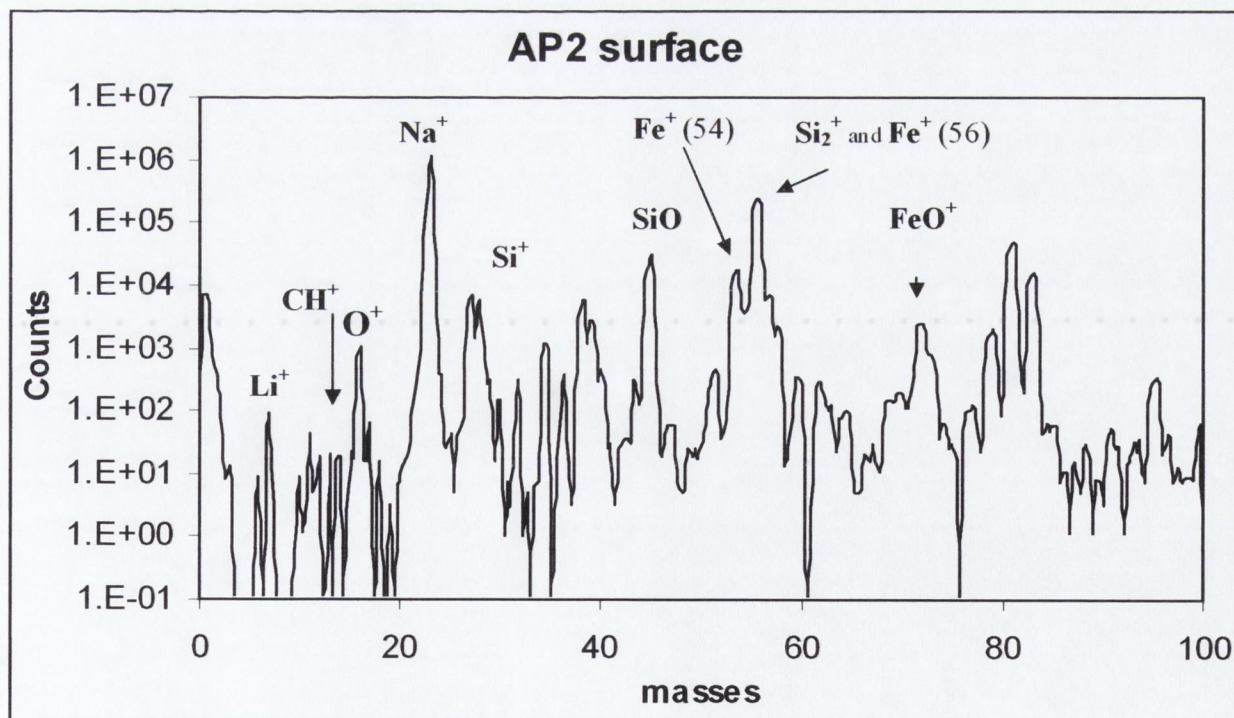


Figure 4.17 SIMS measurement on the surface of porous silicon-magnetite composite.

Depth profiling was performed by intensity measurements of secondary ions with masses: 13 (CH); 16 (O); 28 (Si); 29 (Si); 23 (Na), 35 (LiSi); 54 (Fe), 56 (Si₂ or Fe isotope with masse 56) and 72 (FeO). The porous silicon used for SIMS was studied up to a depth of 11 μm. For depth profiling, secondary ions are used from 10% of all scanned area and the results is presented in figure 4.18. The surface depth of the composite was calculated from the average rate of sputtering, *i.e.*, depth of pore/time.

The depth profile shows a decrease in intensities of ions with the masses: 23 (Na), 44 (SiO) and a slight increase of intensities of ions with masses 28 (Si), 54 (Fe), 56 (Si₂ or Fe _{Fe mass 56}), 72 (FeO _{Fe mass 56}). The ratios of ions intensities helps to determine the concentration of the metal oxide (Si or Fe) at different depths. It can be seen the same character of ratios for Fe(54)/Si(28), Fe(56)/Si(28) and their corresponding masses FeO(72)/Si(28).

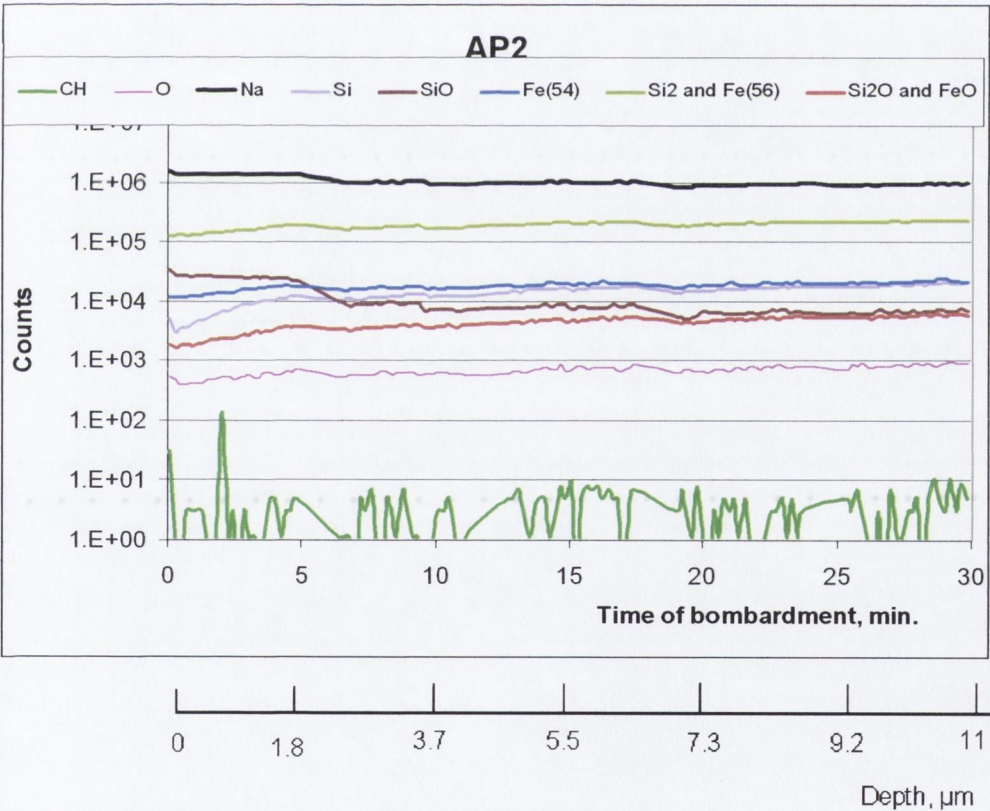


Figure 4.18 Depth profile on porous silicon–magnetite composite.

Figure 4.19 shows the ratio of intensities of ions in porous silicon–magnetite composite up to a depth of 11 μm .

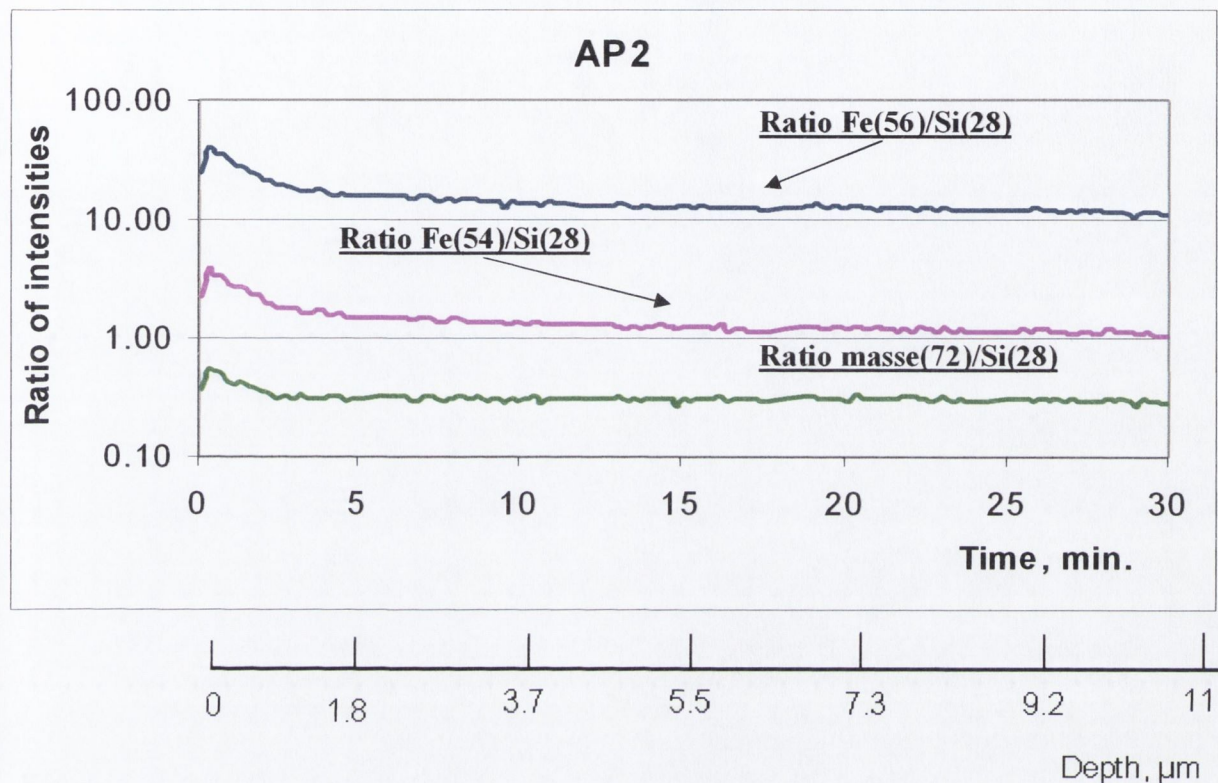


Figure 4.19 Ratio of intensities of ions in porous silicon–magnetite composite.

The depth profile measurements showed that an increase in intensity of iron oxide is prevailing. Thus it can be concluded that the magnetic nanoparticles are deposited quite well inside in the pores.

The positive ion spectrum in porous silicon to a depth of 11 μm is presented in the figure 4.20.

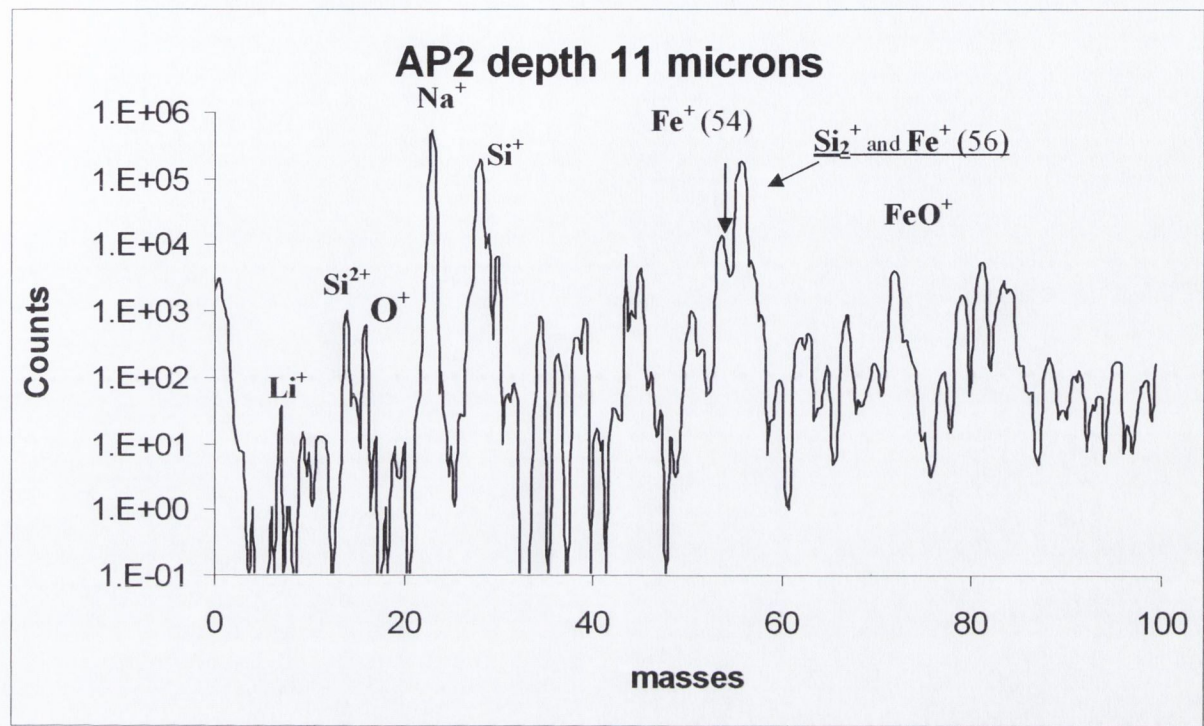


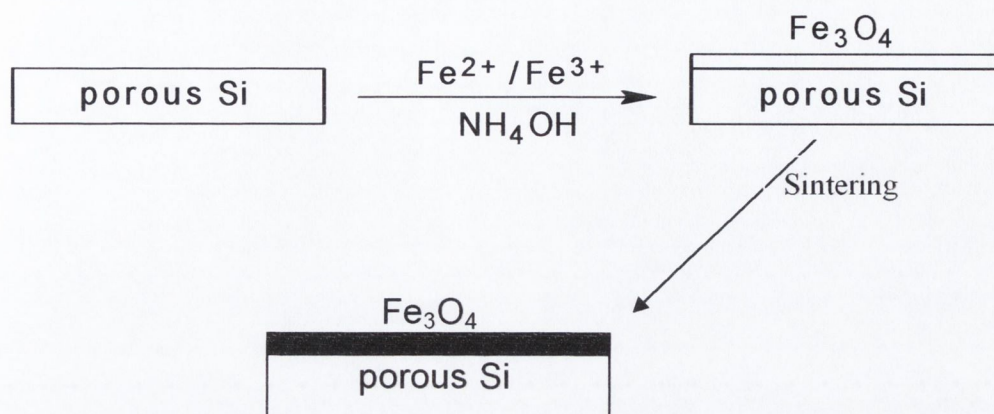
Figure 4.20 The positive ion spectrum to a depth 11 μm in porous silicon–magnetite composite.

The positive ion spectrum obtained for PS-magnetite composite at a depth of 11 μm is similar to that obtained on surface of the composite, which revealed the uniform distribution of the nanoparticles inside the pores of silicon. The counts of Fe^+ ions from a pore depth of 11 μm in the spectrum indicate the presence of magnetite. Thus the results from SIMS confirm the presence of iron oxide nanoparticles is distributed deep inside the porous silicon.

4.2.3 Sintering of magnetite–porous silicon composites

The porous silicon–magnetite composite material was prepared analogously by co-precipitation method using an initial porous silicon samples with randomly distributed pores. The average pore diameter of the porous silicon samples are 2 – 3 μm . The dried composite samples were subjected to heat treatment separately at two different

temperatures 350°C and 450°C under high vacuum (10^{-5} Torr) for three hours. A schematic representation of the method is shown in scheme 4.4.



Scheme 4.4 Schematic representation of the preparation of sintered PS–magnetite composite.

The magnetite-porous silicon sample, which was annealed at 350°C for 3hrs, was initially characterised by X-ray diffraction. Figure 4.21 compares the patterns of blank annealed porous silicon and magnetite introduced porous silicon annealed at 350°C/3hrs.

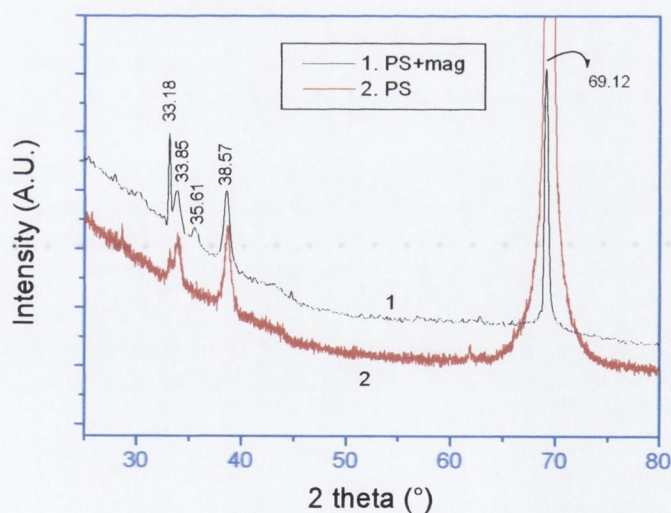


Figure 4.21 XRD patterns of porous silicon–magnetite composite (annealed at 350°C/3hrs).

The observed reflections in the annealed sample correspond to both magnetite-porous silicon sample and porous silicon. The annealed magnetite composite sample exhibited sharp high intensity reflections compared to the broader reflections observed in the sample before annealing. This confirms the grain growth upon annealing.

The Raman spectrum of the sample after the heat treatment at 350° C/3hrs in vacuum is shown in figure 4.22.

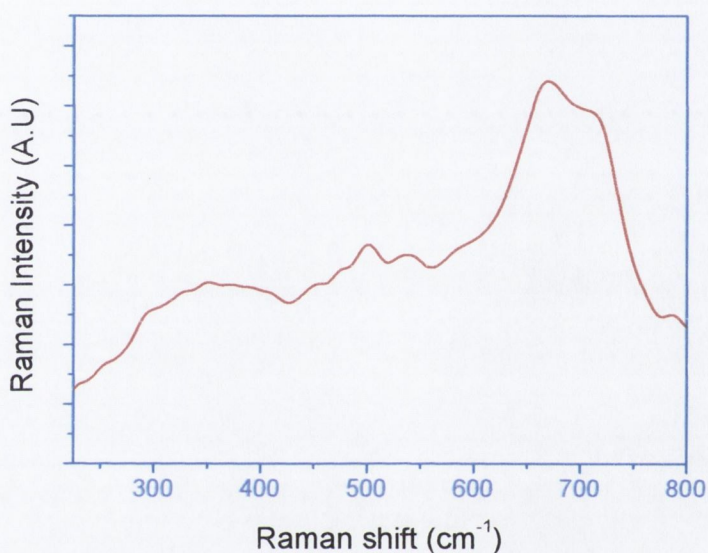


Figure 4.22 Raman spectrum of porous silicon–magnetite composite (annealed at 350°C/3hrs).

The characteristic band at 667cm⁻¹ corresponds to magnetite. Annealing leads to broadening of band in the spectrum. The magnetite–porous silicon composite sample annealed at 450°C/3hr in vacuum was also studied using Raman spectroscopy, showing the similar band characteristic of magnetite.

The as-prepared free magnetite nanoparticles were annealed in vacuum (10⁻⁵ Torr) at 350°C for 3 hours with the aim to increase the magnetisation by reducing the surface spin disorder. Figure 4.23 compares the magnetisation of annealed magnetite particles at 300 K and 5 K.

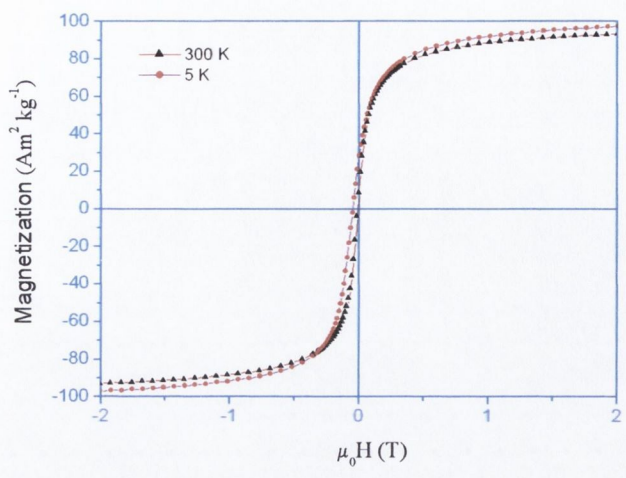


Figure 4.23 Magnetisation curves of annealed magnetite powder measured at 300K and 5K, after annealing.

It is quite clear that the magnetisation increases after the annealing, from 56 Am²Kg⁻¹ to 97 Am²Kg⁻¹. The increase in magnetisation upon annealing could be attributed to the growth in particle size, reduction in surface and spin disorder. A reduction in the surface spin disorder (observed in the composites) towards super magnetic limit can usually leads to a reduction in magnetisation.³⁸

Similar studies were performed on magnetite-porous silicon samples annealed at 350°C/3 hours is compared in figure 4.24.

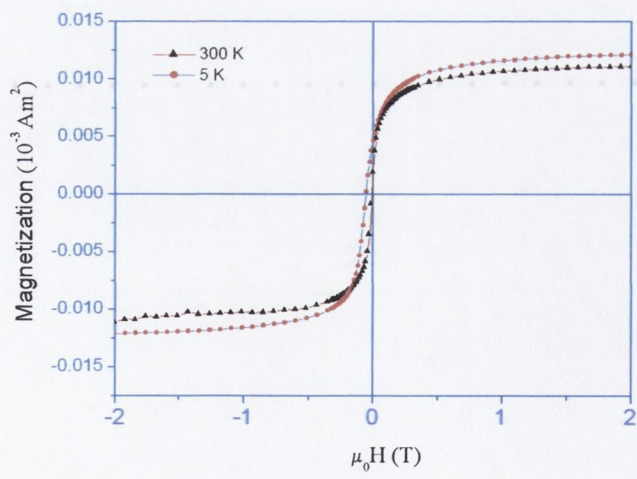


Figure 4.24 Magnetisation of magnetite–porous silicon measured at 300K and 5K, after annealing in vacuum at 350°C /3hours.

Magnetoresistance studies have been performed up to 2T magnetic field on the annealed magnetite-porous silicon composite. The laboratory prepared porous silicon-magnetite composite samples are found, prior to annealing, to be insulating and show no magnetoresistance. After annealing the sample in vacuum at 450°C for 3 hours, its conductivity is induced significantly. It can be shown in figure 4.25 that the resistance decreases significantly with increasing magnetic field.

The magnetoresistance ratio,

$$\frac{\Delta R}{R} = \frac{R(0)-R(H)}{R(0)} \times 100$$

where, $\Delta R/R$ is the change in the electrical resistance of a substance when it is subjected to magnetic field. $R(0)$ is the resistance in zero field and $R(H)$ is the resistance in any field for example 1T, 2T *etc.*

at room temperature in 2T is 0.35 %. This value is slightly lower than value of 1-2 % normally observed in epitaxial magnetite thin films.³⁹

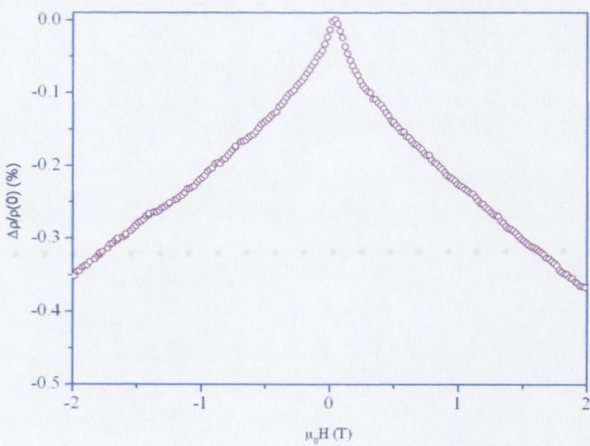


Figure 4.25 Room temperature magnetoresistance of annealed magnetite-porous silicon sample.

Finally, the annealed magnetite-porous silicon samples were analysed using SEM. The images of the PS-magnetite annealed at 450°C for 3 hours under high vacuum (10^{-5} Torr) are presented in figure 4.26. The SEM of the annealed samples shows an ordered arrangement of micro particles in linear arrays, presumably, due to the grain growth and fusion of the particles.

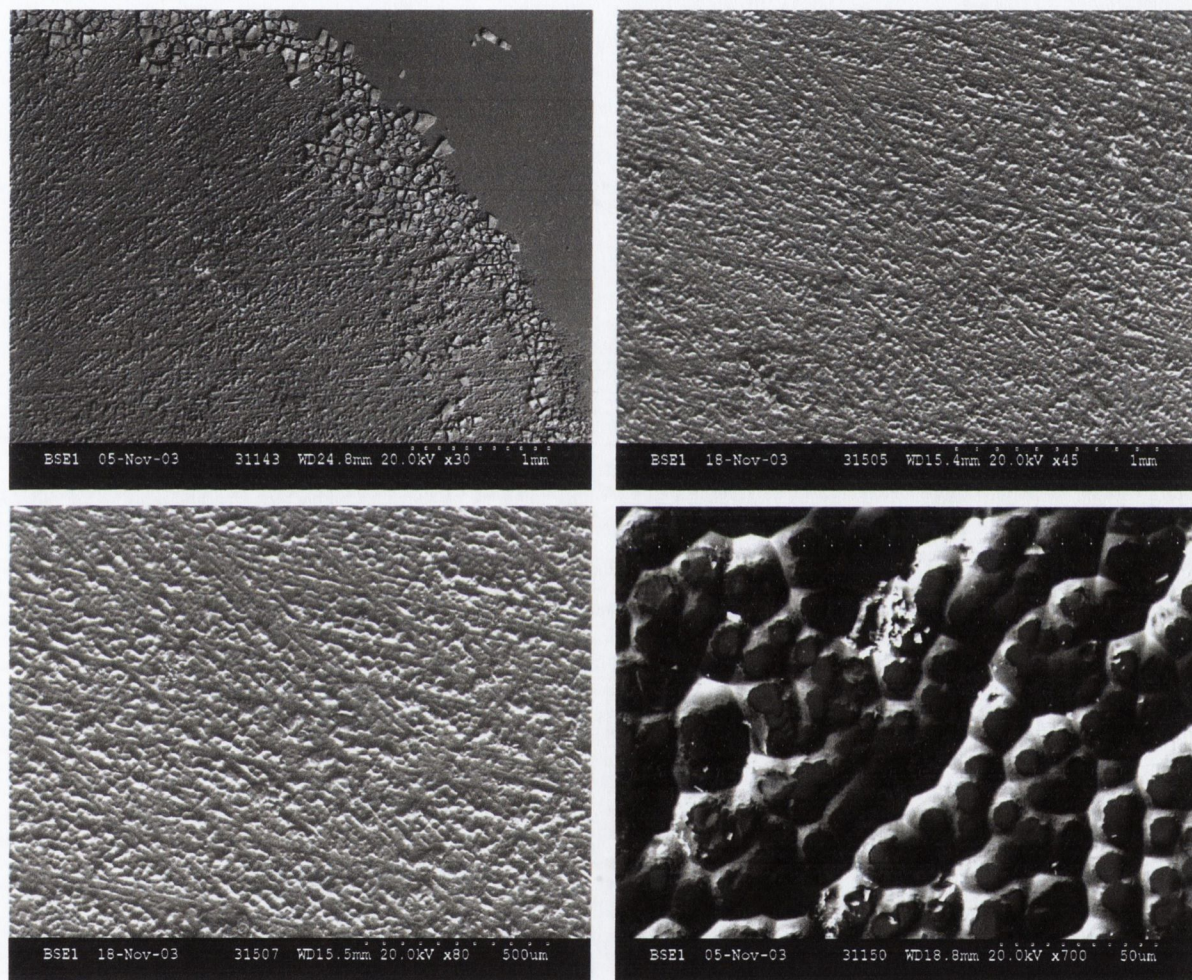


Figure 4.26 SEM images of porous silicon-magnetite composite annealed at 450°C for 3 hrs (at different magnifications).

It is well known that the small particles tend to grow in size when subjected to heat treatment,⁴⁰ by 10 ± 5 μm . In the present work, the particle growth is facilitated by the porous silicon template. This was also confirmed by X-ray diffraction pattern taken on

sample before annealing which showed broadness of reflections, indicating on the small size of the particles before the annealing.

4.3 Conclusions

Several different porous silicon–iron oxide composites have been prepared using various approaches.

We have prepared iron oxide layers on hydroxyl-terminated porous silicon using metallorganic precursors and sol-gel processing. The layers have been characterised by FTIR and Raman spectroscopy.

We have demonstrated that magnetite-porous silicon composites can also be prepared by *in situ* co-precipitation of magnetic iron oxide nanoparticles from the mixture of iron ($\text{Fe}^{3+}/\text{Fe}^{2+}$) salts used with ammonia solution. We have found that this process results in the self-organisation of magnetite nanoparticles into dendrite- or fractal-like magnetite structures on porous silicon samples. Although the mechanism of the fractal formation is not fully understood, we presume it must involve a DLA model in combination with the porous substrate effect and dipole-dipole interactions between the nanoparticles. The sintering of porous silicon magnetite composites in vacuum resulted in the formation of the micron size linear arrays of magnetite microparticles on porous silicon. The formation of these arrays most likely can be explained by the grain growth and fusion of magnetite nanoparticles. Sintered magnetite–porous silicon samples demonstrated relatively low room temperature magnetoresistance.

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V

**Preparation and
Characterisation of Porous
Silicon-Aluminosilicate
Xerogel and Glass
Composites**

5.1 Introduction

One of the very important applications for porous materials is to serve as host matrices for various components. Porous silicon has been a subject of numerous and detailed studies after the discovery of room temperature photoluminescence in microporous silicon.¹ An incorporation of sol-gel and glass materials into porous silicon opened up new ways in the development of optical composite materials.² The development of components for photonics applications is growing. The enormous demand for telephone, broadband internet, and digital television services has stimulated, in recent years, a rush for the introduction of optical links. Indeed, optical communications may solve most of the problems related to interconnection bottlenecks³ and speed limitations⁴ of electronics, offering very large bandwidth,⁴ high noise immunity,⁵ reduced power dissipation and crosstalk.⁶ The luminescence properties of rare-earth (RE) ions in a silica host matrix are of interest for either fundamental aspects and for the numerous industrial applications mainly concerning optoelectronics and optical communication technology.⁷ For example, RE doped glasses are used as optical fibres and amplifiers, remote chemical sensors, and solid state lasers.⁷ Most of the applications for these materials are based on the unique fluorescence emission of RE ions related to the closed 4f electronic configuration of RE elements. Trivalent lanthanide ions produce intense luminescence and their spectra represents the sets of narrow bands in the range from ultraviolet (Ce) to visible (Eu, Tb) and infrared (Er, Nd, Yb) due to intra-4f electron transitions. Emission from lanthanide ions has high efficiency, low temperature quenching, sharp spectral bands and high coherence.⁸ Europium is widely used for fabrication of red-emitting materials.⁹ There is a major interest in erbium-doped materials due to their applications in optoelectronic devices operating at 1.54 μm .^{10,11} This wavelength corresponds to maximum transmission and minimal losses in silica based optical fibres and is outside the range of wavelengths focused on the retina of the human eye.¹¹ An example of one of the major current applications for the RE-doped glass materials is the general use of erbium (Er)-doped fibre amplifiers (EDFA) for optical communication.¹²

Porous silicon has shown to be a promising host matrix for different materials because of its large surface area.^{2,13} Although there are various methods of incorporating rare-earth ions into the porous silicon matrix; the sol-gel processing provides a convenient and cost

effective approach for preparing doped glass samples for optical studies. Current techniques are quite expensive, time consuming, require specialised equipment, and are limited to very shallow doping profiles.² It is logical therefore, that attention should now shift towards a sol-gel doping approach to fabricate doped nanocomposite materials. This method is potentially cheaper and simpler compared to the existing techniques.¹⁴ Also, the sol-gel method allows one to obtain xerogel films by dipping or spin coating. One of the advantages of sol-gel method is the possibility of controlling the doping components of the gel at the stage of preparing a sol. Usually the doping components that must enter into the composition of the gel are introduced at the stage of preparation of a sol in the form of nitrates or chlorides, which, while being heated decompose into volatile components and oxides that modify the oxygen-cationic frame² (oxygen-cation network *e.g.*, of it is silica, then oxygen-silicon network) of the xerogel film. For the efficient up-conversion fluorescence¹² high erbium concentrations are required: however, in the case of high concentrations, the Er^{3+} ions form clusters that results in self-quenching of the luminescence.⁹ Consequently, a key material requirement is the isolation of Er^{3+} ions from each other. The sol-gel process is ideal in this respect. Since it is a chemical process involving mixing of different species at molecular level, a high homogeneity (and as result low losses and good dispersion of Er^{3+} ions) can be achieved. The sol-gel derived films provide surface modification of the entire surface of porous silicon, affecting the chemical bonds at its surface.¹⁵ Recently, researchers have extended this field of research and have devoted their efforts to the introduction of sol-gel coatings into porous networks, including porous silicon, to form nanocomposite materials. The first experiments with silica gel films doped with erbium were carried out on a 5- μm - thick mesoporous silicon density of 1.3 g/cm^3 .^{16,17} Lopez *et al.*,¹⁸ report on porous silicon doped with rare earth metal ions by cathodic electrochemical migration. Gaponenko *et al.*,¹⁶ reported on spin-on technique and dip coating technique for the depositing erbium containing xerogel on porous silicon.¹⁶ In fact deposition methods can be as simple as “dipping” into the liquid sol-gel phase.¹⁹ Sols with a low viscosity may penetrate mesoporous solids meaning that the chemical content of interior surfaces can be tailored to give new properties. These properties would be dependent on the pore size, its shape and morphology. Macroporous silicon, which exhibits a regular pore morphology, microchannel glass and also porous anodic alumina with

regular vertical porous channels are of particular interest.²⁰ The simplicity and reduced cost of room temperature deposition onto porous structures could conceivably pave the way for the next generation of rare-earth opto-electronic devices. It is anticipated that precision coating of carefully selected porous materials may form the basis of future technologies exploiting light emission from lanthanides spanning the ultraviolet, visible and infrared range.

5.1.1 Aims of this work

This part of the project is focused on the rare earths metal ion (erbium and europium) doped, aluminosilicate xerogel and glass materials incorporated into a porous silicon matrix. The macroporous silicon samples are suitable for hosting the sol-gel materials compared to the microporous silicon (pore size less than 10 nm) samples, as the diameter of the pores in microporous samples are insufficient for penetration of the sol through the channels of the pores.²⁰ The ultimate goal of this research is to develop a new approach for the fabrication of microcylindrical emitters using porous membranes and sol-gel processing techniques. Microcylindrical light emitting devices are promising for the development of super small lasers for networking with a size comparable to that of an optical communication fibre core.²¹ We plan to introduce the hydroxylated porous silicon samples into the rare earth doped aluminosilicate sol prior to its conversion into gel inside the porous silicon matrix. In the present work we are going to use a new way of incorporating rare earth doped aluminosilicate xerogel into porous silicon matrix by vacuum filtration method. The same technique of sol-gel incorporation into porous matrices is to be extended to other porous matrices such as microchannel glass matrices. The final objective was to investigate the rare earths doped aluminosilicate-porous silicon composite materials before and after thermal treatments. The prepared porous silicon-rare earths doped aluminosilicate composites are to be characterised using various instrumental techniques such as FTIR, Raman, Photoluminescence (PL) spectroscopy, confocal microscopy, Scanning Electron Microscopy (SEM), EDX (Energy Dispersive X-ray), Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC).

5.2 Results and Discussion

5.2.1 Preparation and characterisation of rare earth doped aluminosilicate xerogel-porous silicon composite material

The preparation of rare earths (erbium and europium) doped aluminosilicate xerogel-porous silicon composites was carried out according to the scheme shown in figure 5.1. The aluminosilicate sol was prepared as previously described by Nogami *et al.*²² In brief, the hydroxylated porous silicon samples were introduced to rare earths doped aluminosilicate sol prior to its conversion into the gel. TEOS (Tetraethoxyorthosilane), was first hydrolysed for 1 h at room temperature with an ethanol-water-acid mixture in the molar ratios 1: 1: 2.7×10^{-3} per mole of $\text{Si}(\text{OC}_2\text{H}_5)_4$. Aluminium isopropoxide, $\text{Al}(i\text{-OC}_3\text{H}_7)_3$, was added to this solution, followed by stirring for 15 min at 70°C . After cooling to RT, the required rare earth salts were added and the solution was then stirred for 1 h. The resultant homogenous solution was hydrolysed by adding ethanol-water-acid in the molar ratios 4: 1: 1.1×10^{-2} per mole of $\text{Si}(\text{OC}_2\text{H}_5)_4$. For the preparation of Er^{3+} and Eu^{3+} doped aluminosilicate sol, erbium iso-propoxide precursor, and europium iso-propoxide or europium chloride precursors were used respectively.

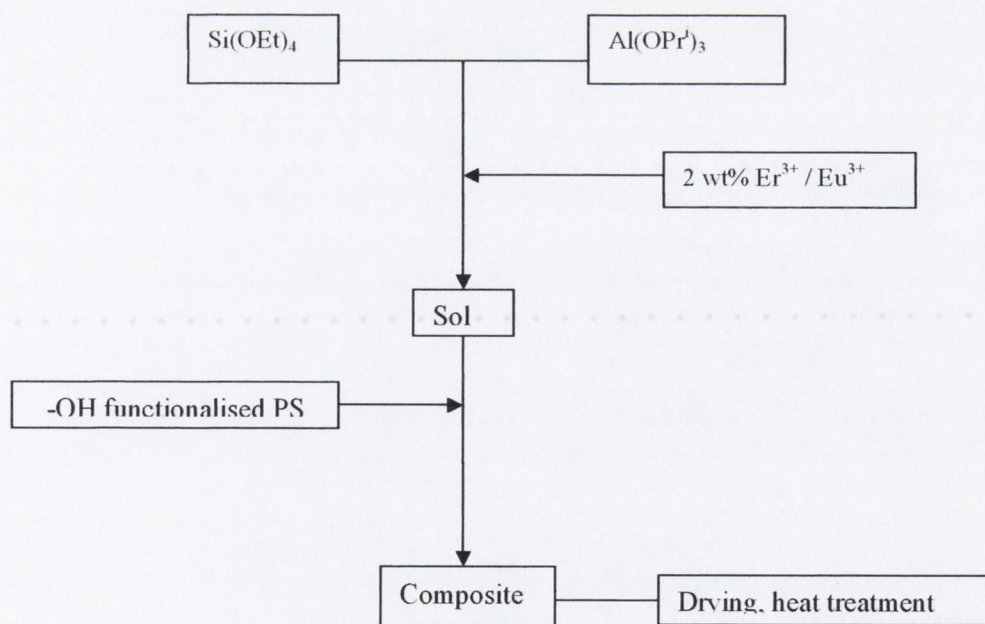


Figure 5.1 Schematic representation of the preparation of porous silicon-rare earths doped xerogel composites.

The as-prepared composite materials were characterised before and after thermal treatment. The SEM images of xerogel-porous silicon composites are shown in figure 5.2 with different magnification. According to these images, the pores are uniformly filled with the xerogel.

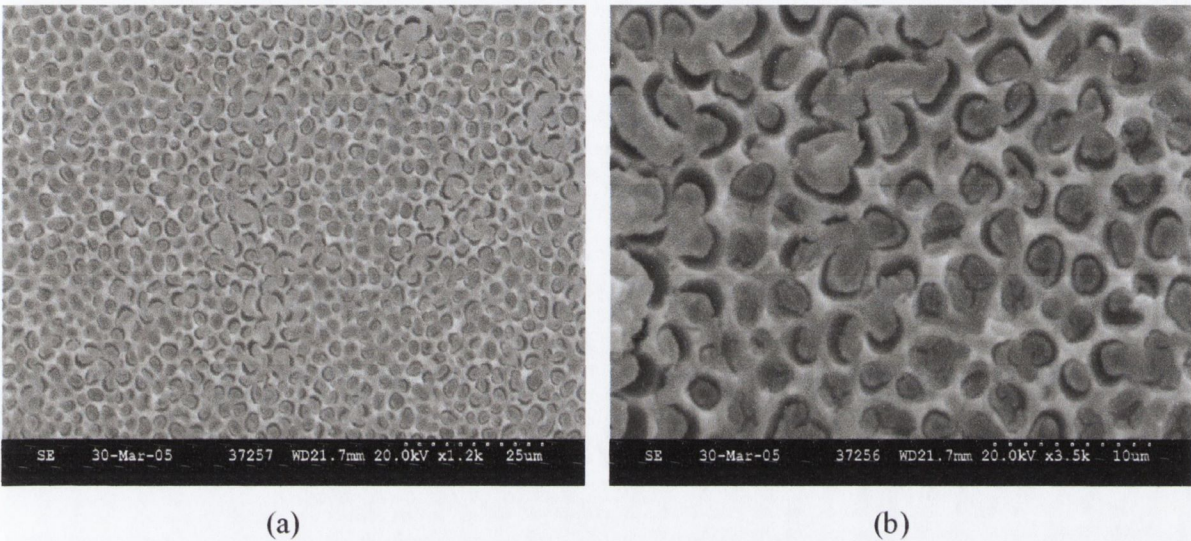


Figure 5.2 (a) and (b) SEM images of porous silicon–rare earth doped xerogel composite (non-thermally treated samples).

FT-IR spectra of aluminosilicate xerogel at room temperature, samples heat treated at 500°C and 800°C are presented in figure 5.3.

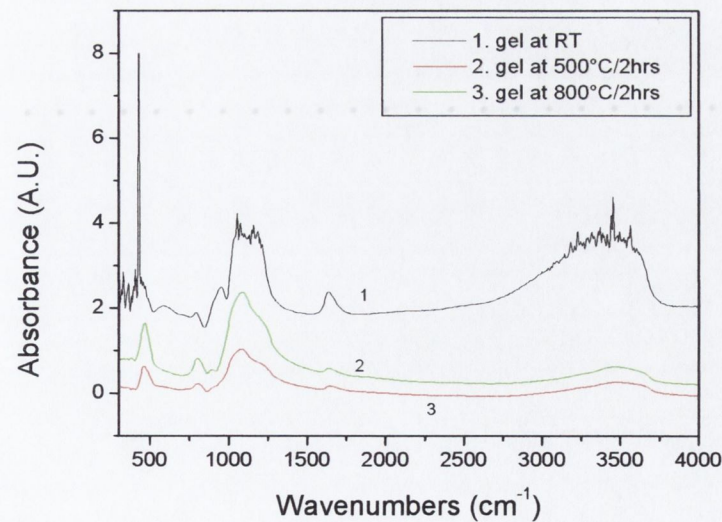


Figure 5.3 FT-IR spectra of aluminosilicate gel heat treated at different temperatures.

The FT-IR spectra revealed the bands associated with gel network. The most prominent region of the spectra corresponding to silica gels lies between 1000 and 1300 cm^{-1} as it was reported in the literature.^{23,24,25} The characteristic peak and shoulder seen at approximately 1086 and 1220 cm^{-1} were assigned to asymmetric stretching vibrations of three dimensional Si-O-Si network.²⁶ A weaker peak seen at approximately 799 cm^{-1} corresponded to the symmetric stretching vibration of the Si-O-Si network.^{23,27,28} A peak assigned to the bending mode of the Si-O-Si bond has been observed at around 460 cm^{-1} and is reported by others.^{23,24} In addition to the characteristic Si-O-Si vibrations, a peak observed at 960 cm^{-1} in the gel at low temperature was assigned to Si-O⁻ groups.^{29,30} This peak disappeared at higher temperature due to dehydroxylation of the surface siloxane groups.³¹ A broad peak observed in the O-H stretching region centred at approximately 3500 cm^{-1} was also assigned to surface hydroxyl groups.

The FTIR spectrum of the rare earth doped (Er^{3+}) aluminosilicate xerogel-porous silicon samples is presented in figure 5.4. The IR spectrum revealed bands associated with xerogel network vibrational modes centred around 800, 930, 1071, 1647 and 3423 cm^{-1} . The peaks associated with porous silicon composite have the same peaks associated with the aluminosilicate gel at room temperature. The main difference is the sharpness of the Si-O-Si asymmetric band at around 1070 cm^{-1} compared to the aluminosilicate gel. This might be due to the influence of the porous silicon that the gel is confined inside the matrix and leads to the more packed gel structure.

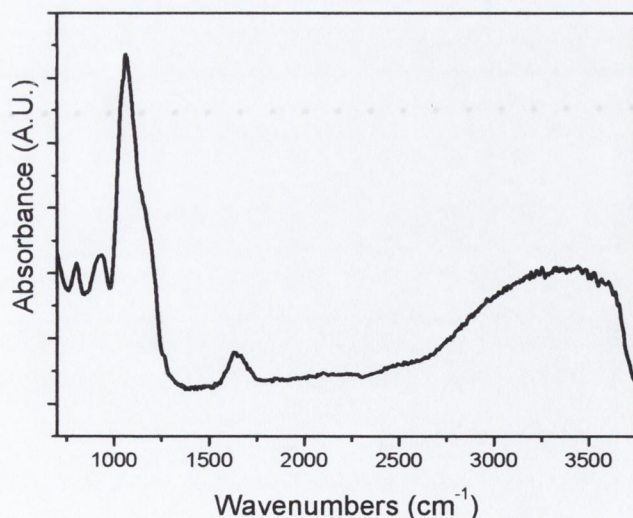


Figure 5.4 FT-IR spectrum of erbium doped aluminosilicate xerogel-porous silicon composite.

The rare earth (Er^{3+}) doped aluminosilicate xerogel samples were sintered at 200°C for 2hrs and 800°C for 2hrs. A typical sintering regime for the samples sintered at 800°C is schematically presented in figure 5.5.

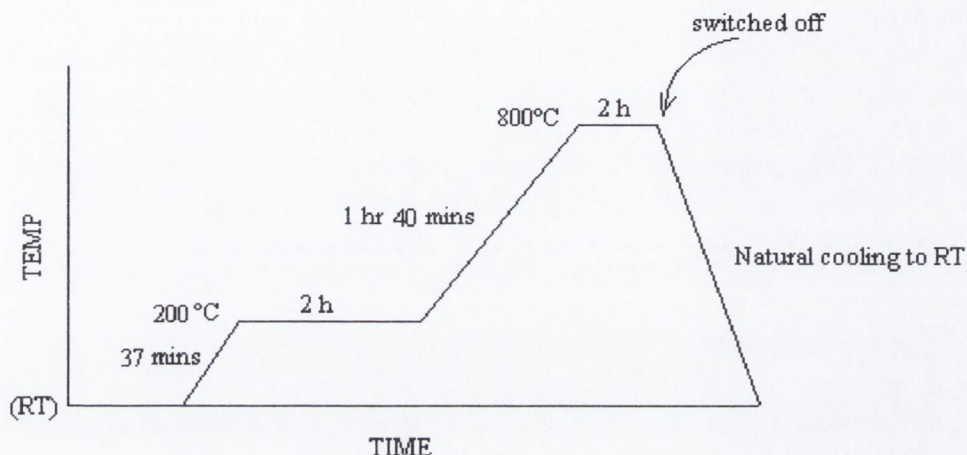


Figure 5.5 A typical sintering regime for rare earth doped aluminosilicate xerogel samples.

The TGA curve on the aluminosilicate xerogel and its derivative are presented in figure 5.6 a & b respectively. The weight loss in the region less than 225°C is attributed to the loss of bonded water. The weight loss in the region 640°C to 680°C can be due to the long alkoxide chains present in the gel. This presence of organic groups may be responsible for the broad and intensive luminescence we observed in the gel as discussed in the later sections of this chapter. The corresponding derivative showed the sharp peak responsible for the % weight change in the gel as represented in figure 5.6b.

The presence of the characteristic bands for Si-O and Si-O-Al bands in the sintered samples was further confirmed by FTIR and Raman spectroscopy. The Raman spectra of the porous silicon-aluminosilicate composite show peaks at 1141 and 1295 cm^{-1} which are attributed to Al-O and Si-O-Al stretches respectively (figure 5.7).³²

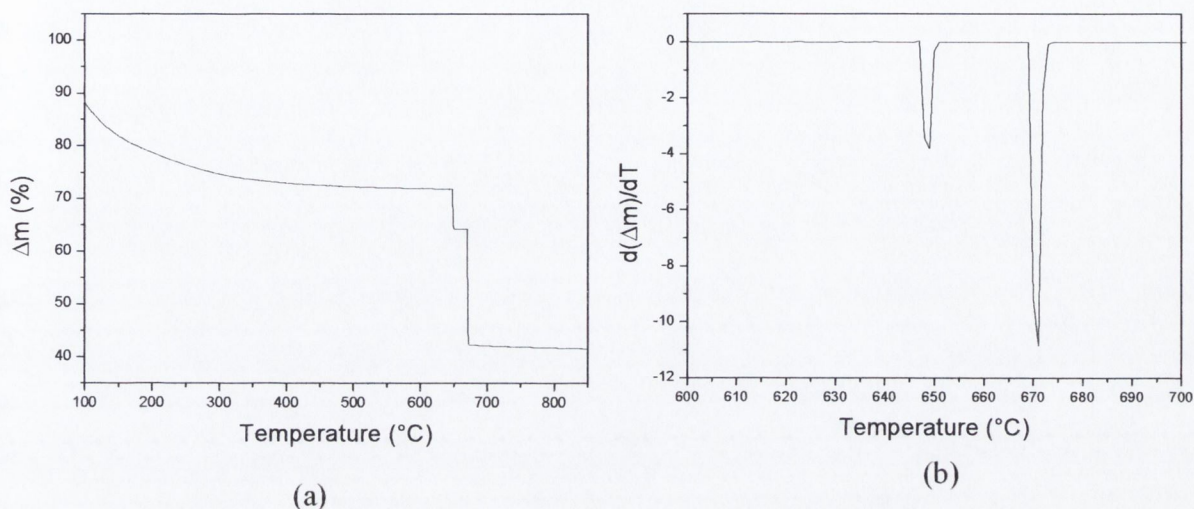


Figure 5.6 TGA diagrams of the aluminosilicate xerogel sample (a) percentage weight change (b) derivative of percentage weight change.

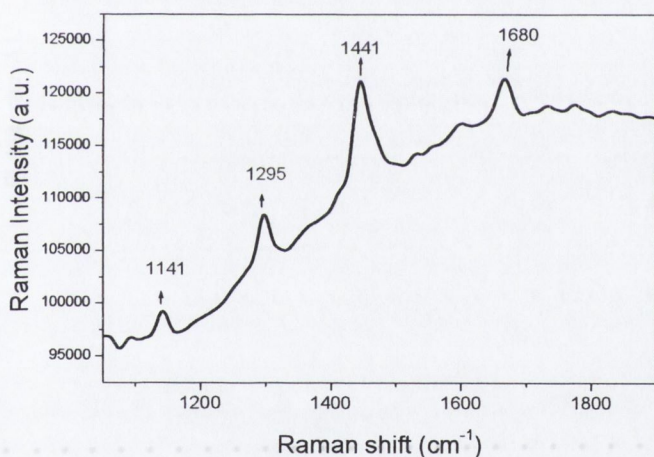


Figure 5.7 Raman spectrum of the erbium doped aluminosilicate-porous silicon composite.

The photoluminescent studies on erbium doped xerogel after the thermal treatment at two different temperatures (200°C and 800°C) are presented in figure 5.8. The spectra show the visible room temperature erbium luminescence under 514.5 nm excitation. Three different bands centred at 522, 545, and 658 nm are observed [figure 5.8(b)]. They corresponds to the radiative transitions from the levels $^2H_{11/2}$, $^4S_{3/2}$, and $^4F_{9/2}$ to the ground level $^4I_{15/2}$.³³

The photoluminescent spectrum for the sample heated at 200°C/2hrs shows {figure 5.8(a)} a broad intensive band. This broad luminescence band is most likely due the presence of organic luminescent species, as it has been previously reported³⁴ and this broad band covers up the rare earth bands. Meanwhile the sample heated at 800°C does not contain luminescent organic species and its PL spectrum shows narrower erbium bands, which are typical for Er-doped alumino-silicate glass matrix. When heated at higher temperature, the gel loses water and organic compounds, that leads to the formation of glass. The structural changes after heating is clearly represented in PL spectra (figure 5.8). As the temperature used for heat-treating the samples increases the PL increase in intensity and J-splitting begins to appear which indicates that the degeneracy is being lifted by an asymmetric ligand field.^{35,36}

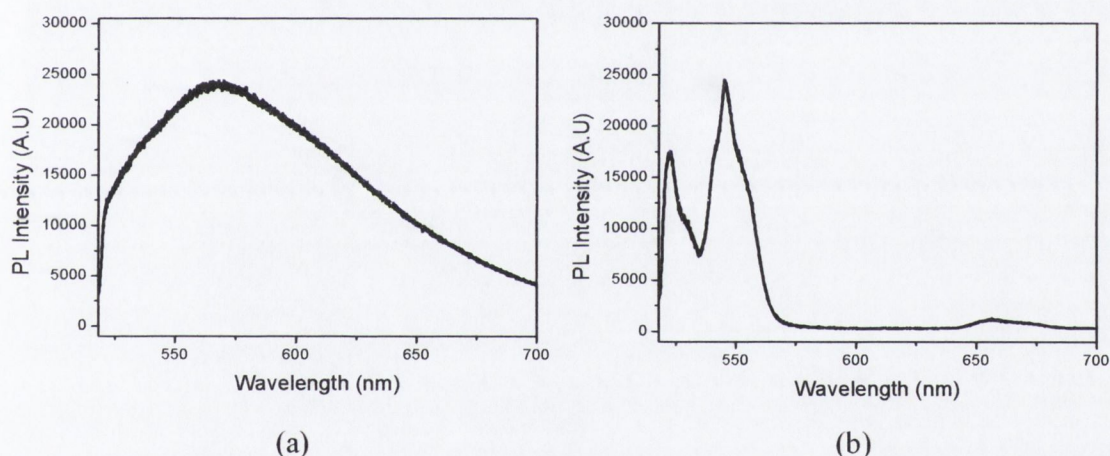


Figure 5.8 PL spectrum of erbium doped xerogel heat treated at (a) 200°C (for 2hrs) and (b) 800°C (for 2hrs).

Similar processes were performed for europium doped porous silicon-xerogel samples.

The europium doped xerogel-porous silicon composite shows the photoluminescence as shown in figure 5.9. The observed luminescence bands correspond to the optical transitions of Eu^{3+} ions in the porous silicon matrix but the intensity of bands is very low compared to the europium doped glass-porous silicon samples. It has been reported that the presence of

-OH groups as well as the clustering of rare earth ions discussed above may promote the PL quenching. The study of aqueous solutions of lanthanides demonstrated that aqua molecules may quench significantly the luminescence due to exchanging the energy of electron excitation of trivalent lanthanide ion by higher oscillation of -OH bond.³⁶ Thus the quenching by hydroxyl groups oscillation plays an important role in non radiative energy transfer.

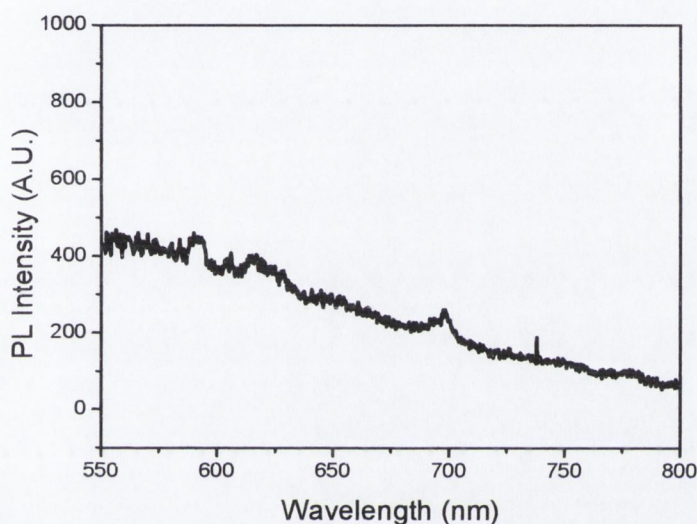


Figure 5.9 PL spectrum of europium doped aluminosilicate-porous silicon composite.

The sintering regimes for the europium doped aluminosilicate-porous silicon composites heated at two temperatures were the same as shown in figure 5.5. The composites were then dried and polished to remove any residual xerogel from the surface of porous silicon. The top view SEM image showing the glass filled pores is presented in figure 5.10(a). The cross-sectional SEM image presented in figure 5.10(b) showed the partial filling of the pores with the aluminosilicate glass. EDX analyses were carried out on the polished part of the sample and also inside the pores. The resultant EDX spectra are presented in figures 5.11(a) & (b). The silicon peak in EDX can be both from glass and the substrate. The EDX is showing no presence of rare earth, as the amount of lanthanide compounds used was very low.

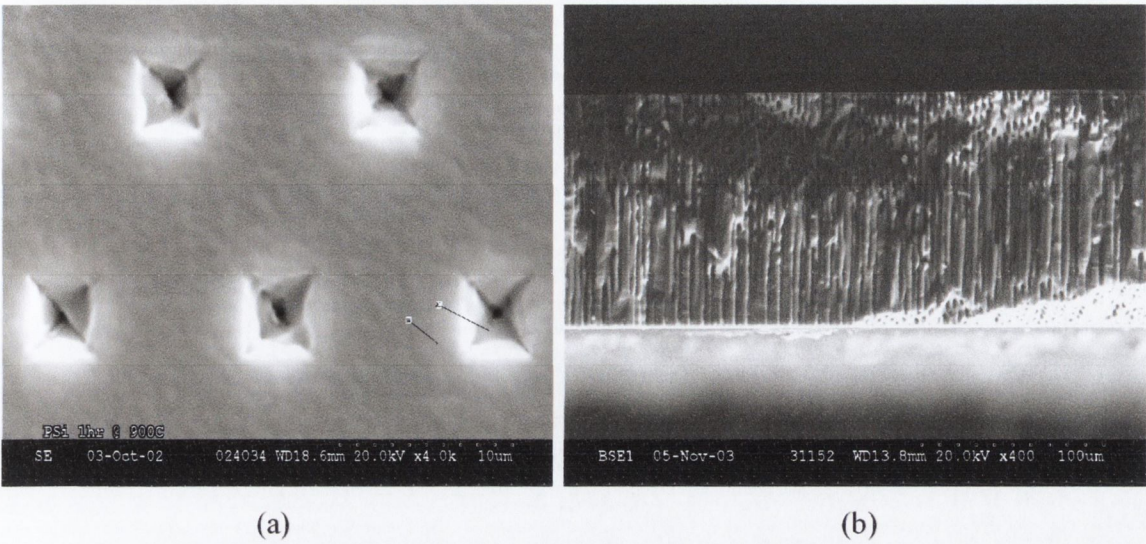


Figure 5.10 (a) SEM image showing the heat-treated rare-earth doped aluminosilicate–porous silicon composite (The surface of the sample was polished to remove any excess of xerogel from the top surface). (b) Cross-sectional SEM image of the aluminosilicate-porous silicon composite.

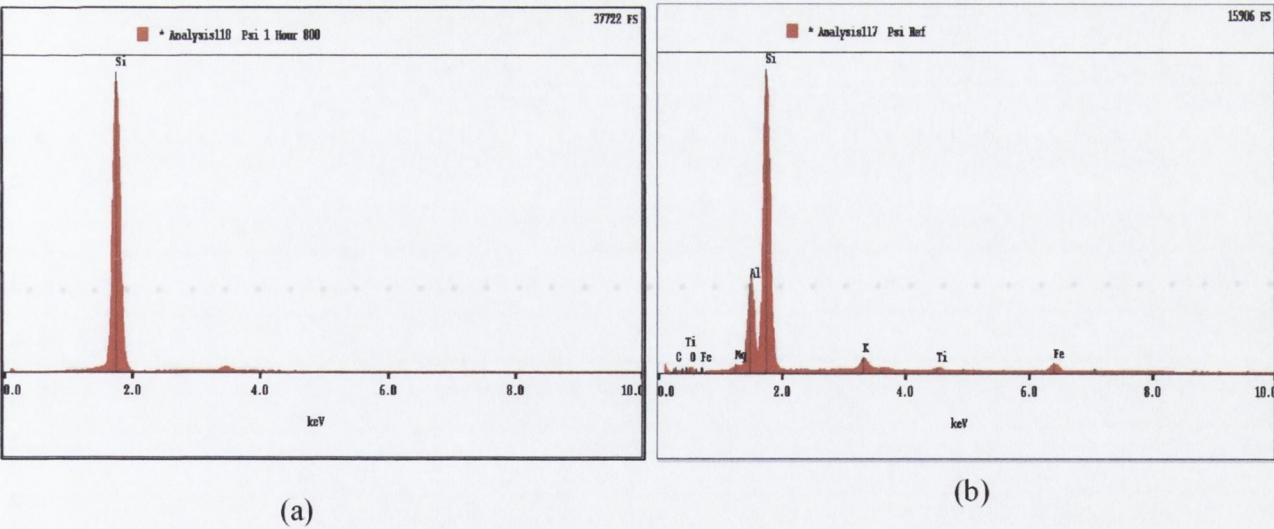


Figure 5.11 EDX analysis carried out on the polished part of the rare-earth doped glass–porous silicon sample (a) and inside the pores of silicon (b).

The PL spectrum of the europium doped aluminosilicate glass-porous silicon composite sintered at 800°C for two hours is presented in figure 5.12. The presence of a number of sharp peaks in the spectrum is caused by the $f-f$ transitions in europium (III). The optical bands centred at 587, 598, 617, 653, 702 nm originating from the electronic transitions between the levels of trivalent europium ion $^5D_0 \rightarrow ^7F_0$, $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$, $^5D_0 \rightarrow ^7F_3$ and $^5D_0 \rightarrow ^7F_4$ respectively. The peaks corresponding to the different wavelength are similar to those reported in the literature.⁸

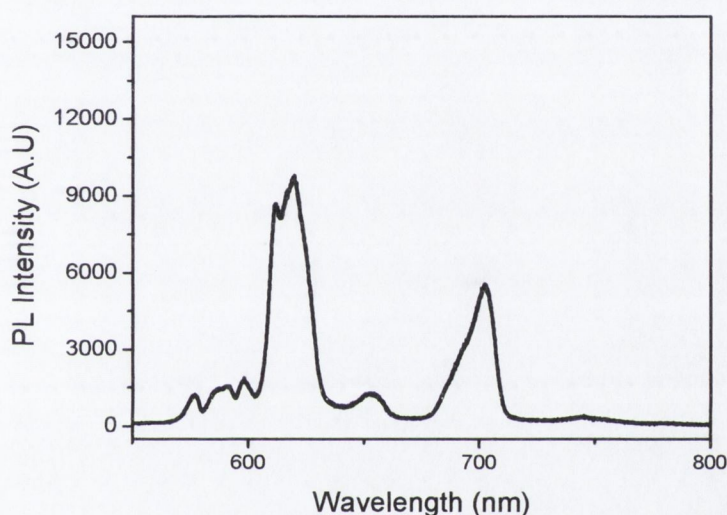


Figure 5.12 PL spectrum of porous silicon-europium doped aluminosilicate glass composite sintered at 800°C for two hours.

It has been reported in Eu^{3+} doped aluminosilicate system that the effect of the Al^{3+} addition assists in dispersing the Eu^{3+} ions in the silica glass as Eu^{3+} ions bonds preferentially with alumina.³⁶ As the glass is densified, in which the strong Si-O bonds are formed due to the progressive enhancement of condensation reactions, Eu^{3+} ions are more embedded in the aluminosilicate network. Thus Eu^{3+} ions should be separated by alumina polyhedra in aluminosilicate glass.

5.2.2 Preparation and characterisation of rare earth doped xerogel-porous silicon composite material by vacuum infiltration method

The rare earths (Er^{3+} and Eu^{3+}) doped aluminosilicate xerogel were introduced to porous silicon according to the scheme shown in figure 5.13. The incorporation of xerogel inside the porous silicon membrane was performed under the vacuum. In brief, the rare earth doped aluminosilicate sol is introduced onto porous silicon samples before the gelation point and vacuum is applied such a way that the “sol” will infiltrate to the pores of silicon. Most of the methods reported to date for the preparation and modification of optical fibres are based on fibre drawing and CVD methods.³⁷ Here we report the preparation of rare earth doped aluminosilicate xerogel/glass fibre using porous silicon and microchannel glass templates. To the best of our knowledge the method used here for infiltration is reported for first time.

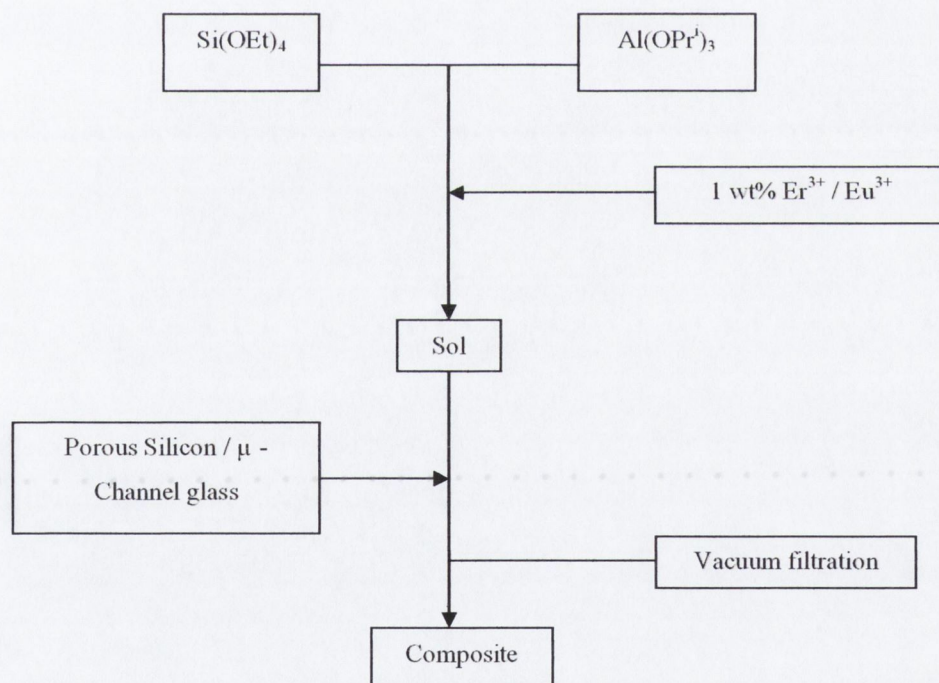


Figure 5.13 Schematic representation of the preparation of PS / μ -channel glass-rare earth doped xerogel composite.

The incorporation of xerogel inside the porous silicon matrix by vacuum method leads to fascinating results. The cross-section of the xerogel-porous silicon composite was examined under optical microscope and is presented in figure 5.14.

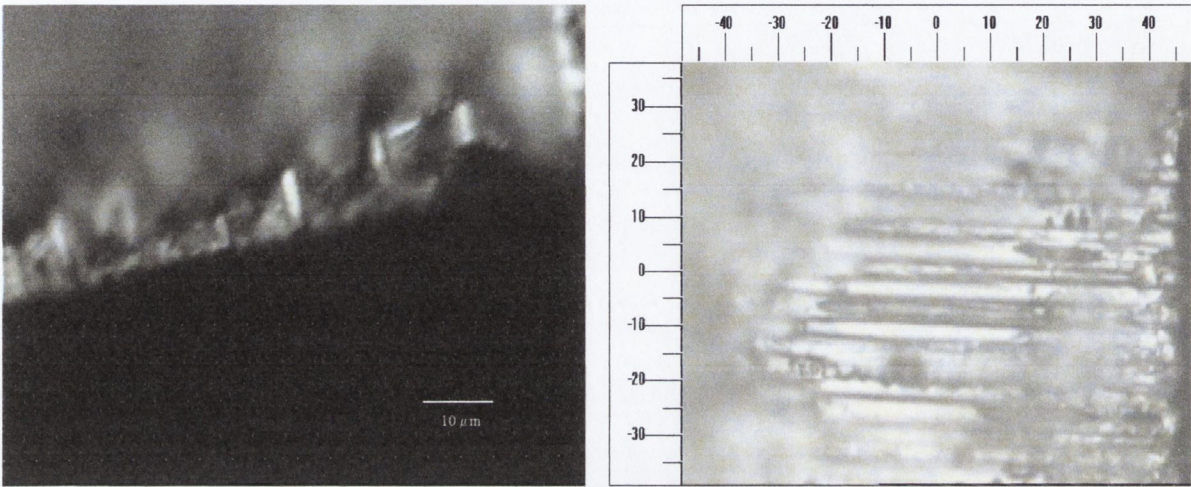


Figure 5.14 Optical images of rare earth doped xerogel-porous silicon composite with 50X objective.

The optical image showed formation of fibres inside the porous silicon matrix. This was further confirmed by SEM (figure 5.15).

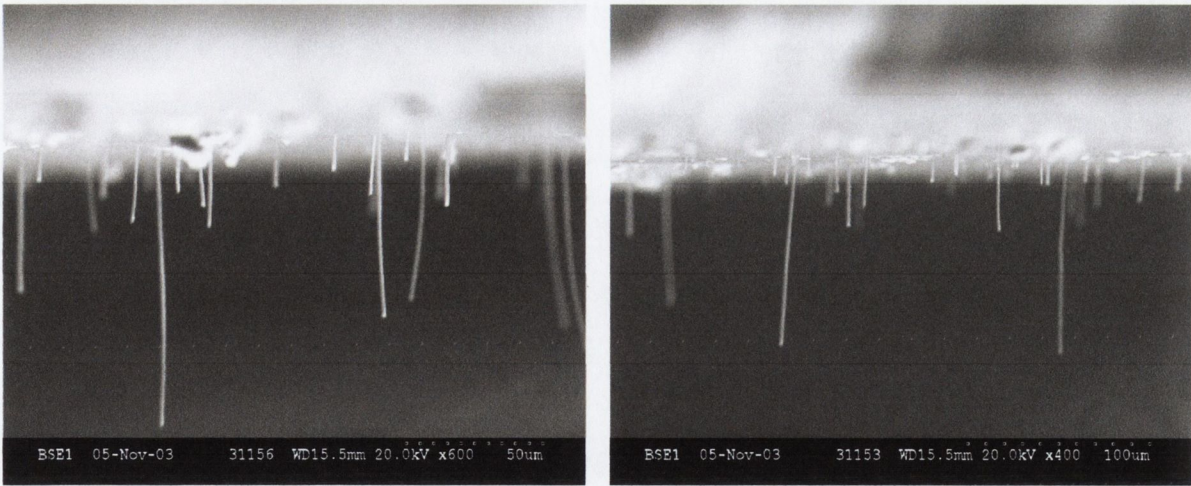


Figure 5.15 SEM images of aluminosilicate xerogel-porous silicon composite.

The SEM images revealed xerogel fibres, which are formed on the surface of porous silicon samples. The fibres were pulled through the porous silicon membrane under vacuum. The fibres have an approximate length of 100 μm and a diameter of 2-3 μm .

The luminescence studies on the fibres are presented in figure 5.16. The excitation wavelength used was 633 nm. The studies revealed the broad band emission between 600 and 800 nm. The sharp peaks occurred in the spectrum are most likely due to the Raman modes. The broad band luminescence is caused by the presence of organic species³⁴ inside the sol-gel matrix.

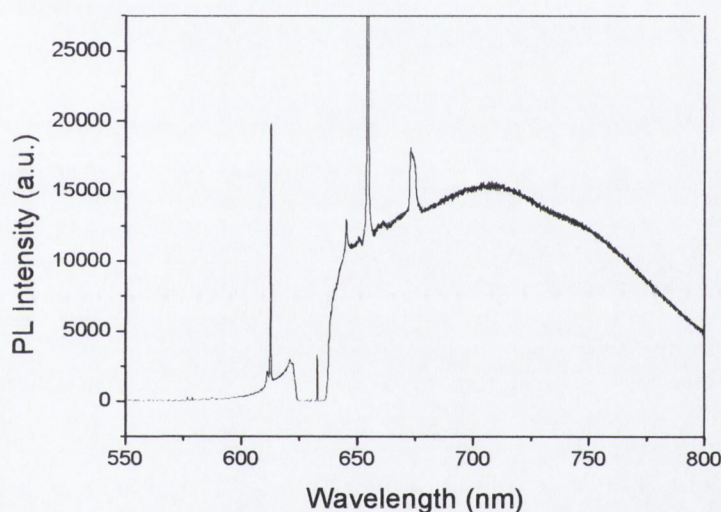


Figure 5.16 PL spectrum of aluminosilicate xerogel fibres.

The same experimental procedure as explained above has been applied on porous silicon membrane samples of different pore morphology. The samples were annealed at 500°C for 2 hours and the SEM images are presented in figure 5.17. The plan view SEM image (figure 5.17a) shows the encapsulation of the gel inside the porous silicon matrix and the cross-sectional SEM image (figure 5.17b) shows the presence of aluminosilicate fibres inside the porous matrix. The SEM image revealed the porous silicon samples containing aluminosilicate fibres of different star-like morphology.

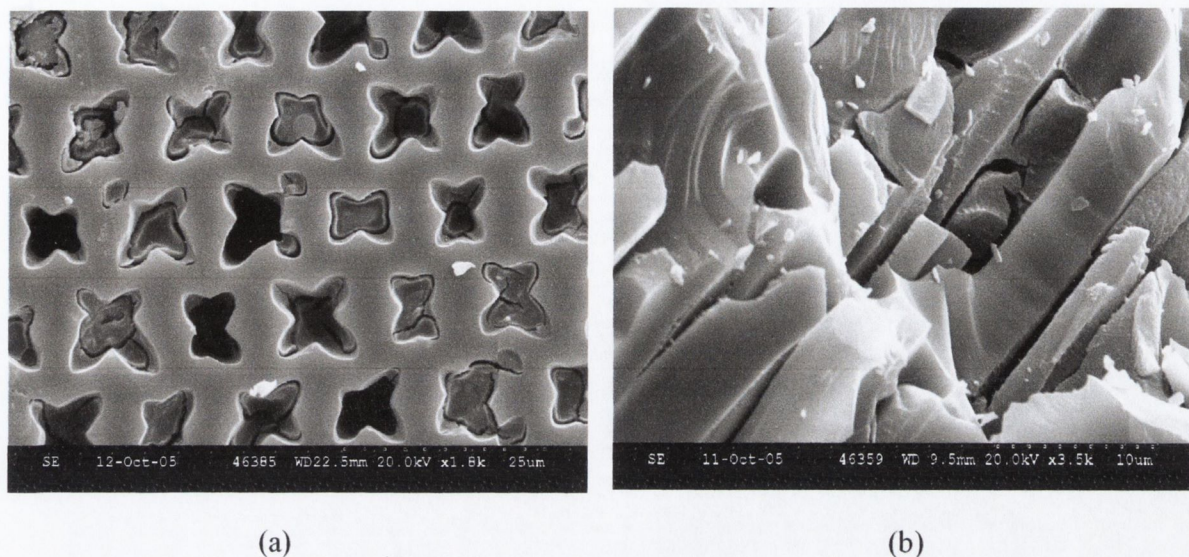


Figure 5.17 SEM images of aluminosilicate glass-porous silicon composite annealed at 500°C for 2hrs. (a) Plan view of the sample (b) Cross-sectional image.

5.2.3 Preparation and characterisation of rare earth doped xerogel-microchannel glass composite material by vacuum filtration method

The rare earth (Eu^{3+}) doped aluminosilicate xerogel was introduced to micro-channel glass matrix according to the scheme shown in figure 5.13. In brief, the aluminosilicate sol was prepared using TEOS and aluminium isopropoxide as starting materials. The alkoxide was hydrolysed using ethanol-water-acid mixture in the molar ratio 1: 1: 2.7×10^{-3} per mole of $\text{Si}(\text{OC}_2\text{H}_5)_4$ for an hour. Aluminium isopropoxide, $\text{Al}(\text{i-OC}_3\text{H}_7)_3$, was added to this solution followed by stirring for 15 min at 70°C. After cooling at RT, europium salts were added and stirred for an hour. The final hydrolysis was done by adding ethanol-water-acid in the molar ratio 4: 1: 1.1×10^{-2} per mole of $\text{Si}(\text{OC}_2\text{H}_5)_4$. For the preparation of Eu^{3+} doped aluminosilicate sol, europium isopropoxide/chloride precursors were used.

The incorporation of gel inside the glass matrix was performed under the vacuum (figure 5.18). Then the micro-channel glass samples have been heated at 500°C for 2 hours. Heating above 500°C will results in the deformation of microchannel glass, which is not suitable for our experiment. After that, the samples were cross-sectionally cut into pieces. It

was expected to form the microfibrils, similarly as it was observed in the porous silicon-glass composites before.

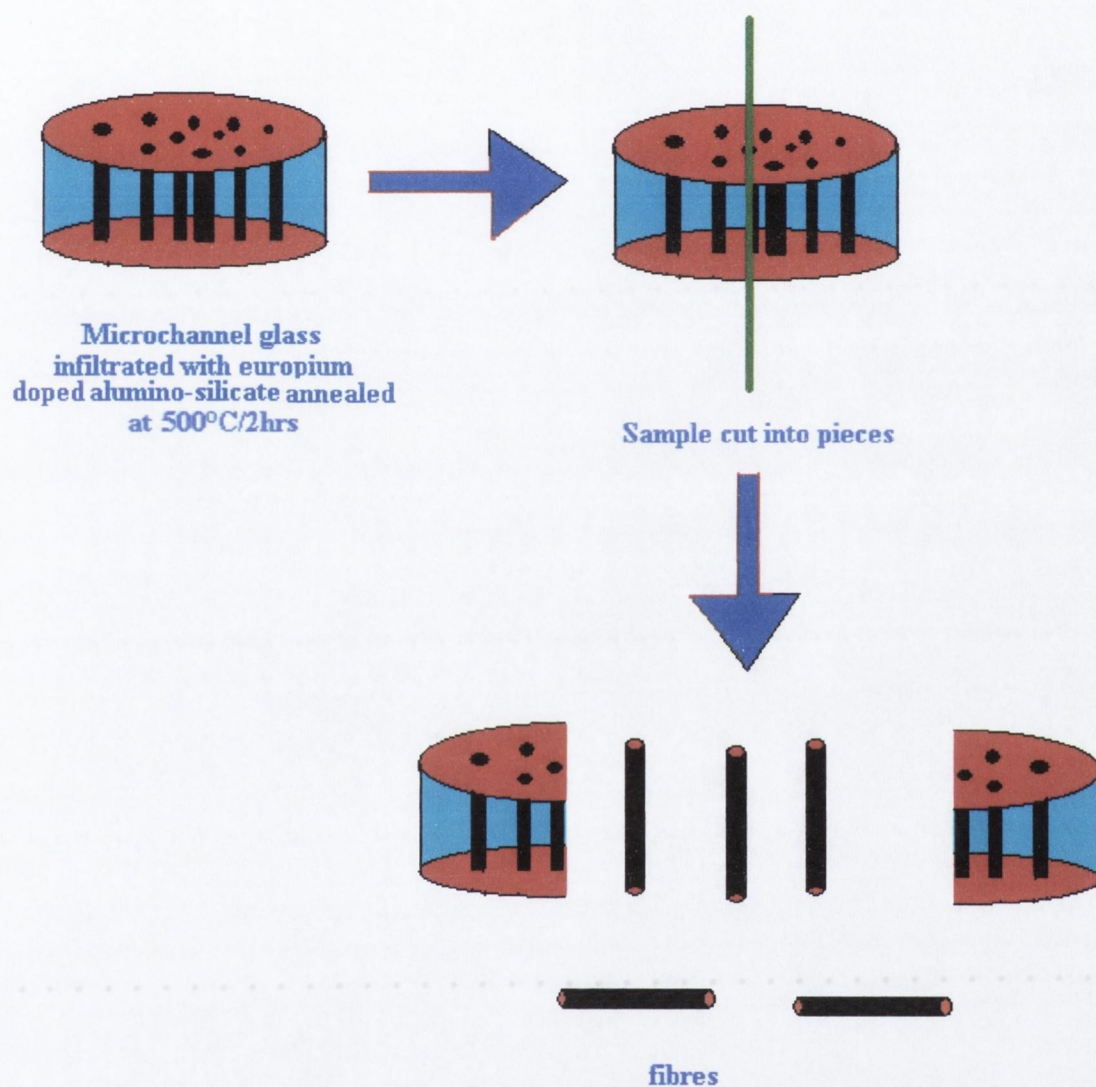


Figure 5.18 A sequential schematic diagram showing the aluminosilicate fibres drawn out from the microchannel glass matrix.

The rare earth doped aluminosilicate fibres, which were isolated from the microchannel glass matrix were examined using the optical microscope (figure 5.19). The individual fibres have been found to have different lengths of microns and the diameter around 8 μm .

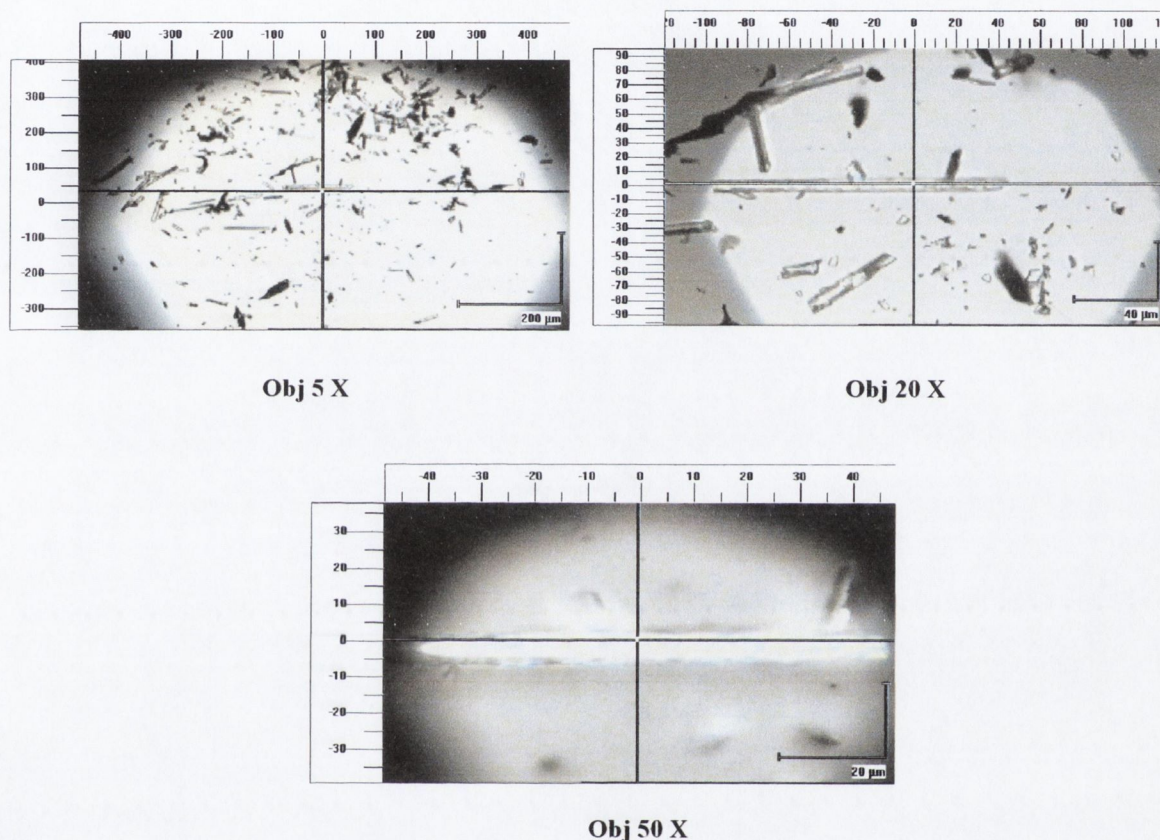


Figure 5.19 Optical microscopy images of individual fibres isolated from the microchannel glass matrix at different objectives.

Then the microchannel glass-rare earth doped aluminosilicate xerogel composites were studied by SEM. The pores of the micro-channel glass were uniformly filled by the xerogel as can be seen from the SEM images (figure 5.20 a & b). The enlarged image of the filled pores (figure 5.20b) shows xerogel microtubes inside the pores. Some reduction in size of these xerogel fibres can be attributed to the drying effects, as it is well known that xerogel shrinks in size upon drying.³⁹

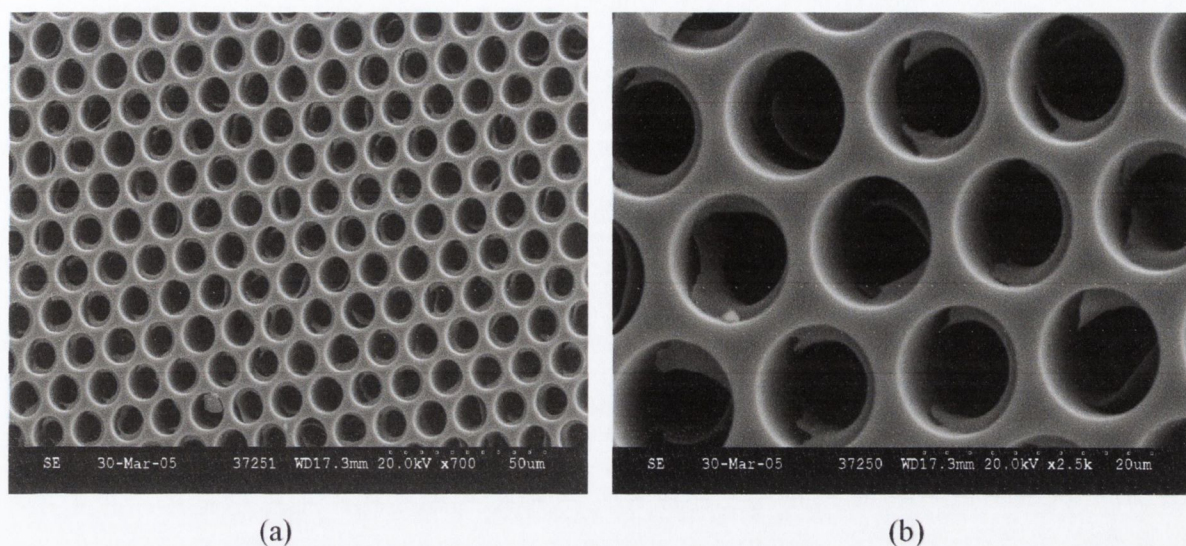


Figure 5.20 (a) and (b) SEM images of rare earth doped xerogel-micro channel glass composite (before thermal treatment).

The rare earth doped xerogel-microchannel glass composite were heated at 500°C holding the sample at the same temperature for two hours. The SEM images of the annealed samples are presented in figure 5.21 a & b.

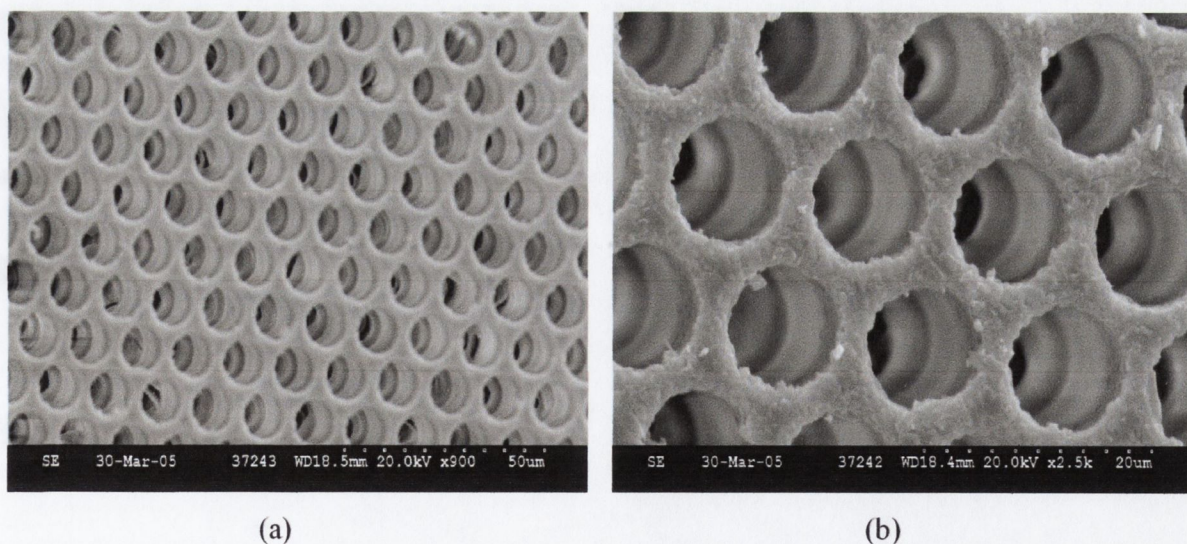


Figure 5.21 (a) and (b) SEM images of μ-channel glass-rare earth doped glass composite after heat treatment at 500°C for 2 hours.

The SEM images revealed the further shrinkage of the xerogel fibres at higher temperatures. An EDX analyses of the rare earth doped aluminosilicate xerogel and the glass inside the micro-channel glass matrix showed the presence of both silicon and aluminium. The SEM images of the rare earth doped xerogel fibres are presented in figure 5.22. The SEM images showed an individual fibre drawn outside the microchannel glass matrix. The images confirmed the cylindrical nature of the fibre inside the pore. The individual fibre has a length of more than 200 μm and a diameter of 6-7 μm , which is consistent with the optical images and also with the diameter of the microchannel glass (8-9 μm). The rest of the fibres were broken or damaged during the preparation. The fibre presented in the SEM image showed uniform and smooth walls. Thus by using this method of preparation, it is possible to fabricate fibres of length more than 200 μm .

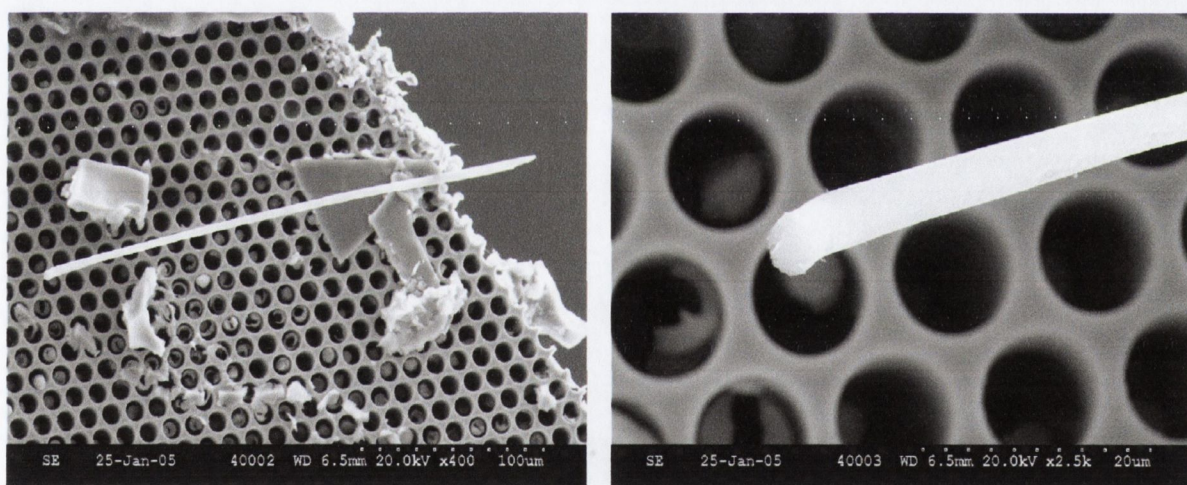


Figure 5.22 SEM images of microchannel glass–rare earth doped xerogel composite fibre before heat treatment.

The heat treated (500°C for 2 hours) rare earth doped gel–micro-channel glass composite samples were characterised by SEM measurements on a cross-section and the images are presented in figure 5.23. The images clearly show the tubular hollow nature of the rare earth doped alumino-silicate glass samples. Further, the annealed microchannel glass

samples were subjected to a small cut (as shown in schematic diagram, figure 5.18) with an intention to get free standing fibres. As expected the result of which was the freestanding aluminosilicate fibres of good aspect ratio. The SEM images of the freestanding aluminosilicate fibres are presented in figure 5.24.

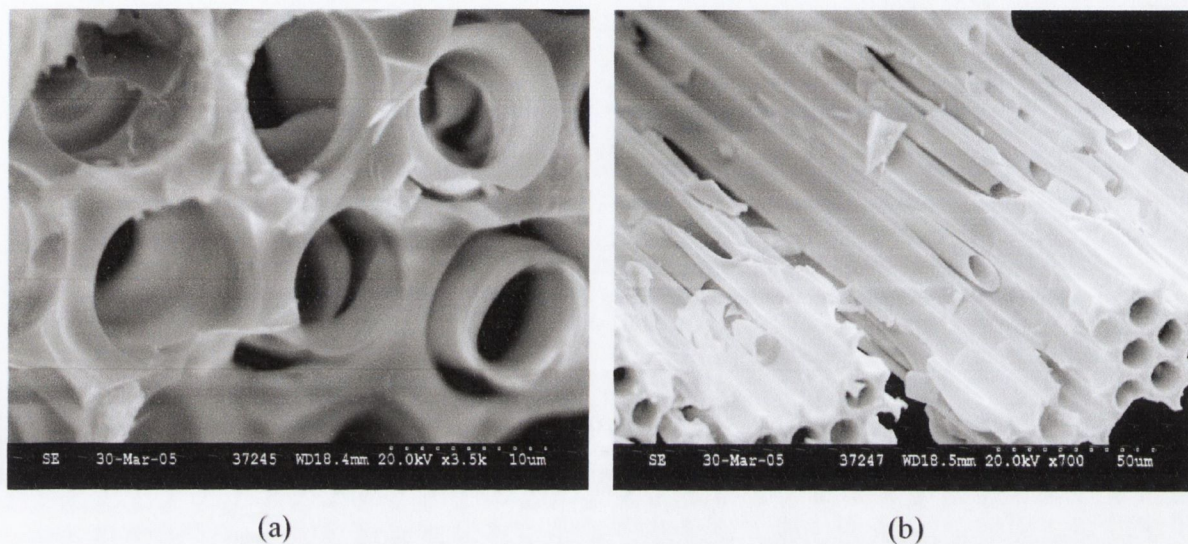


Figure 5.23 SEM images of μ -channel glass-rare earth doped glass composite fibre (after heat treatment at 500°C/2hrs). (a) & (b) Cross-sectional images.

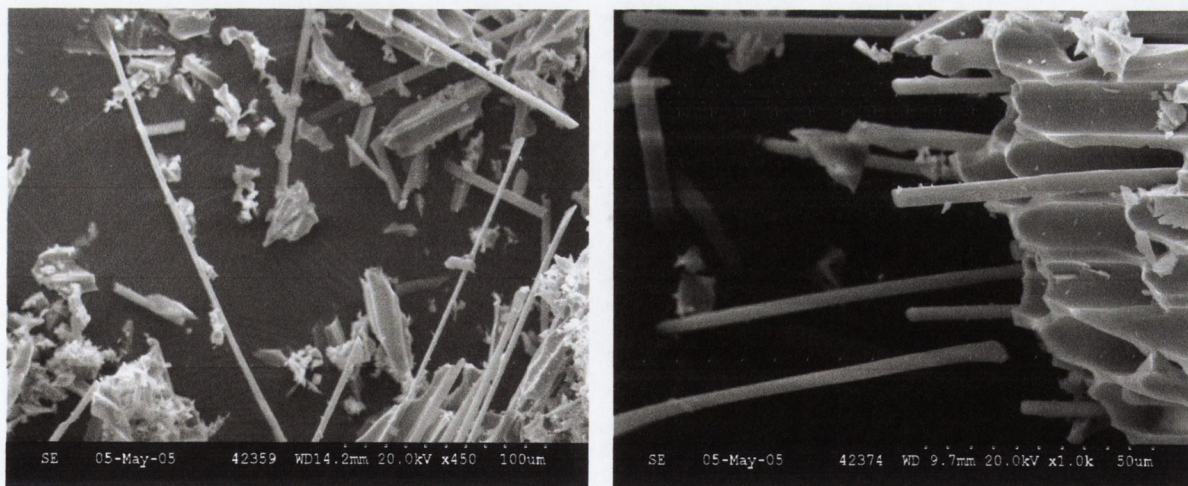


Figure 5.24 SEM images of freestanding aluminosilicate fibres outside the matrix.

5.2.3.1 PL measurements on the microchannel-xerogel composite

The luminescence studies were carried out in the microchannel-xerogel composites using PL spectroscopy and fluorescent confocal microscopy (MicroTime 200 confocal microscope). Figure 5.25 shows the PL spectrum of xerogel inside the pores from freshly prepared sample. The excitation wavelength of 633 nm was used in this PL measurement. There is a presence of a very broad intensive band between 500 and 800 nm containing more narrow peaks centred at 595, 618, 653, 700 nm originating from the electronic transitions between the levels of trivalent europium ion $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$, $^5D_0 \rightarrow ^7F_3$ and $^5D_0 \rightarrow ^7F_4$ respectively.⁸

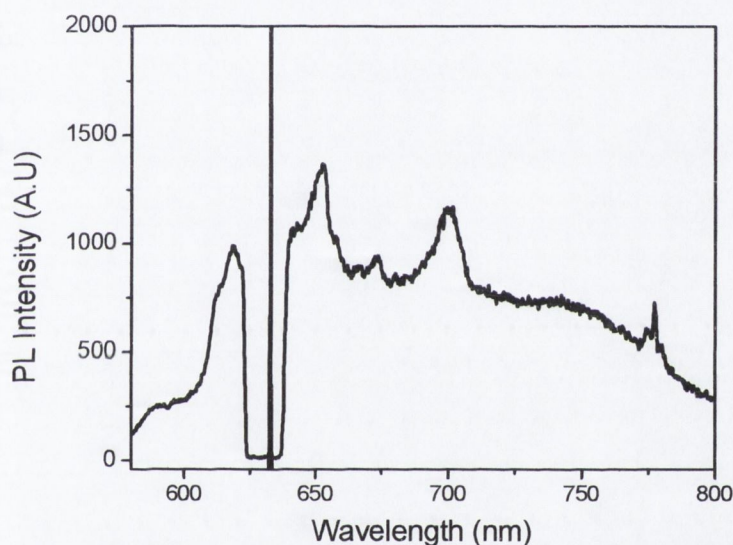


Figure 5.25 Room temperature PL spectra of europium containing aluminosilicate xerogel inside the pores of μ -channel glass.

5.2.3.2 PL measurements on an individual fibre isolated from the microchannel glass matrix

The aluminosilicate-microchannel glass prepared by vacuum filtration technique was subjected to annealing at 500°C for 2 hours as explained before. The composites were cut and individual fibres were isolated as showed previously in the schematic diagram (figure 5.18). The individual fibres isolated from the microchannel glass matrix and were investigated by PL spectroscopy.

The PL spectrum of the bulk aluminosilicate gel sample, which was heat treated at 500°C for 2 hours, is presented in figure 5.26. The emission spectra of the bulk aluminosilicate sample heated at 500°C for 2 hours showed a broad luminescence ranging between 520 and 800 nm.

There is no rare earth luminescence peaks have been detected. In this case rare earth luminescence is covered up by more strong and broad luminescence bands of organic species trapped inside the xerogel matrix. The thermal decomposition of organic in xerogel results in a substitution of Si atoms with carbon giving strongly luminescent species. A similar type of observation for xerogels was reported before by M. J. Sailor *et al.*³⁴ The aluminosilicate gel was prepared under the same conditions as that for the microtube formation. The aluminosilicate gel was then heated at 500°C for 2 hours. The elemental analysis of the annealed gel showed the carbon and hydrogen content of 0.32% and of 0.56% respectively.

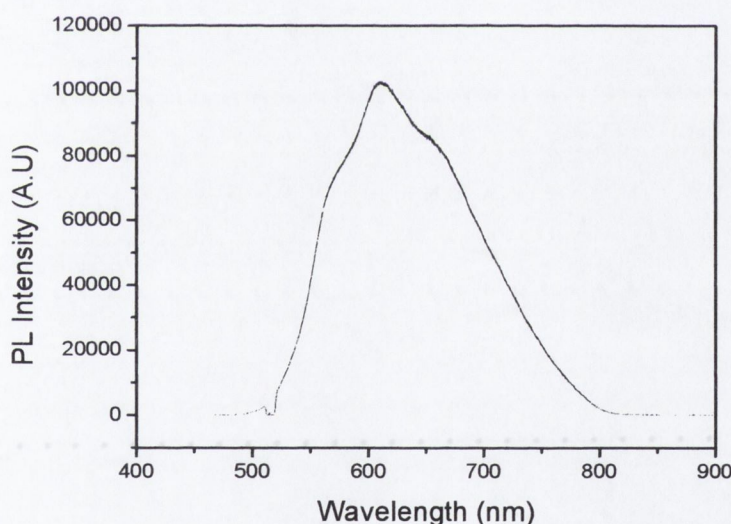


Figure 5.26 PL measurement on the bulk aluminosilicate gel sample heat treated at 500°C/2hrs.

The PL measurements were done on the individual fibre is shown in the optical images (figure 5.27). The optical images are numbered in the order of the distance from middle of fibre where the PL measurements were carried out. For example, fbr2_1 is taken as the middle of the fibre and fbr2_2, fbr2_3 *etc.*, in the order of distance away from fbr2_1.

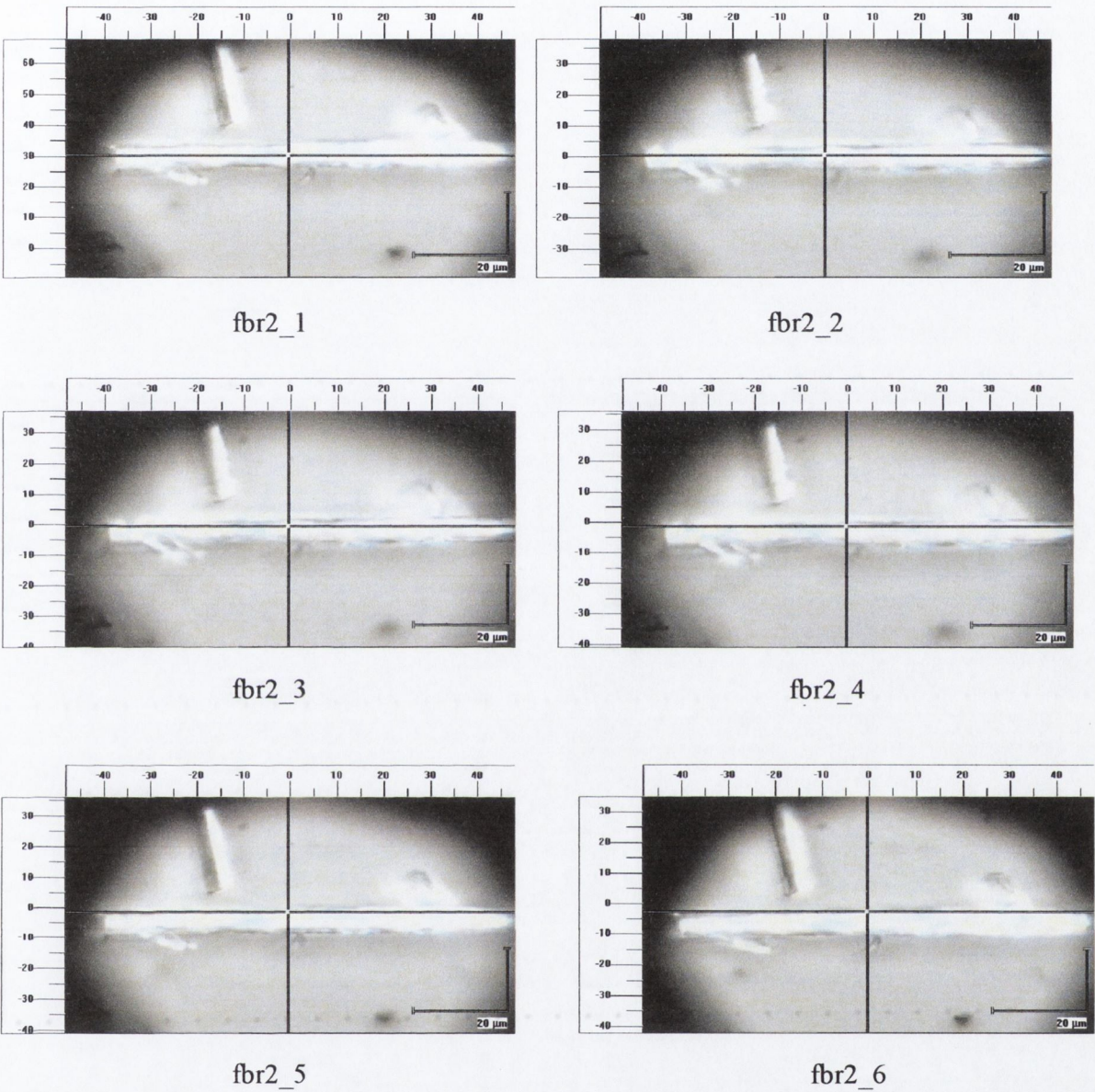


Figure 5.27 Optical microscopy images of aluminosilicate fibre on which room temperature PL measurements were done.

The PL spectra of the fibre shown in optical images (figure 5.27) are presented in figure 5.28. The PL measurements demonstrated the whispering gallery mode (WGM) resonances

in the microtubes. Whispering-gallery modes are electromagnetic waves that travel many times in a dielectric microcavities with circular symmetry (spherical, disk and ring-shaped) due to continuous total internal reflections at the curved boundary of surface.⁴⁰

When the microtube is embedded inside a matrix, the spectral distribution of emission and the individual transition probabilities are almost independent of spatial location due to low refractive index contrast between microtube and matrix. Contrastingly, when separated from the matrix, microtube is much more optically dense than its surrounding medium, providing that light in the microcavity can be internally reflected. In this way, light propagating inside the microtube would then be spatially constrained to travel along the rim of a cross section of the tube, and therefore it is said to be trapped in a WGM. An immediate result of this optical confinement is the presence of emission peaks in luminescence spectrum from single microtube as illustrated in figure 5.28. These peaks correspond to optical resonance locations (or WGM) and reflect the fact that transition probabilities are increased for emission wavelength near resonance and decreased for wavelength that do not satisfy resonance conditions.

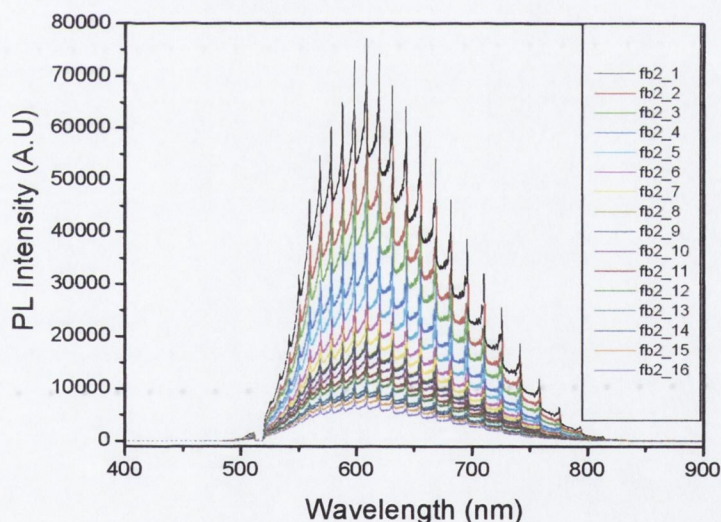


Figure 5.28 PL measurement on the aluminosilicate microtube showing whispering gallery mode phenomenon. (laser power 3 mW)

The PL measurement was extended on the fibre for different laser power (figure 5.29). The spectrum shows an increase in the luminescence with an increase of laser power. With higher laser power the luminescence gets saturated.

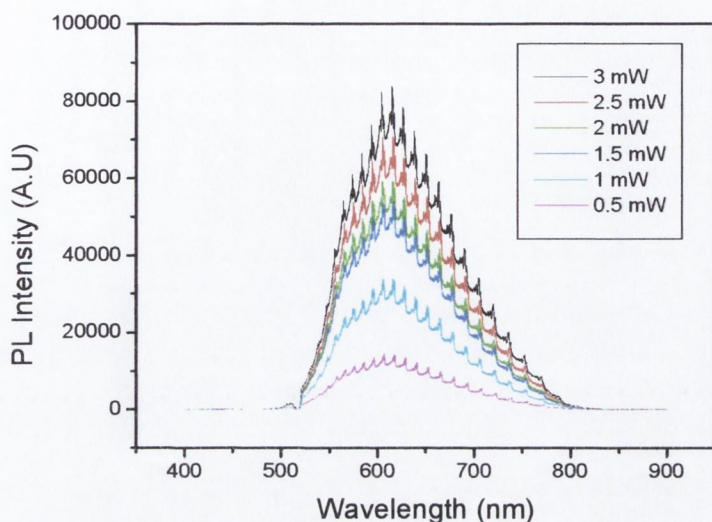


Figure 5.29 PL measurement on the aluminosilicate microtube using different laser powers.

Polarisation measurements were carried out on the middle and edges of the individual fibre. Figure 5.30 shows the PL spectra and the optical images (objective 50X) of the position on the microtube where measurements were done.. The half-wave plate ($\lambda/2$) is used for polarisation switching or circular polarisation. Polarization-resolved micro-photoluminescence spectroscopy can distinguish between transverse electric (TE) and transverse magnetic (TM) polarized modes, i.e., it can be used to determine the state of polarization of a detected resonance line.

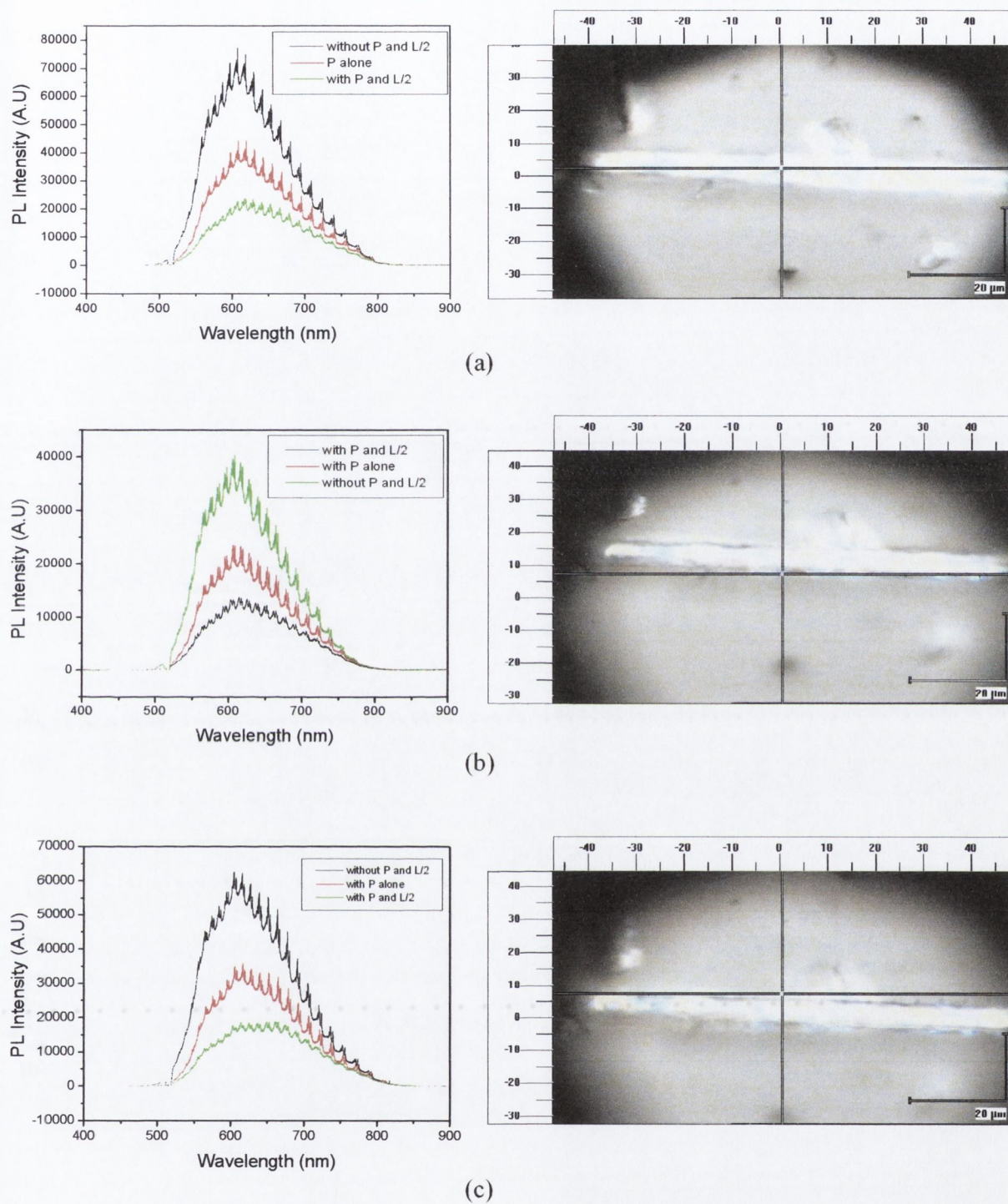


Figure 5.30 Polarisation measurement on the aluminosilicate microtube. The P and L/2 in the inset of the graph stand for polarisation and half-wave plate ($\text{Lamda}/2$) respectively.

The PL measurements on the edge and middle of the microtube doesn't show any difference in the spectra. Polarisation measurements were also done by rotating the microtube at an angle of 45° , which is presented in figure 5.31. The PL spectra showed an increase in intensity on the individual fibre which was done with out polarisation. It can also be seen that the spectral shapes show a difference when compared to figure 5.30 where the measurements were perpendicular to the axis.

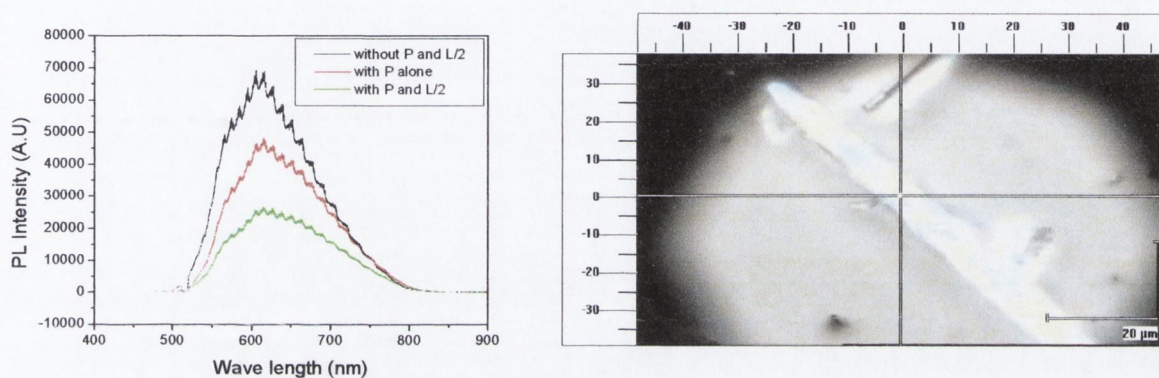


Figure 5.31 Polarisation measurement on the aluminosilicate microtube at an angle of 45° . The P and L/2 in the inset of the graph stand for polarisation and half-wave plate (Lamda/2) respectively.

The experiments were performed on the fibre with different laser power but by using the power filter. A power filter is used to reduce the laser power falling on the sample or in other words to reduce the energy of the pump. The 1% filter was used in the measurement. The PL spectra showed an increase in intensity with laser power. Table 5.1 shows the laser powers used for the experiment. The corresponding spectra are shown in figure 5.32.

Table 5.1 Laser power used for the PL measurement on microtube.

Code	Power (mW)	Code	Power(mW)
t1	20.0	t11	10
t2	19	t12	9
t3	18	t13	8
t4	17	t14	7
t5	16	t15	6
t6	15	t16	5
t7	14	t17	4
t8	13	t18	3
t9	12	t19	2
t10	11	t20	1.5

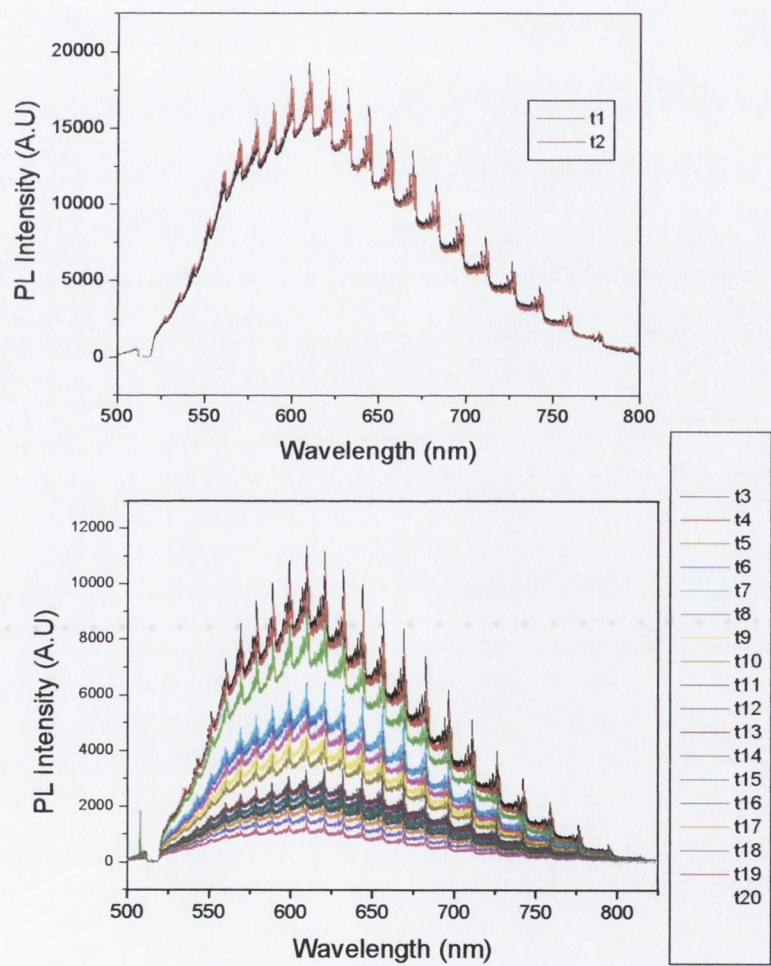


Figure 5.32 PL measurements of aluminosilicate microtube using different laser power and by using 1% power filter.

The confocal microscopy images of the aluminosilicate microtubes annealed at $500^{\circ}\text{C}/2\text{hours}$ and isolated from the microchannel glass was presented in figure 5.33. The images show luminescent centres on the microtube. The distribution of luminescent centres is uniform through out the microtube. In this case every pixel in the lifetime image gives the lifetime at particular position in space (x,y). The lifetime image of the array of aluminosilicate microtubes in a micro-porous glass matrix (figure 5.33a) clearly demonstrates distribution of emitting species over microtube crosssection. Fluorescence lifetime image of an isolated aluminosilicate microtube is presented in figure 5.34

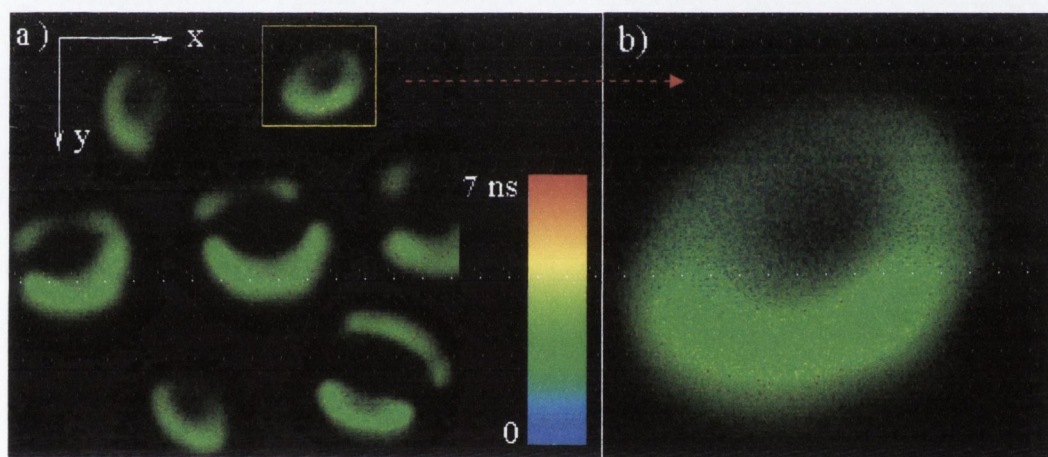


Figure 5.33 Fluorescence lifetime image of aluminosilicate microtubes in a micro-porous glass matrix (a) The image was collected at 250×250 pixel resolution with 4096 time channels; 2 ms acquisition time per pixel and total recording time 6.63 min. Image size: $29.90 \mu\text{m} \times 29.90 \mu\text{m}$. Panel (b) shows enlarged image one of *single* aluminosilicate microtubes in a glass matrix (indicated by frame in panel (a)). In this case the image was collected at the same pixel resolution and recording time, with image size $7.30 \mu\text{m} \times 7.30 \mu\text{m}$. Panels

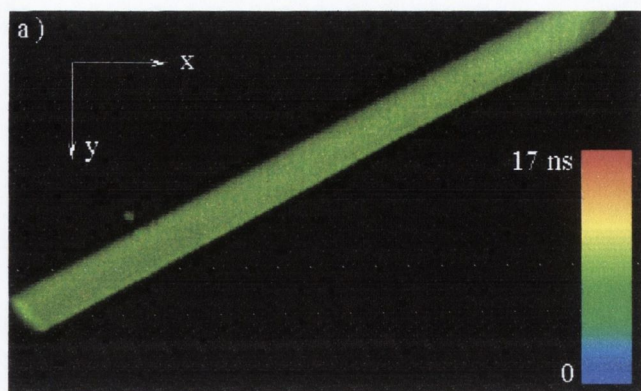


Figure 5.34 Fluorescence lifetime image of an isolated aluminosilicate xerogel microtube. The image was collected at 416×250 pixel resolution with 4096 time channels; 2 ms acquisition time was provided per pixel and total recording time was 9.6 min. Image size: $67.72 \mu\text{m} \times 40.70 \mu\text{m}$.

The life time studies of the microtubes is presented figure 5.35. Decays were measured to 6000-8000 counts in the peak and reconvoluted using non-linear least squares analysis (FluoFit, PicoQuant), using an equation of the form: $I(t) \propto \sum_i \alpha_i \exp(-t / \tau_i)$, where τ_i are the PL decay times. The pre-exponential factors α_i , were taken into account by normalisation of the initial point in the decay to unity. The quality of fit was judged in terms of a χ^2 value (with a criteria of less than 1.1 for an acceptable fit) and weighted residuals. The τ_i and α_i parameters were used then to calculate the average lifetime, τ_{av} :

$$\tau_{av} = \frac{\sum \alpha_i \tau_i^2}{\sum \alpha_i \tau_i}$$

The PL of a single aluminosilicate microtube shows distinct multi-exponential decay. Sum of at least three-exponential functions is required to achieve satisfactory fit to the decay data (figure 5.35a) yielding reasonable plot of weighted residuals (figure 5.35b), χ^2 value 1.1 with corresponding lifetimes in the nanosecond time scale (Table 5.2). Observed multi-exponential decay kinetics is consistent with a PL model that includes multiple emission pathways and is indicative of broad lifetime distribution caused by corresponding distribution of defect or trap states.

The studies showed that the fibres have a PL lifetime averaging 6 to 7 ns. The short life time of the luminescence is due to the presence of C substituted defect centres as described above.³⁴

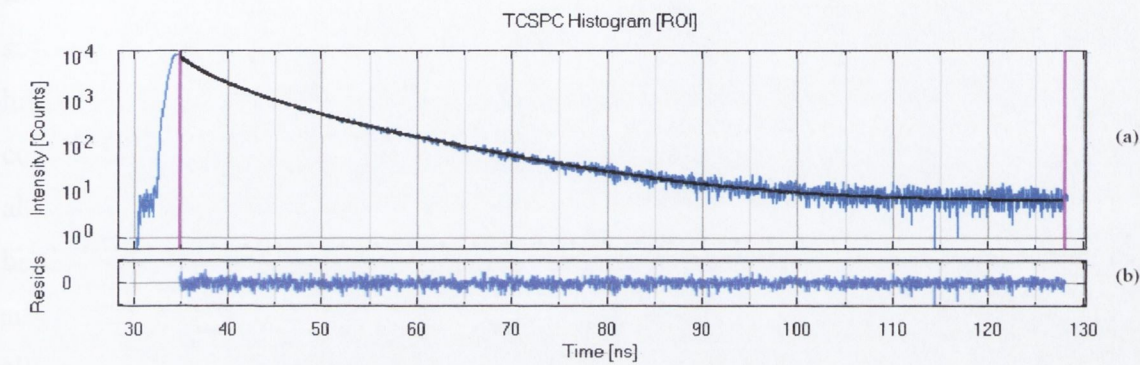


Figure 5.35 Time-dependent PL intensity decay of aluminosilicate microtubes accommodated in microchannel matrix and annealed at 500°C for 2hours. (a) Results of three-exponential analysis of decay curves with corresponding residuals (b).

Table 5.2 Multiexponential fit parameters to the observed PL of single aluminosilicate microtube. α_i is a pre-exponential factor and τ_i is the PL decay time in nanoseconds.

τ_1 (ns)	α_1	τ_2 (ns)	α_2	τ_3 (ns)	α_3	τ_{av} (ns)
1.701	0.28	5.391	0.52	11.742	0.20	7.81

5.3 Conclusions

We have demonstrated that rare-earths (erbium and europium) doped aluminosilicate xerogel or glass -porous silicon composites can be effectively prepared using standard sol-gel processing techniques. We have introduced new method of producing xerogel and glass microfibres and microtubes or capillaries using microchannel glass or porous silicon substrates and sol-gel processing techniques. To the best of our knowledge this technology has not been previously reported or patented. The porous silicon-rare doped xerogel composites have been prepared for the first time by the vacuum infiltration of the aluminosilicate sol inside into porous silicon or microchannel glass membranes shortly before the gelation point. This processing resulted in xerogel micro-fibres attached to silicon substrate. Similar vacuum assisted infiltration of gel in microchannel glass matrix allowed us to produce microtubes or microcapillaries, which demonstrated the whispering gallery mode lasing, which has not been reported for microtube structures to date. The luminescent aluminosilicate xerogel microtubes demonstrated the high-Q resonance modes in emission spectra of single microcavity. Our method of preparation of such structures has unique advantages providing high-quality smallest three-dimensional microcavities with strongly polarized emission. Evanescent field associated with cavity modes was found to extend into the surroundings up to a distance comparable to the external radius of microtube. Nonlinear character of pump-power dependence of microtube emission and strong acceleration of emission decay at high excitation power confirm the occurrence of low-threshold amplified spontaneous emission from single microtube. Potentially these microcavities should be useful for a variety of photonic applications such as microcylindrical light emitters in optoelectronics and optical communications and also as various micro-sensing devices.

Thus both porous silicon and microchannel glass act as good matrixes for the preparation of xerogel and glass microfibres, which might have a range of potential applications.

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VI

Functionalisation of Silicon Surfaces with Cyclopentadienyl and Ferrocenyl Groups

6.1 Introduction

Modification of silicon surfaces with organic reagents has been a field of growing interest for the past ten years.¹ Organic monolayers and thin films on silicon surfaces have been intensively studied in an effort to improve and expand existing microelectronics technology. Thin films of semiconducting organic molecules in particular have been a focal point in order to develop electronic devices such as organic thin-film transistors (OTFTs).^{2,3} Molecular modification of semiconductor surfaces has been significantly advanced in recent years by the development of functional group chemistry on hydrogen terminated silicon surfaces.⁴ Thus Si-CH₂R bonded monolayers were been prepared through reactions between an appropriate organic derivative and hydrogen or hydroxyl terminated silicon surface.^{5,6}

There are various reports on the surface modification of silicon either through surface oxide or direct functionalisation of oxide free surfaces.⁶ Surface modification on porous silicon has generated much interest for the stabilization of photoluminescence.^{7,8} The attachment of organic species to the silicon surfaces by formation of Si-C bonds has been shown to provide greater stability towards oxidation.⁹ Si-C bonded layers are extremely robust and can be prepared by reactions with a variety of reagent including alkenyl and alkynyl groups.¹⁰ There has been directed efforts over the past few years towards the formation of silicon-carbon bonds on porous silicon and the majority of the reactions involved in the passivation of silicon surface was through the formation of these Si-C bonds which directly or indirectly involves heat treatment, use of transition metals and high vacuum condition. The disadvantage of heating is that it can destroy the fragile structure of porous silicon. Several other groups have successfully investigated the formation of silicon-carbon bonds on porous silicon at room temperature through one- or two step wet chemical techniques at room temperature.¹¹⁻¹³ For example Linford and Chidsey have shown that single-crystal silicon surfaces can be derivatized with alkyl monolayers by the photolysis of diacyl peroxides at 90-100°C.^{14,15} Similarly, Lewis and co-workers have functionalised silicon with an alkyl layer in a two-step reaction in which the H-terminated silicon surface is first chlorinated with PCl₅ and then treated with a Grignard reagent at 80°C for 30 minutes to 8 days.¹⁶ Chazalviel and co-workers have grafted methyl groups to porous silicon directly using an anodic electrochemical treatment in ether solutions containing either CH₃Li or

CH_3MgCl .¹¹ Finally, Song and Sailor have successfully functionalised porous silicon surfaces with aryl compounds by using aryllithium reagents.¹⁸ In all of the above cases, the Si-C bonded species have been observed to significantly hinder the rate of surface oxidation of porous silicon.

There are also reports on surface modification by forming Si-O-C bonds on the surface and also *in situ* functionalisation of porous silicon surfaces during electrochemical formation process in ethanoic hydrofluoric acid solution.¹⁹ Although there are several publications on organic and metallorganic functionalisation on silicon surfaces, there is only one report on ferrocene functionalised silicon surfaces²⁰ and in this work vinylferrocene and hydrosilylation processes have been used to attach ferrocene functionality *via* alkyl spacer to the porous silicon surface.

6.1.1 Aims of this work

Most of the research on silicon surface functionalisation above is based on organic chemistry approaches. The main objective of this part of our work is to develop new organometallic methods for silicon surface functionalisation. This involves preparation and characterisation of new ferrocene and cyclopentadienyl functionalised macro- and micro-porous silicon surfaces, where ferrocene or cyclopentadienyl- fragments are bonded to the PS surface either directly *via* cyclopentadienyl rings or *via* propylsiloxy- spacers. We believe that organometallic approaches to functionalise silicon surfaces allow us to develop new porous silicon materials with possible applications for chemo- and bio-sensors, and opto-electronics. Chemical surface functionalisation can tune and stabilise properties of porous silicon that is absolutely essential for sensor and electronics applications. Therefore it is very important to develop new efficient methods for chemical modification of porous silicon surfaces and to find a treatment preventing the long-term instability, while maintaining the large specific surface area and improving simultaneously its sensitivity and selectivity. In addition, the attachment of cyclopentadienyl groups to the surface of PS *via* spacers and without spacers is new strategy, which can be used for the preparation of metallocene functionalised silicon surfaces with possible applications in molecular electronics.²¹ The main characterisation methods used in this work for new functionalised

silicon materials are FTIR and photoluminescence (PL) spectroscopy. In addition we used XPS for flat silicon and SIMS for porous silicon characterisation.

6.2 Results and Discussion

6.2.1 Functionalisation of porous / flat silicon surfaces with ferrocene moieties

In this work, the functionalisation was performed on both meso- and macro- porous silicon surfaces. The mesoporous silicon was prepared using a standard procedure of anodic etching of *p*-type Si(100) wafer with 1:1 48wt% HF(aqueous)/EtOH in a Teflon cell. The macroporous silicon samples were prepared by electrochemical etching in 4% HF in DMF with silicon sample of resistivity 10 Ω cm. SEM images of some of the macroporous silicon samples used for the present studies are presented in figure 6.1. The pore diameters are in the range 0.5 – 5 μ m. The SEM images show both a patterned sample (figure 6.1a) as well as a non-patterned sample (figure 6.1b).

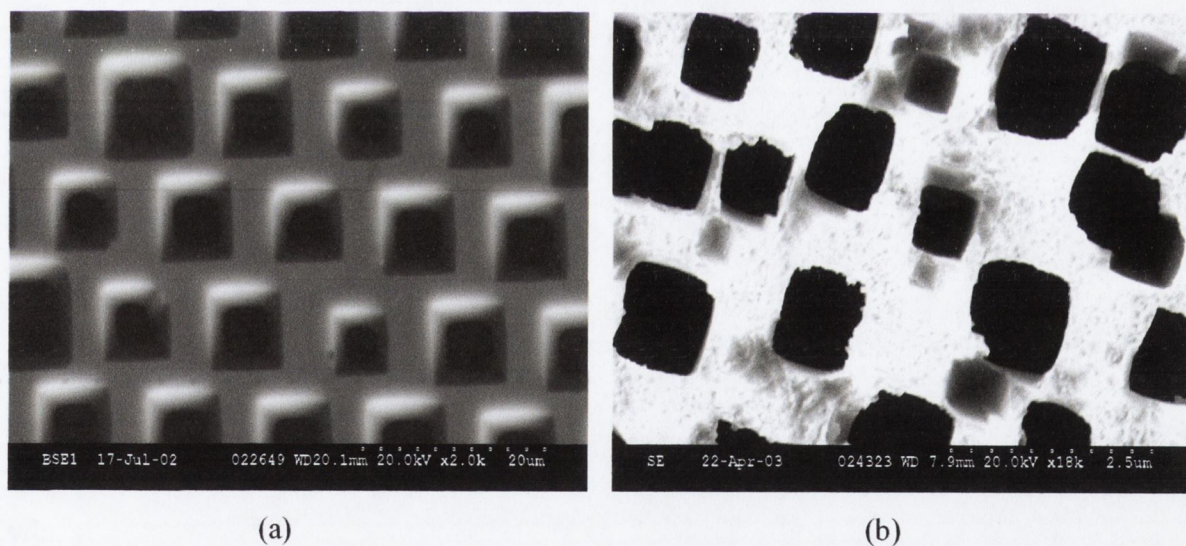
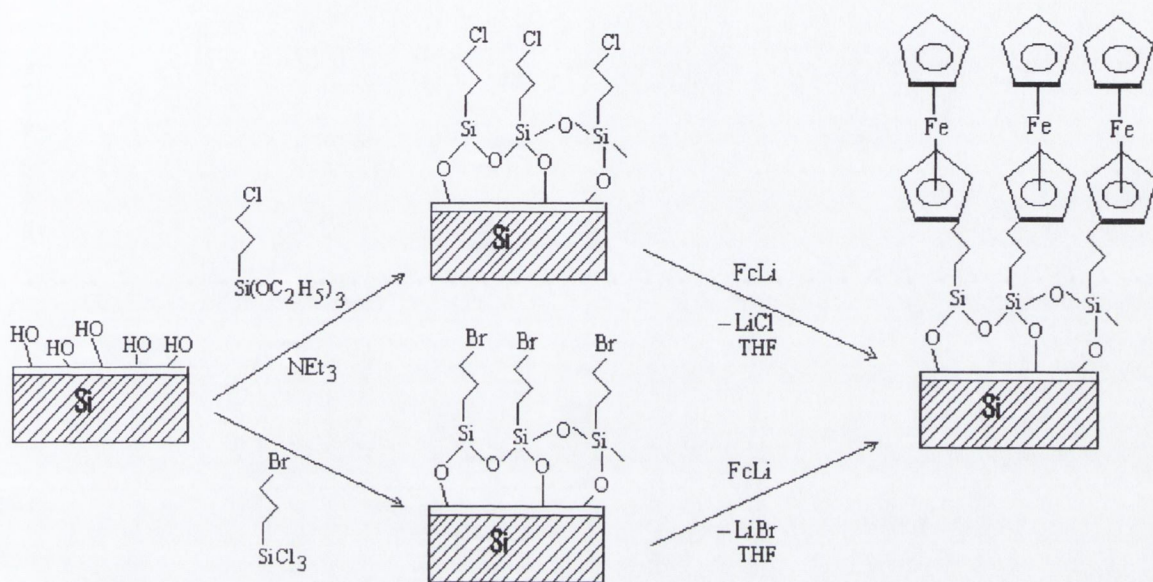


Figure 6.1 SEM images of macroporous silicon samples with different pore diameters used for functionalisation. (a) patterned sample. (b) non-patterned sample.

The ferrocene groups were attached to the Si surface either *via* organic (3-halogenopropyl) siloxy spacer or directly *via* cyclopentadienyl-rings of ferrocene. The samples containing spacers were prepared according to scheme 6.1.



Scheme 6.1 Bonding of ferrocene to the porous silicon surface through (3-halogenopropyl) siloxy-spacer.

A clean hydroxylated PS surface was first treated with (3-chloropropyl) triethoxysilane in the presence of catalytic amounts of NEt_3 to introduce the chloroalkyl functionality on the porous silicon surface. The process was monitored by FTIR spectroscopy (figure 6.2), which clearly showed the presence of Si-O-Si bands in the range of $1000\text{--}1100\text{ cm}^{-1}$, CH_2 vibrations at 2934 , 2848 and 1263 cm^{-1} . A similar approach was used to introduce a bromopropyl ($-\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$) functionality, by treatment of the hydroxylated silicon surface with the (3-bromopropyl) trichlorosilane. FTIR spectra of the bromoalkylated surface show the same bands corresponding to the Si-O-Si stretch in the range of $1000\text{--}1100\text{ cm}^{-1}$, CH_2 vibrations at 2934 , 2848 and 1263 cm^{-1} and $\text{CH}_2\text{-Br}$ stretch at 1240 and 1300 cm^{-1} .

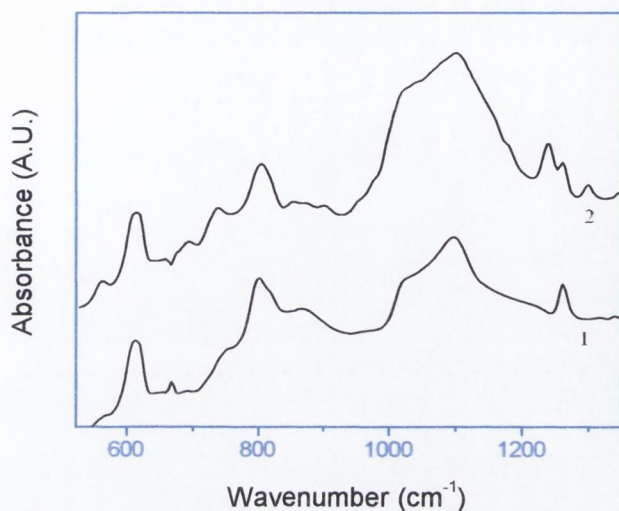
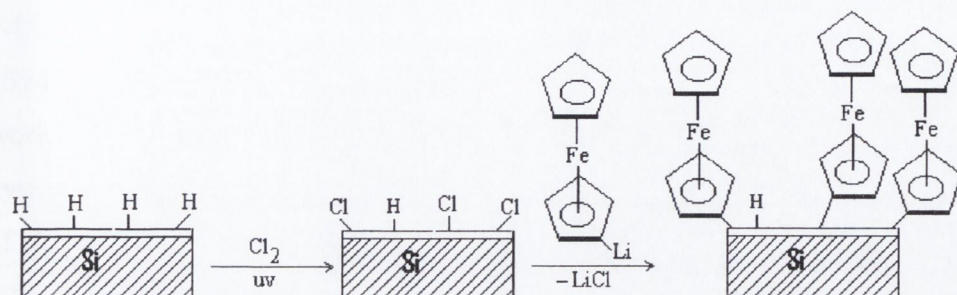


Figure 6.2 FTIR spectra of $(\text{OC}_2\text{H}_5)_3\text{Si}(\text{CH}_2)_3\text{Cl}$ (**1**) and $\text{Cl}_3\text{Si}(\text{CH}_2)_3\text{Br}$ (**2**) spacers bound to macroporous Si surface.

The bromo- or chloro- alkyl functionalised surfaces were then treated with the solution of lithiated ferrocene²² in dry THF at ambient temperature for overnight. After that, the samples were washed first with dry THF, then with dry hexane and dried in vacuum. The FTIR spectra (Table 6.1) of the sample contain CH_2 , SiC and Si-O-Si bands of the spacers and characteristic ferrocene (cyclopentadienyl) bands at 3098 cm^{-1} and 815 cm^{-1} .

Direct bonding (without a spacer) of ferrocene groups to the PS surface was performed according to scheme 6.2. The chlorinated porous silicon sample surface was prepared by UV-initiated reaction between chlorine gas and the silicon-hydride terminated surface. The chlorine-functionalised surface was then treated with lithiated ferrocene in dry THF at ambient temperature for overnight.



Scheme 6.2 Direct bonding of ferrocene to porous silicon surface.

Table 6.1 Assignment of the IR bands for modified PS²⁰

Assignment	Ferrocene/PS (bonded <i>via</i> spacer using $[(OC_2H_5)_3Si(CH_2)_3Cl]$, $\{cm^{-1}\}$)	Ferrocene/PS (bonded directly to Si), $\{cm^{-1}\}$
$\nu_{Cp}(CH)$	3098	3098
$\nu(CH_2)$	2848, 2934	-
$\nu(C=C)$	1449, 1516	1448, 1514
$\delta(CH_2)$	1228, 1280	-
$\nu(CC)$	1107	1098
$\nu(Si-O-Si)$	1000-1100	-
$\delta(CH)$	1018	1018
$\nu(SiC)$	803	800
$\pi(CH)$	815	818

The FTIR spectra (Table 6.1) of the sample show characteristic ferrocene (cyclopentadienyl) bands at 3098 cm^{-1} and 818 cm^{-1} . In addition an intensive SiC band [$\nu(\text{SiC})$] at 800 cm^{-1} and the bands corresponding to C=C stretching vibrations (1448 and 1514 cm^{-1}) are observed. These bands have not been observed in previously published work²⁰ on bonding of ferrocene *via* vinyl-spacer using the hydrosilylation of silicon-hydride terminated surfaces. Thus FTIR spectroscopy has given clear indication of bonding of ferrocene species to the Si surface. It should be mentioned that an experiment on interaction of original non-functionalised ferrocene with porous silicon surface (*without chemical bonding*) was also performed in dry THF solution. The FTIR spectra (figure 6.3) for this sample is different when compared to the two previous cases (bonding of ferrocene with and without spacer on the Si surface). In particular, vibrational bands belonging to Si-C have not been observed for the sample treated with original non-lithiated ferrocene.

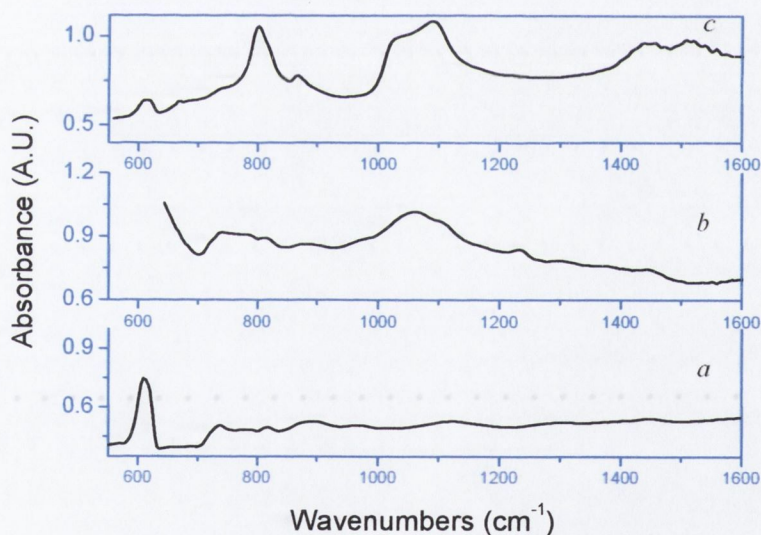


Figure 6.3 FTIR absorbance spectra of: bare macroporous silicon (**a**), macroporous silicon filled with ferrocene without covalent bonding (**b**), and ferrocene chemically bonded to the macroporous silicon surface (**c**).

It should be noted that measurements of the PL spectra of porous silicon (after oxidation and oxide removal in HF solution) at room temperature show the presence of a band at ~ 700 nm, which was substantially reduced in intensity after functionalisation of porous silicon surface {for both bonding of ferrocene functionalities via spacers and direct bonding} (figure 6.4 a & b).

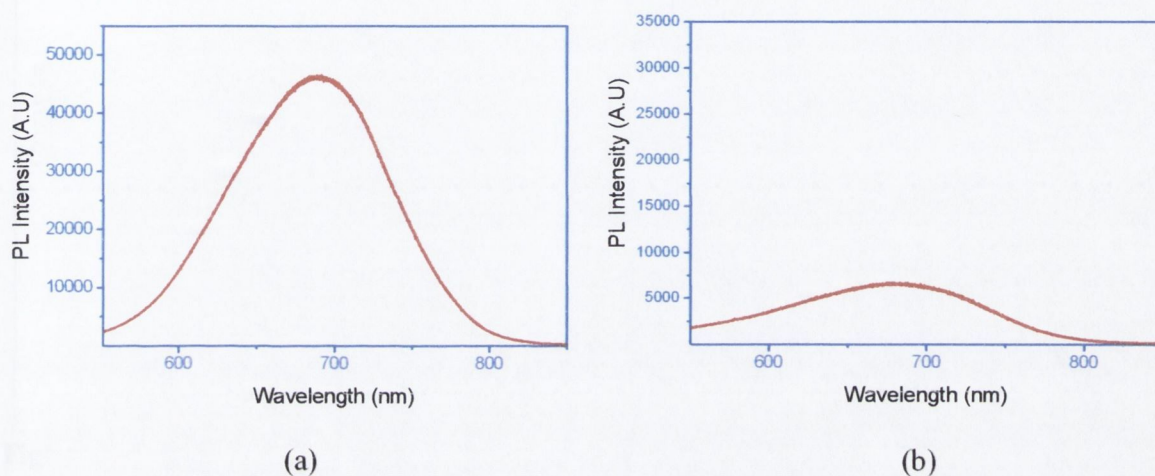


Figure 6.4 Photoluminescence of the porous silicon sample before (a) and after (b) functionalisation with ferrocene.

The most possible reason for the quenching of the luminescence in porous silicon is attributed to the presence of covalently bonded ferrocene species acting as efficient non-radiative traps on the porous silicon surface.²³ So it is possible that the interaction of the ferrocene moiety with silicon orbitals introduces states of appropriate energy for non-radiative quenching to occur.

The SIMS (Secondary Ion Mass Spectrometry) measurement is carried out on the surface of porous silicon as well as on the porous region (both surfaces are bonded with ferrocene). The secondary positive ion spectrum on the surface of the silicon sample is presented in figure 6.5 and it was compared with the positive ion spectrum on the pores of silicon (in a depth of $7\text{ }\mu\text{m}$), which is presented in figure 6.6. The spectrum showed the distribution of ions on the surface and inside the pores. It can be seen that the counts of Li^+ is more on the surface than on the pores, but the counts of Fe^+ on both the surface and pores, remains almost the same suggesting that the Li^+ on the surface can be mainly from the LiCl which

was not completely removed from the surface or from the Li^+ species left over from the hydrolysis and oxidation of FcLi resulting in LiOH and Li_2O impurities.

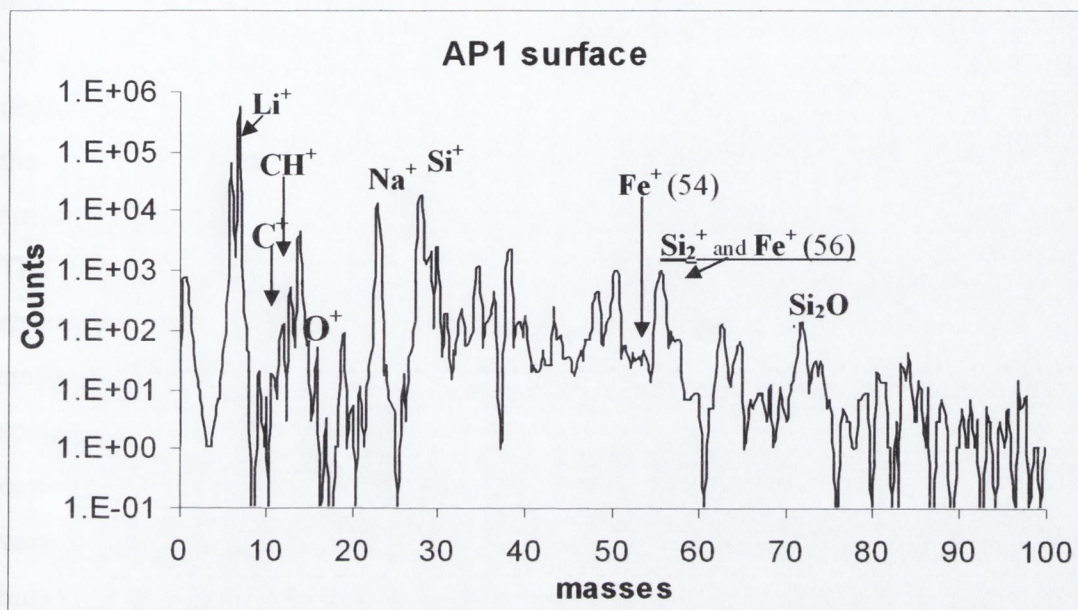


Figure 6.5 The secondary positive ion spectrum on the surface of porous silicon sample.

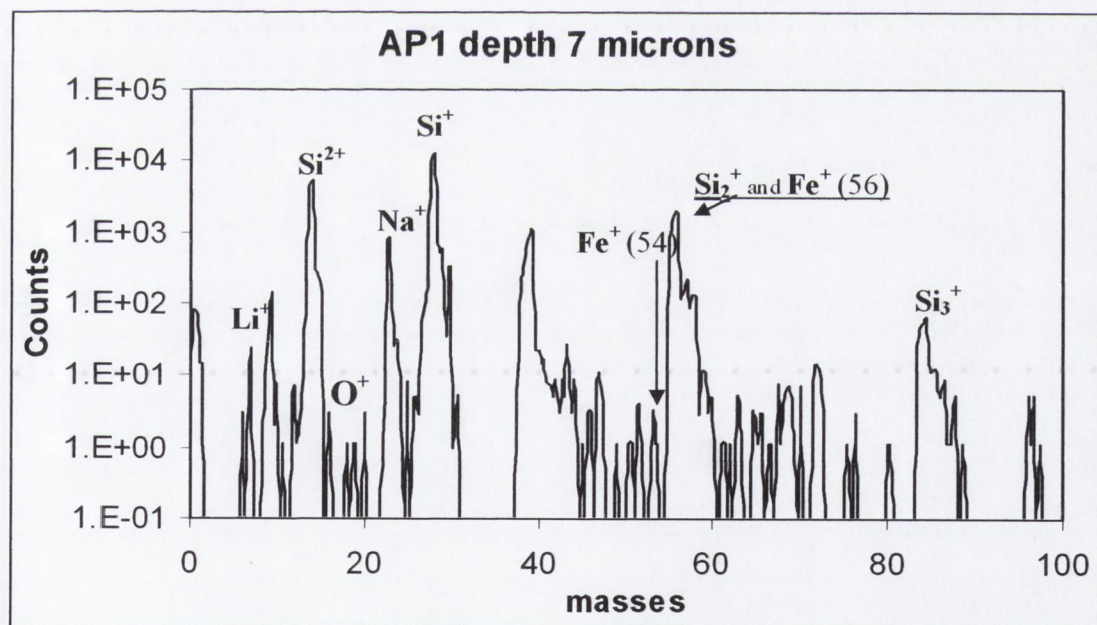


Figure 6.6 The secondary positive ion spectrum on the pores of porous silicon sample (at a depth of $7\text{ }\mu\text{m}$).

Depth profiling was performed by intensity measurements of secondary ions with masses: 13 (**CH**); 16 (**O**); 28 (**Si**); 23 (**Na⁺**), 29 (**Si**); 35 (**LiSi**); 54 (**Fe**), 56 (**Si₂** or **Fe** isotope with mass 56) and 72 (**FeO**) and is presented in (Appendix I figure 1). The depth profile was calculated from the average rate of ion sputtering, at different depth of the pores. From the depth analysis it can be concluded that the density of the **-CH** groups and **Fe** decreases in the depth of pores which reflects that ferrocene is concentrated mostly close to the top surface.

The SIMS measurement on the ferrocene samples bonded to porous silicon *via* spacer (3-chloropropyltriethoxysilane) is studied and the secondary positive ion spectrum on the surface of the silicon sample is presented in figure 6.7. It was compared with the ion spectrum on the pores of silicon (in a depth of 2.4 μm), which is presented in figure 6.8. By comparing the two spectra (figure 6.7 and 6.8) it is clear that the concentration of **Fe** ions is very low in a depth of 2.5 μm and this can be due to the micropores, which precludes the bulky spacer group together with ferrocene not to go into the pores. This is also clearly seen in the depth profile analysis on the sample (Appendix I figure 2).

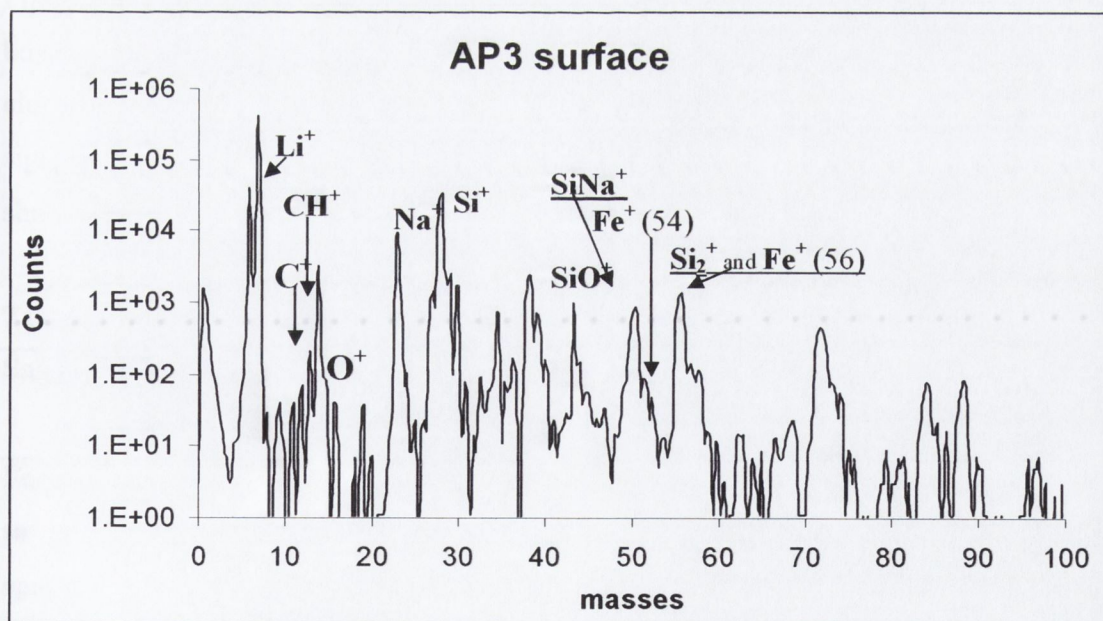


Figure 6.7 The secondary positive ion spectrum on the surface of porous silicon sample.

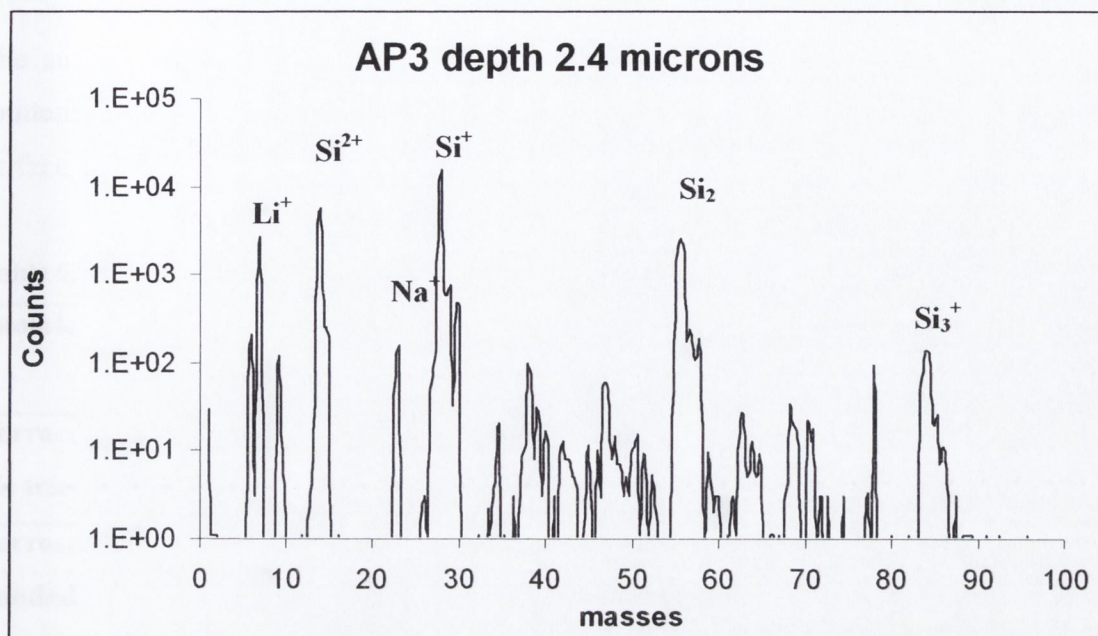


Figure 6.8 The secondary positive ion spectrum on the pores of porous silicon sample (at a depth of 2.4 μm).

Flat crystalline silicon samples were taken as models for porous silicon to study the bonding of ferrocene moieties by XPS. The samples were handled in air and therefore are cleaned by sputtering Ar^+ ions to reduce surface contamination, which can block off Fe signal. The surface compositions of samples (in atomic percents) before sputtering are shown in the table 6.2.

Table 6.2 Surface compositions of samples before sputtering.

Sample description	Sample code	Si (%)	C (%)	O (%)	Fe (%)
Ferrocene bonded to Si via triethoxy spacer	Q4	23.7	47.1	28.6	0.6
	Q13	28.2	37.3	34.4	less than detectable
Ferrocene directly bonded to Si.	Q14	26.4	40.0	33.1	0.5
	Q15	39.1	18.6	41.9	less than detectable

The surface composition after sputtering is presented in table 6.3. The samples after sputtering showed an increase in Si (%) and a decrease in C (%), which indicates that surface contamination has been removed after sputtering.

Table 6.3 Surface compositions of samples after sputtering.

Sample description	Sample code	Si (%)	C (%)	O (%)	Fe (%)
Ferrocene bonded to Si via triethoxy spacer	Q4	29.5	33	36.9	0.6
	Q13	38.8	15.6	45.3	0.3
Ferrocene directly bonded to Si.	Q14	34.7	21.4	43.2	0.6
	Q15	49.8	10.1	38.8	0.8

A deconvolution of the different contributions (by fitting procedure) relative to the Fe2p spectrum is presented in figure 6.9. The weakness of the signal made it difficult to perform deconvolution in accuracy.

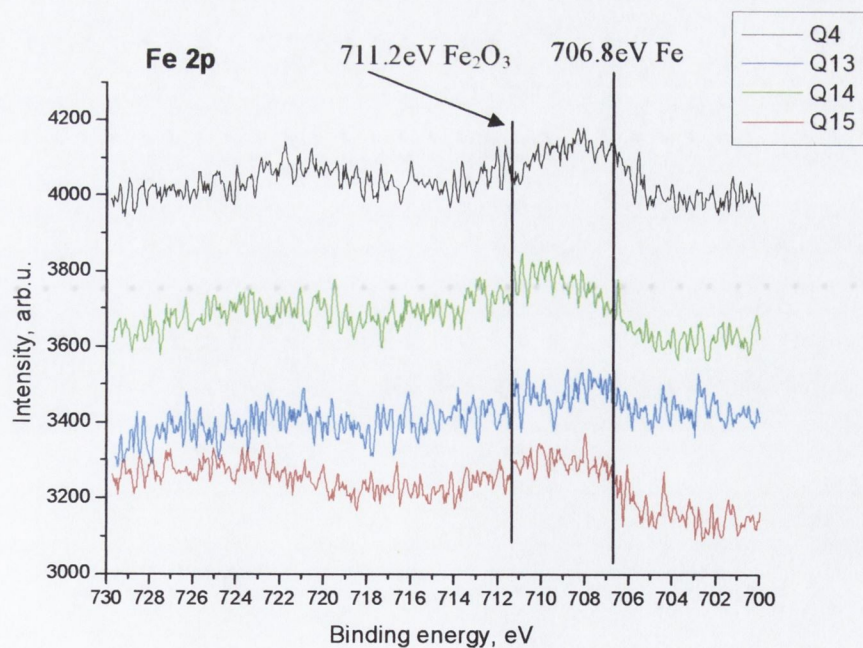


Figure 6.9 A deconvolution of different contributions relative to Fe2p XPS peak.

The position of Fe 2p_{3/2} at 708.5 eV is reported^{24, 25} as Fe in oxidation state of +2. From the analysis of different oxidations states, it has been found that the binding energy of 708.5 eV is comparable with that of 709 eV as for Fe²⁺ ions.²⁶ Thus the corresponding BE (binding energy) values are identical to the literature data for ferrocene salts. A comparison of relative atomic ratios of our samples with the reported wet chemistry functionalisation of H-terminated Si(100) with vinylferrocene²⁵ is presented in table 6.4.

Table 6.4 A comparison of relative atomic ratios of functionalised silicon sample with reported article.

	Sample code	Fe/Si	C/Fe	C/Si	O/Si
Reported with vinyl ferrocene²⁴	-	0.035	15.9	0.53	0.35
Our samples after sputtering	Q4	0.02	55	1.12	1.25
	Q13	0.08	52	0.4	1.18
	Q15	0.017	35.7	0.62	1.24

Figure 6.10 shows Si (2p) XPS spectrum of ferrocene sample bound to Si *via* triethoxy spacer. The shoulders in the main peak have been resolved and the spectrum was fitted with peaks corresponding to Si-O species (at BE's 103.25 eV), Si-C-O (102.15eV), Si-C (101.25eV), Si-H (100.15 eV) and Si-Si (98.3 eV). The chemical shifts of Si-H and Si-C bonds are too small to observe relative to the lattice Si atoms.¹⁶ The presence of Si-O species can be due to interstitial oxygen. The chances of oxidation of the silicon samples cannot be ruled out. The presence of Si-C-O bands can be caused by the oxidation of triethoxy spacer groups after binding. We can also conclude that the surface coverage is not complete which might be the reason for Si-H peaks in the spectrum. Thus XPS spectrum of Si (2p) region confirms the binding of ferrocene species to silicon surface *via* triethoxy spacer group. The binding of the ferrocene moiety to silicon *via* spacer was also confirmed by XPS spectrum on Q13 sample and is presented in figure 6.11. The spectrum shows the peaks corresponding to the surface species same as that observed in sample (Q4) with an exception of Si-H peaks.

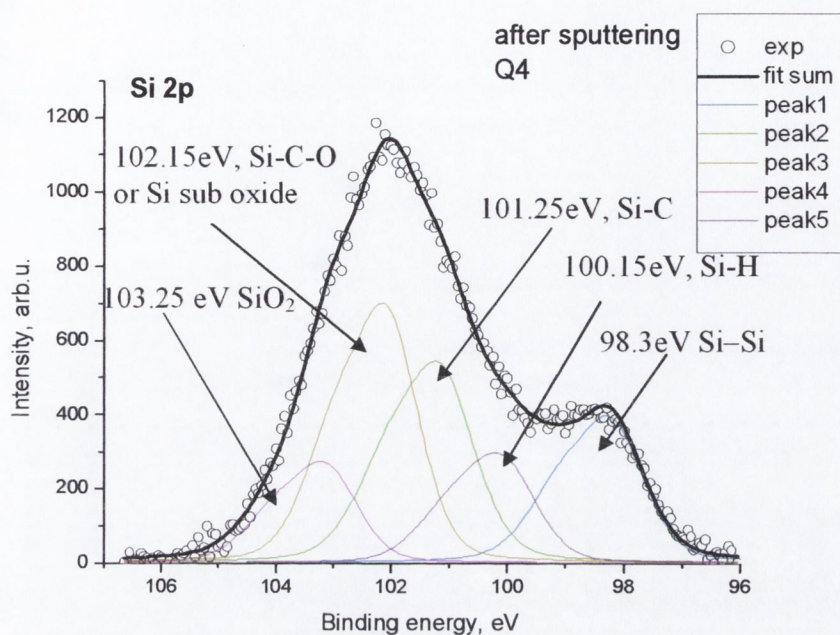


Figure 6.10 Si (2p) region of XPS for ferrocene bonded to silicon *via* triethoxy spacer.

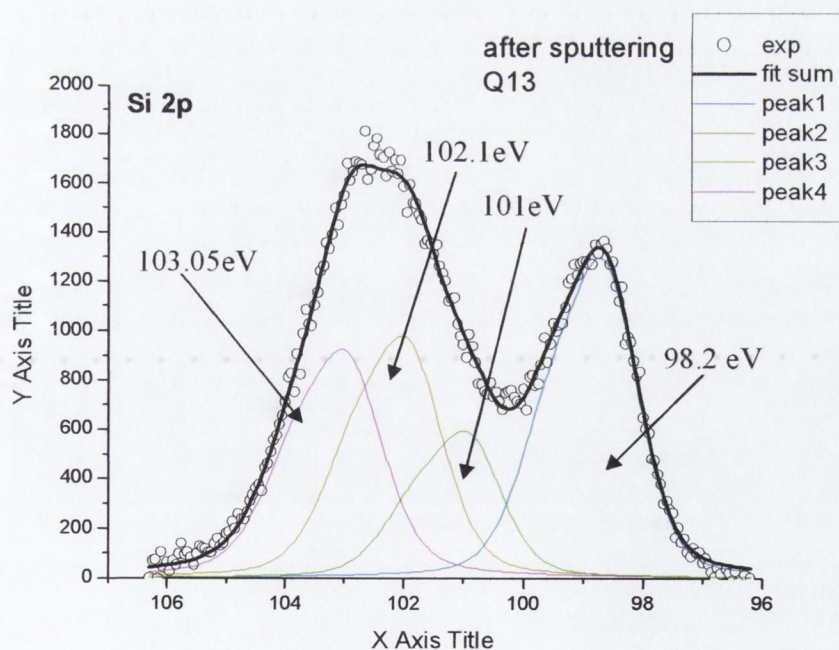


Figure 6.11 Si (2p) region of XPS for ferrocene bonded to silicon *via* triethoxy spacer.

The Si (2p) XPS spectrum of the sample with ferrocene directly bonded to silicon is presented in figure 6.12. The main resolved peaks are corresponding to Si-O species (BE's 103.05 eV), Si-C-O (102.05eV), Si-C (101eV), and Si-Si (98.55 eV). The presence of Si-C-O species suggested that a possible oxidation might have happened.

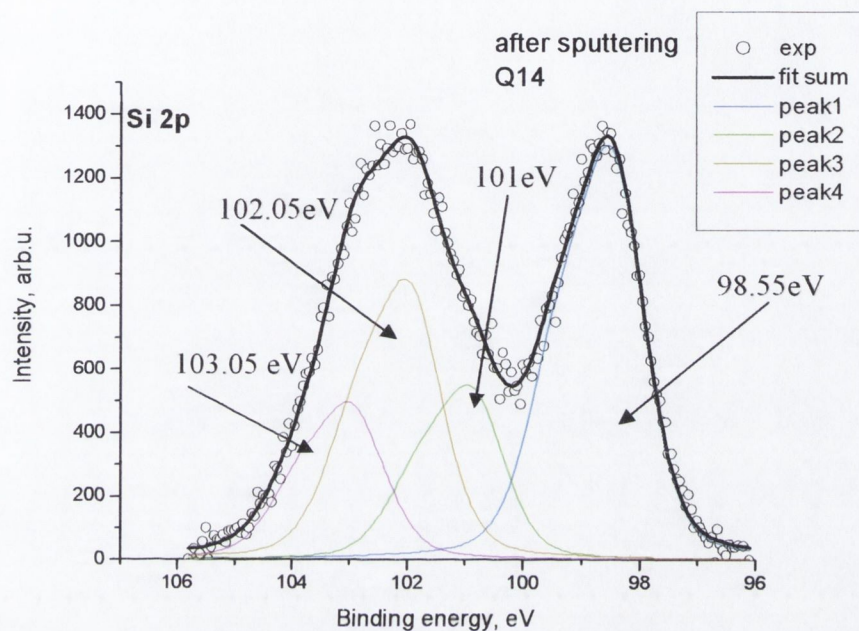


Figure 6.12 Si (2p) region of XPS for ferrocene bonded directly to silicon.

Figure 6.13 shows the C (1s) XPS spectrum for ferrocene sample bonded to Si *via* the triethoxy spacer. The main peak has been resolved and well fitted with four peaks, which corresponds to various species like C-C or methylene carbons (BE of 284.6 eV), C-O (285.7 eV), C-Si (283.35 eV) and C-Fe (282.3 eV). The BE for C-Si appeared at a lower binding energy with a negative chemical shift. This observed negative shift is consistent with the XPS studies on Si-C in the literature.²⁷ The peak at 282.3 eV can also be attributed to C-Si. Thus the C (1s) XPS spectrum confirms the attachment of the ferrocene functionalised to the silicon surface (*via* the spacer group). The second silicon sample (Q13), which was functionalised with ferrocene *via* spacer, has been subjected for XPS and the peak positions indicated the presence of ferrocene and spacer groups on the surface of silicon. The results were consistent with the XPS measurements repeated for various samples.

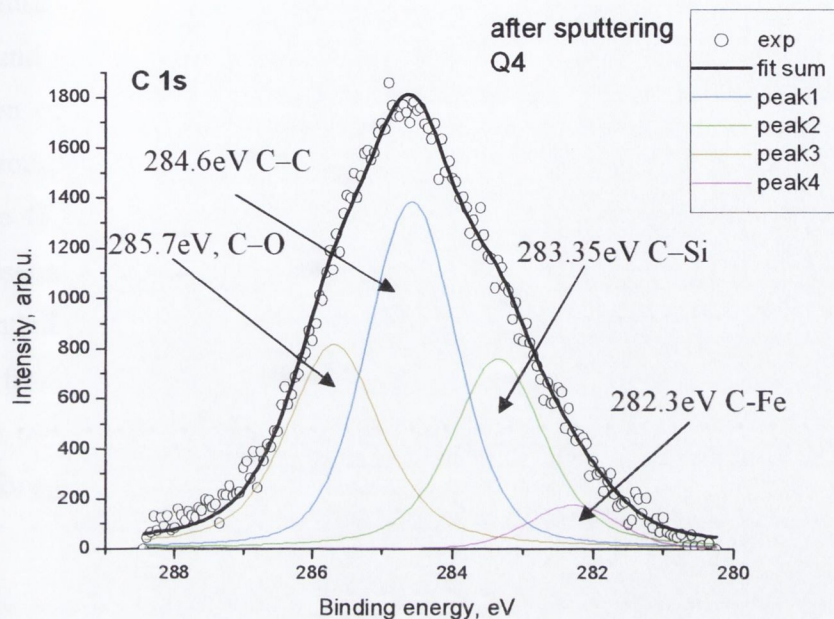


Figure 6.13 C (1s) region of XPS for ferrocene bound to silicon *via* spacer group.

Figure 6.14 shows the C (1s) XPS spectrum for silicon sample functionalised directly with ferrocene.

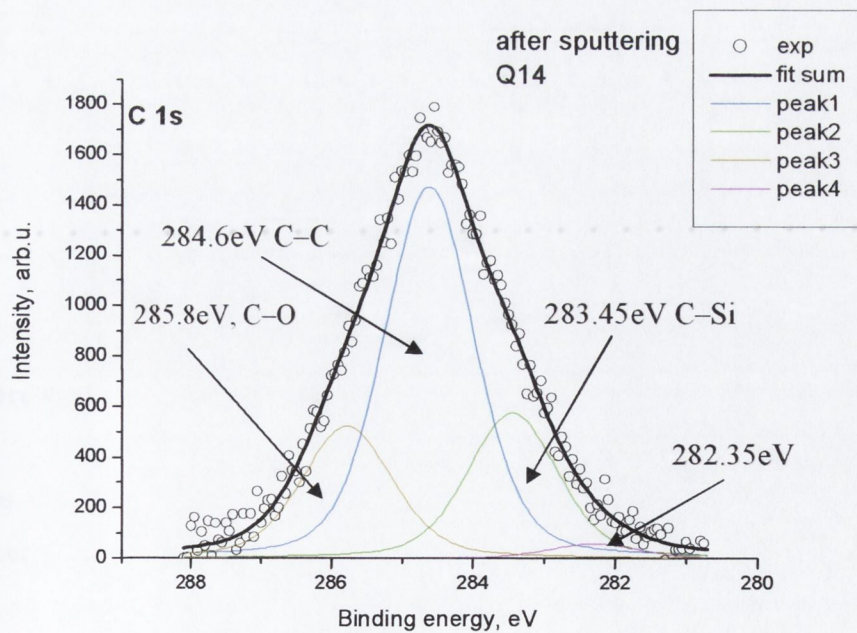


Figure 6.14 C (1s) region of XPS for ferrocene bound directly to silicon.

Similarly above, C (1s) region of XPS showed the peaks with BE's corresponding to the bound ferrocene species. The spectrum also indicates the possible oxidation that might have been occurred. The peak at 284.6 eV attributed to C-C or methylene carbon indicated the ferrocene group on silicon surface.²⁸

The O (1s) region of XPS of silicon sample functionalised *via* spacer with ferrocene is presented in figure 6.15. The spectrum show the peaks corresponding to various oxygen bonded species and the peak at 532.65 eV is attributed to Si-O or Si-O-C species which can be from the siloxy- spacer group on silicon surface. The peak at 531.9 eV is attributed to the residual Si-OH from the unreacted silicon surface which was hydroxyl terminated before functionalisation.

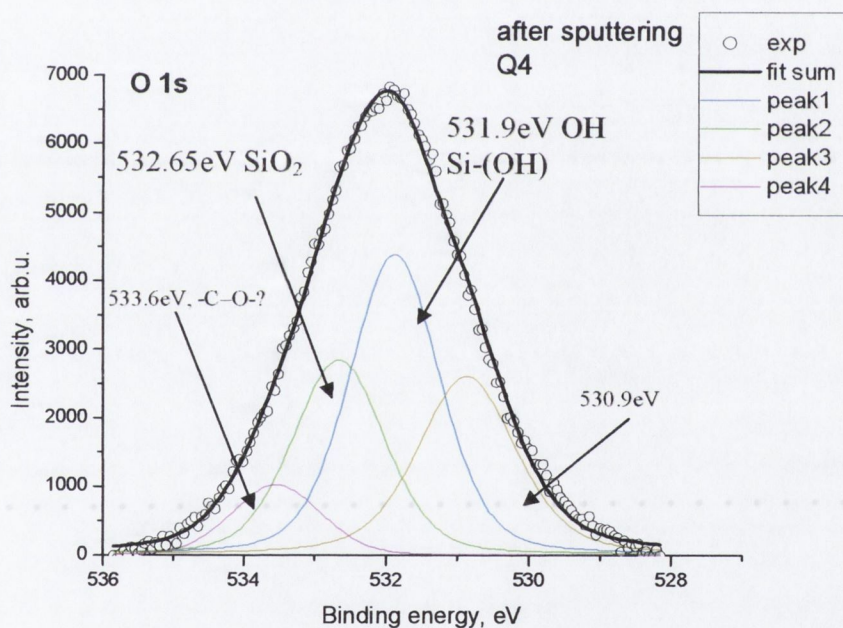


Figure 6.15 O (1s) region of XPS for ferrocene binded to silicon *via* spacer group.

Thus O (1s) XPS spectrum of silicon sample functionalised with ferrocene *via* triethoxy spacer showed the various Si-O species attached to the surface of silicon.

6.2.2 Functionalisation of porous / flat silicon surfaces with cyclopentadienyl moieties

Although there are several publications on the interaction of cyclic molecules such as cyclohexene and cyclohexadiene with silicon surfaces,^{29,30} very little work has been carried out on the binding of five membered rings to silicon surface.³¹ In this section a chemical binding of cyclopentadienyl (Cp) functionality to porous silicon surfaces is discussed. The mesoporous silicon was prepared using a standard procedure of anodic etching of *p*-type Si(100) wafer with 1: 1 48% HF(aqueous)/EtOH in a teflon cell. The macroporous silicon samples were prepared by electrochemical etching in 4% HF in DMF with silicon sample of resistivity 10 Ω cm. Figure 6.16 shows SEM images of some of the macroporous silicon samples used for the present studies. The pore diameters are in the range 0.5 – 3.5 μ m.

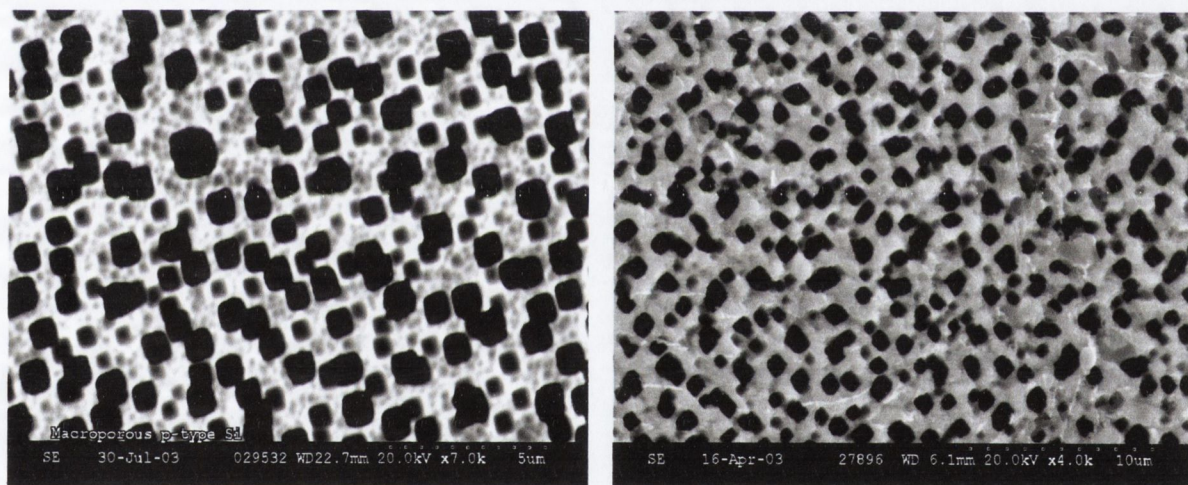
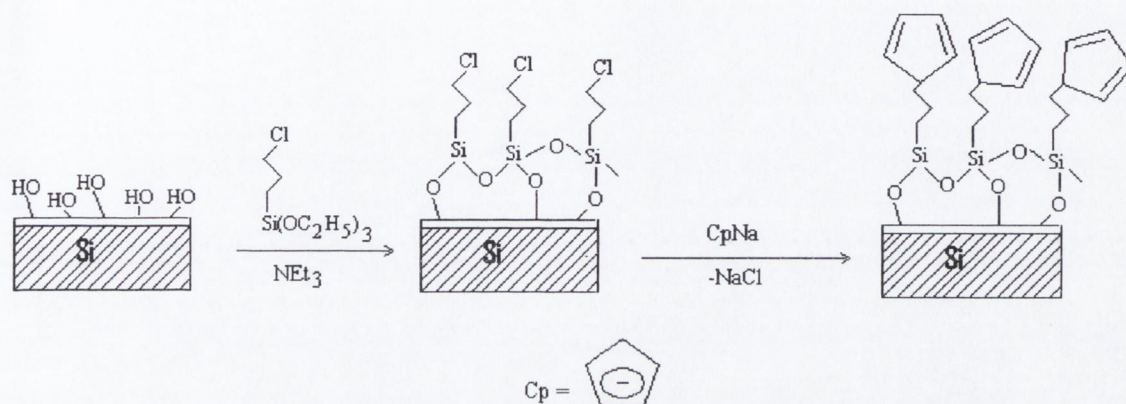


Figure 6.16 SEM images of macroporous silicon sample with different pore diameters used for the functionalisation.

The cyclopentadienyl groups have been bound to the silicon surface either *via* organic (3-halogenopropyl) siloxy spacer or directly *via* C-Si/surface bond. Cp-modified PS sample with (3-chloropropyl) siloxy spacer was prepared according to scheme 6.3. A clean hydroxylated PS surface was first treated with (3-chloropropyl) triethoxysilane to introduce the chloroalkyl functionality. The process was monitored by FTIR spectroscopy (Figure

6.1), which clearly shows the presence of Si-O-Si bonds in the range $1000\text{--}1100\text{ cm}^{-1}$, CH_2 vibrations at 2934 , 2848 and 1263 cm^{-1} .

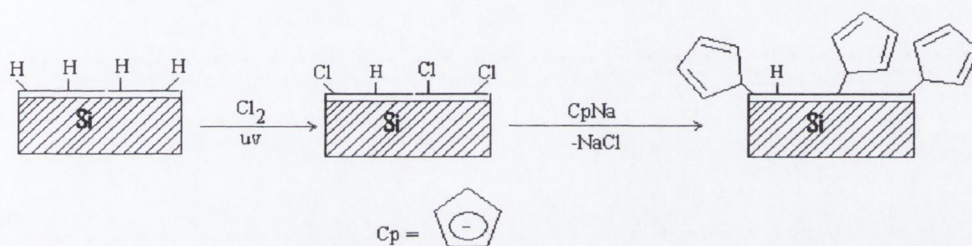


Scheme 6.3 Bonding of cyclopentadienyl groups to the porous silicon surface through (3-chloropropyl) siloxy spacer.

The chloroalkyl- functionalised surfaces were then treated with a solution of sodium cyclopentadienide (CpNa) in THF at ambient temperature for overnight. The samples were washed with dry THF and then dried in vacuum. The FTIR spectra (Table 6.5) of the samples contain bands corresponding to CH_2 , SiC, and Si-O-Si groups of the spacers and characteristic cyclopentadienyl bands.

Direct bonding (without spacer) of cyclopentadienyl groups to the porous silicon surface was performed according to scheme 6.4. The chlorinated silicon surface was prepared using UV-initiated reaction of chlorine with the clean silicon-hydride terminated surface. The chlorine-functionalised surface was then treated with solution of CpNa in dry THF at ambient temperature for overnight. The FTIR spectrum (Table 6.5) of the sample contained characteristic cyclopentadienyl bands at 816 and 815 cm^{-1} , and SiC bands at 798 and 803 cm^{-1} , which indicate the presence of cyclopentadienyl ring attached to the surface. It should be noted that the SiC band at 803 cm^{-1} is much more intense when cyclopentadienyl is

directly bound to the PS surface. In addition, two bands appear at 1440 and 1720 cm^{-1} , which belong to C=C stretching vibration of cyclopentadiene. A broad peak at 2100 cm^{-1} revealed the presence of Si-H species on the PS surface.¹³ FTIR spectra showing the bonding of Cp via propyl-spacer and directly to the silicon surface are presented in figure 6.17.



Scheme 6.4 Direct bonding of cyclopentadienyl to silicon surface.

Table 6.5 Assignment of the IR bands for Cp-modified porous silicon.²⁰

Assignment	Cp/PS (bonded <i>via</i> spacer [(OC ₂ H ₅) ₃ Si(CH ₂) ₃ Cl], {cm ⁻¹ }	Cp/PS (bonded directly to Si), {cm ⁻¹ }
$\nu(\text{CH}_2)$	2964	-
$\nu(\text{SiH}_x)$	-	2100
$\nu(\text{C}=\text{C})$	1449, 1670	1449, 1720
$\delta(\text{CH}_2)$	1200	1172, 1254
$\nu(\text{CC})$	1099	1105
$\nu(\text{Si-O-Si})$	1000-1100	-
$\delta(\text{CH})$	1021	1020
$\nu(\text{SiC})$	798	803
$\pi(\text{CH})$	816	815

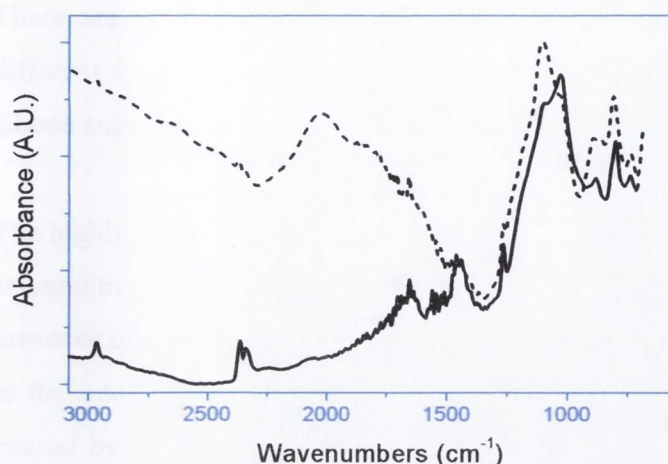


Figure 6.17 FTIR spectra of cyclopentadienyl bonded *via* propyl-spacer (solid line) and directly to the silicon surface (dotted line).

The XPS analysis of Cp-functionalised flat silicon sample with direct bonding of Cp fragments to silicon surface is presented in the figures 6.18 – 6.20. The high resolved C (1s) spectrum (Figure 6.18) show the major peak with BE at 285.00 eV, which is attributed to CH and CC bonds in Cp. The spectrum also contains a weak peak at 282.7 eV, which is assigned to a SiC bond, that confirms the bonding of silicon substrate to the cyclopentadienyl moiety.

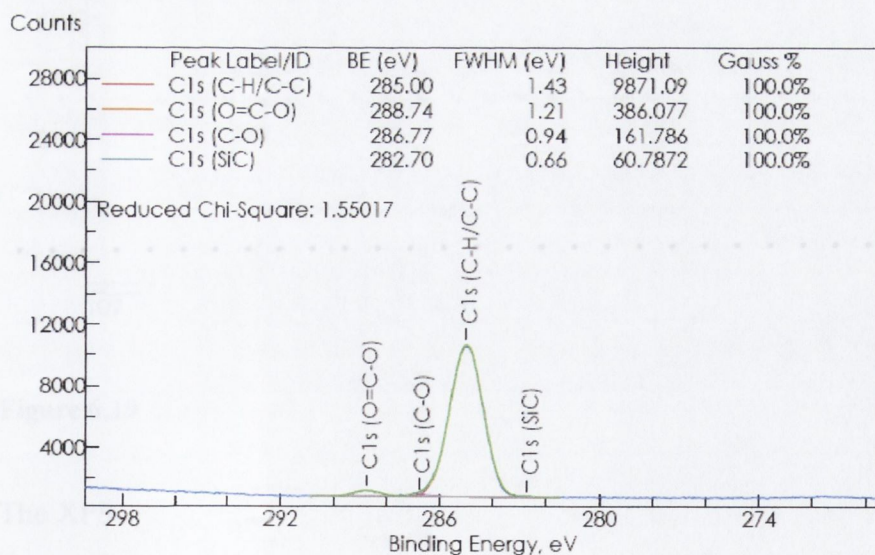


Figure 6.18 C (1s) region of XPS for the Cp-functionalised silicon. The blue colour code represents the measured spectrum and the other colour codes represent modelled peaks.

There are also small peaks with BE's of 286.77 eV and 288.74 eV, corresponding to different C-O bonds, which are most likely formed due to partial oxidation of CpNa on silicon surface during the storage, transportation and transfer into the XPS machine.

The highly resolved Si (2p) core level spectrum (Figure 6.19) of this sample is considerably asymmetric because of different silicon binding states contributing to the total signal. The presence of highly intense Si-O and SiO₂ peaks with BE's at 102.23 and 103.21 eV are due to the interstitial oxygen, which is common in Czochralski prepared samples, or may be caused by the partial oxidation of Si-Cl surfaces. The spectrum showed also peaks with BE's at 98.29 eV and 99.01 eV which are attributed to SiH or Si-Si bonds. It indicates the presence of Si-H bonds, which were not completely converted to the Si-Cl bonds during the halogenation process. The small peak with BE at 100.25 eV is assigned to the Si-C bond, corresponding to Cp fragments covalently bonded to the silicon surface.

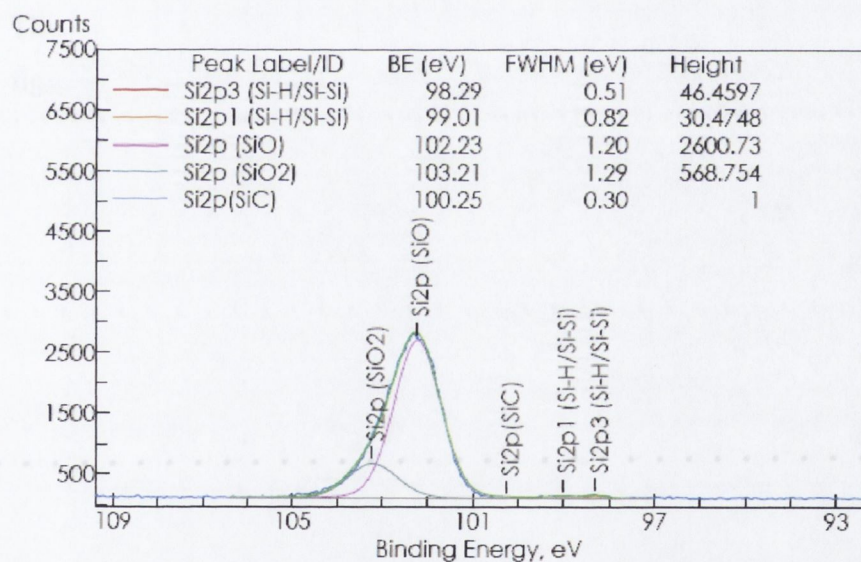


Figure 6.19 Si (2p) region of XPS for the Cp-functionalised silicon.

The XPS spectrum of Cl (2p) core level spectrum is presented in figure 6.20. The spectrum shows peaks with BE's at 202.24 and 200.62 eV corresponding to Cl (2p) after the reaction with CpNa and the non-reacted Si-Cl bonds. Presumably NaCl was not fully removed by washing from the silicon sample after the treatment.

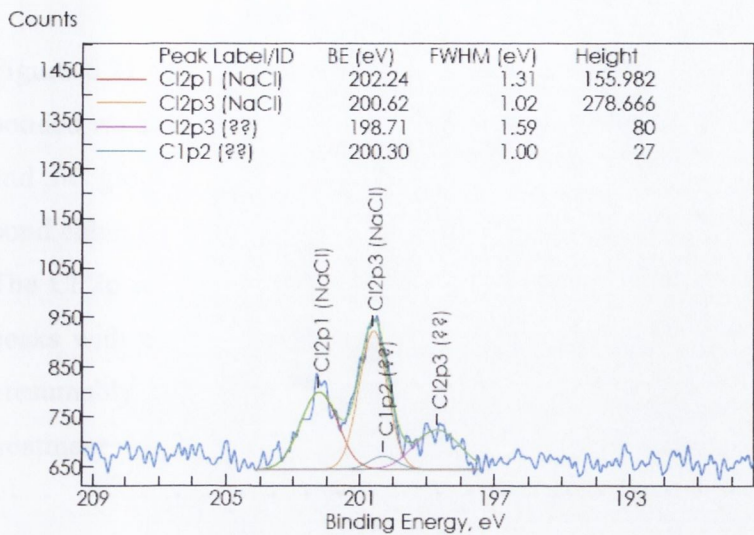


Figure 6.20 Cl (2p) region of XPS for Cp-terminated flat silicon. The blue colour code represents the measured spectrum and the other colour codes represent modelled peaks.

The XPS results of Cp functionalised silicon samples bonded *via* spacer is presented in figures 6.21 – 6.23.

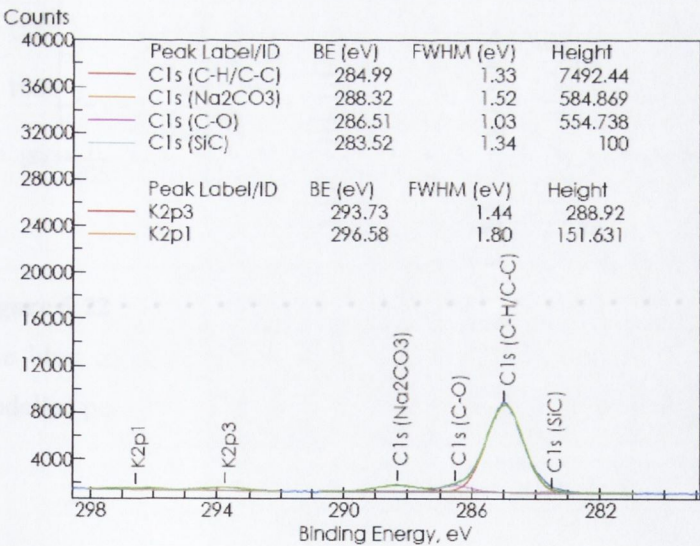


Figure 6.21 C (1s) region of XPS for the silicon sample, where Cp is bonded to silicon *via* spacer. The blue colour code represents the measured spectrum and the other colour codes represent modelled peaks.

Figure 6.21 shows the C(1s) region of XPS for the silicon sample which is having Cp bonded *via* a alkyl spacer group. The BE's at 284.99 eV and 283.52 eV are attributed to CH and SiC groups respectively. The binding energy at 284.99 eV can also be attributed to C-C bond either from the spacer group or from the Cp group.

The Cl 2p region of the XPS for this sample is presented in figure 6.22 and it shows the peaks with a BE's of 200.27 eV and 201.97 eV, which are attributed to NaCl salt that is presumably not removed completely during washing of the silicon sample after the treatment.

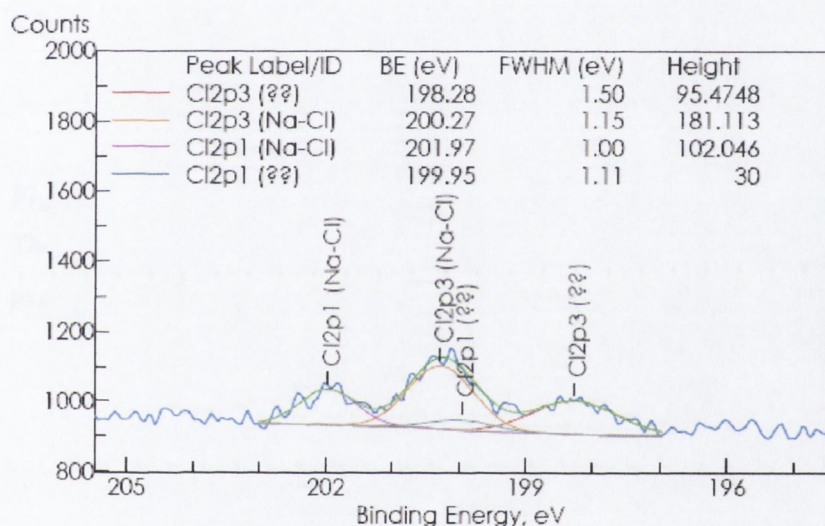


Figure 6.22 Cl (2p) region of XPS for the silicon sample, where Cp is bonded to silicon *via* spacer. The blue colour code represents the measured spectrum and the other colour codes represent modelled peaks.

Figure 6.23 shows the Si (2p) XPS core level spectrum and depicts the different bonds that can be formed due to Si-H (at BE's of 98.08, 98.63) and Si-O bonds (at BE's of 103.40 and 102.49 eV). It also contains peaks with BE at 99.87 eV corresponding to SiC band which

can be from spacer. The presence of Si-H groups indicates that the hydride groups on the silicon are not completely converted to Si-Cl bonds (at BE's of 198.28 and 199.95 eV).

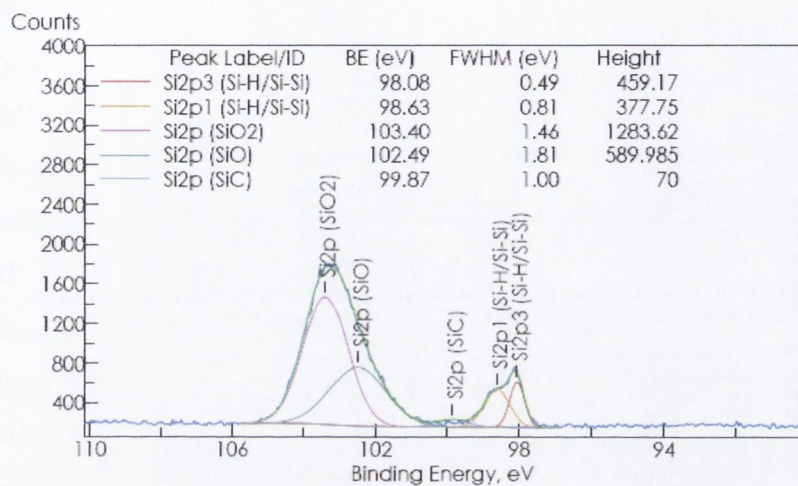


Figure 6.23 Si (2p) region of XPS for the silicon sample where Cp is bonded to silicon *via* spacer. The blue colour represents the measured spectrum and the other colour codes represent modelled peaks.

6.3 Conclusions

Thus we have shown that silicon both flat and porous can be effectively functionalised with ferrocene and cyclopentadienyl groups using new organometallic approaches. We have developed two methods to functionalise silicon surfaces with the ferrocene or cyclopentadiene: *via* alkylsiloxy- spacer groups and by direct bonding to the silicon surfaces. We demonstrated that the functionalised silicon surfaces can be conveniently characterized by XPS, FTIR, SIMS and PL (where appropriate) spectroscopy. All these techniques have proven the formation of new species and their covalent binding to the silicon surfaces after their treatment. Although in some cases only a partial functionalisation of the entire surface was achieved leaving unreacted initial groups. Further studies using STM and AFM techniques in combination with computer simulation will be necessary to understand these systems in more details. This, however, is beyond the scope of this project and should be done in the future. We also believe that new cyclopentadienyl and metallocene functionalised surfaces might find potential applications in sensing and molecular electronics.

6. 4 References

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VII

Experimental

7.1 General procedures

7.1.1 Starting materials and chemicals

All chemicals were purchased from Aldrich unless otherwise stated. Czochralski-grown single crystal *p*-type silicon samples of (100) orientation were used for the present studies unless otherwise stated. The thicknesses of the wafers used were in the range of 300- 400 μm . The silicon samples were having different resistivity ranging from low resistivity samples to high resistivity samples. The resistivity of silicon samples was determined by using the four-point probe method. The wafers were treated with BOE (buffer oxide etch) to remove any oxide layer and cleaned with cleaning solution (1: 10 HF: H_2O) and dried by using spin rinse dryers.

A thin film of aluminium (150 nm in height) was vacuum deposited on the backside of the wafer by metal depositor to provide uniform electrical contact. The silicon wafer with Al thin film was then annealed under vacuum at 450°C for 30 minutes. Additionally Ga-In alloy was deposited instead of aluminium film, by rubbing into the backside of the wafer. The silicon samples were sliced into square pieces of $1.5 \times 1.5 \text{ cm}^2$ in dimension by using a carbide scribe.

7.1.2 Preparation of electrolytes

The electrolyte used for the preparation of porous silicon was based on hydrofluoric acid. HF was purchased from Lennox Laboratories Supplies Ltd. Aqueous solutions of HF are usually not prepared from 100% HF, but by dilution from commercially available aqueous solutions of higher concentrations, *e.g.*, 48 wt% of HF.¹ All electrolytes were prepared with extra safety precautions. Electrolytes used for electrochemical etching of silicon can be categorised according to their constituents into two types: aqueous or organic electrolytes. The solutions to which ethanol or surfactants (to reduce the surface tension) were classified under aqueous electrolyte.² In the experiments mentioned in this thesis, a solution of 200 ml of electrolyte solution was prepared. Deionised millipore water (18.2 M Ω) was used for dilution.

The stock solution of 48 wt% HF was always used for the preparation of the electrolyte solutions. A series of different volume % solutions, was prepared by taking the required volume of stock solution and diluting it with the millipore water. For example, 7 vol%

solution was prepared by taking 7 ml of HF and 93 ml of water. So the ratios in the experimental section are vol: vol.

The various compositions of HF based electrolytes were prepared with either organic or aqueous solvents. The electrolytes used for the present investigations are classified into aqueous and organic electrolytes as given in table 7.1. The electrolyte composition and concentration calculations are given in table 7.2.

Table 7.1 Classification of electrolytes into aqueous and organic electrolytes.

Aqueous Electrolytes (vol/vol)	Organic Electrolytes (vol/vol)
7% HF in H ₂ O	4% HF in DMF
1: 1: 1 HF: C ₂ H ₅ OH: H ₂ O + 0.001 M CTAC (surfactant)	15% HF in DMF + 0.11 mol.l ⁻¹ TBAP (surfactant)
5: 9: 26 HF: C ₃ H ₈ O: H ₂ O	4% HF in formamide
1: 1 HF: C ₂ H ₅ OH	10% HF in acetonitrile

Table 7.2 Table for electrolyte preparation and HF concentration.

Electrolytes (vol/vol)	Electrolytes volumes (in ml) or powder (in g)	HF concentration in mol.L ⁻¹
7% HF in H ₂ O	HF: 14 ml H ₂ O: 186 ml	1.94
1: 1: 1 HF: C ₂ H ₅ OH: H ₂ O + 10 ⁻³ M CTAC	HF: 66 ml Ethanol: 66 ml H ₂ O: 66 ml CTAC: 65.6 µl	9.28
5: 9: 26 HF: C ₃ H ₈ O: H ₂ O	HF: 25 ml C ₃ H ₈ O (Isopropanol): 45 ml H ₂ O: 130 ml	3.47
1: 1 HF: C ₂ H ₅ OH	HF: 100 ml Ethanol: 100 ml	13.92

4% HF in DMF	HF: 8 ml DMF: 192 ml	1.11
4% HF in FA	HF: 8 ml FA: 192 ml	1.25
15% HF in DMF + 0.11 mol.L ⁻¹ TBAP	HF: 26 ml DMF: 180 ml TBAP: 7.52 g	3.51
10% HF in MeCN	HF: 20 ml MeCN: 180 ml	2.78

7.1.3 Fabrication of porous silicon

The setup for electrochemical etching is a lab designed. A schematic representation of the cell used for electrochemical etching was presented in chapter II (figure 2.1). Rubber O-rings, provided a tight seal to prevent HF leakage. A volume of 10 ml required electrolyte solution is used for etching in the cell unless otherwise stated. The etching was carried out under a constant current (galvanostatic) and the instrument provided a maximum of 2A (electrical current) and 150V (voltage). The sample enclosure of the cell had to be screwed tight to prevent the leakage of electrolyte solution. However, over tightening had to be avoided to prevent sample stressing and inhomogeneous etching. The etching was carried out at ambient temperature (20°C) unless otherwise stated. After etching, the samples were washed with deionised water and dried under a dry nitrogen flow.

7.1.4 Calculation of porosity and growth rate

Porosity is defined as the fraction P of the total volume of the sample V_{ps} that is attributed to the pores V_p :

$$P = \frac{V_p}{V_{ps}}$$

Porosity relates to the ratio of the pore diameter D and the pore wall thickness w , but it contains no information about the absolute dimensions of the porous network. The porosity is usually determined gravimetrically.³

The mass of the porous layer can be determined by weighing the sample before and after anodization. The V_{ps} is given by the layer thickness d and the electrode area A exposed to the electrolyte and the density of silicon.

$$\text{Porosity, } P = \frac{\Delta m}{d \times A \times \rho_{Si}}$$

Where, Δm is the mass of the porous layer (determined by weighing the sample before and after etching), d is the layer thickness and A is the electrode area exposed to the electrolyte. Density of silicon, $\rho_{Si}=2.3828 \text{ g.cm}^{-3}$.

The growth rate of porous layer is calculated by,

$$\text{Growth rate} = \text{Depth of the pores in nm} / \text{etching time in secs}$$

7.1.5 Characterisation techniques

Fourier transform infrared (FTIR) spectroscopy was performed in transmission mode using a Digilab FTS-6000 spectrometer. The sample was placed either in the main chamber of spectrometer, using a Perkin-Elmer micro-sampling attachment, or on the positional stage of a UMA 500 IR microscope. For measurements in the main chamber a wide band MCT detector in the wavenumber range of $450\text{--}6000 \text{ cm}^{-1}$ with a resolution of 2 cm^{-1} and 8 cm^{-1} was used. A narrow band MCT detector with a spectral range of $4500\text{--}750 \text{ cm}^{-1}$ was used in a UMA 500 IR microscope. A total of up to 128 scans were used to increase the signal-to-noise ratio in both cases.

Room temperature Raman and Photoluminescence (PL) spectra were measured with a Renishaw 1000 micro-Raman system. The excitation wavelength used was 514.5 nm from an Ar^+ ion laser (Laser Physics Reliant 150 Select Multi-Line) with a typical laser power of $\sim 3 \text{ W/cm}^2$ (in order to avoid excessive heating) and 633 nm from a HeNe laser. The Raman measurement was carried out with a laser power of $\sim 10 \text{ W/cm}^2$. The 50x magnifying objective of the Leica microscope focused the beam into a spot of about $1 \mu\text{m}$

in diameter. The spectra were corrected for the instrumental set-up, the apparatus function (obtained by using a white light source) was divided by the original function, the white light acts as a standard reference. Typically PL spectra were measured from a few different spots on the external surface of as received porous silicon sample and on the same sample after the functionalisation of the samples.

Magnetic measurements were carried out both at 5 K and 300 K using a MPMS superconducting quantum interference device (SQUID) magnetometer. Magnetoresistance (MR) measurements were performed by the linear four-probe method at room temperature using a MULTIMAG variable flux source in a magnetic field of up to 5 T.

Mössbauer spectra were collected at sample temperatures of 300 K, 150 K and 77 K, in transmission geometry using a constant acceleration spectrometer equipped with a $^{57}\text{Co(Rh)}$ source kept at RT. The velocity calibration was done using $\alpha\text{-Fe}$ and all isomer shift (IS) values are given relative to $\alpha\text{-Fe}$ at RT.

Thermal analysis of oven-dried samples was obtained using Thermo-Gravimetric Analysis (TGA). Thermo-Gravimetric Analysis was carried out using Perkin-Elmer, Pyris TGA.

BET measurements were carried out in Gemini Surface area, Micrometrics (Norcross, USA). BET surface area and BJH (Barrett-Joyner-Halenda) method pore distribution analysis were studied using the instrument. Pore distribution measurements used adsorption-desorption data based on an average adsorption points and desorption for partial pressures (P/P_0) between 0 and 1. N_2 gas was used as an adsorbate gas and measurement time depends on sample but typically 1-2 hours.

The scanning electron microscopy (SEM), images of the samples were obtained using an FESEM (Hitachi S-4300 scanning electron microscope), which was operated at 5.0 kV or 20 kV. The beam-specimen interaction produces a variety of signals including secondary electrons (SE), back-scattered electrons (BE) and X-rays. The low energy secondary

electrons are collected to form the standard image and the high energy back-scattered electrons provide an image with good atomic number contrast. Samples for analysis were mounted on aluminium stubs and coated with gold. Energy dispersive X-ray microanalysis was also carried out on a sample at both normal and low operating voltages to determine the elemental composition.

The transmission electron microscopy (TEM) images were taken on a Hitachi H-7000. The TEM was operated at a beam voltage of 100 kV. Samples for TEM were prepared by deposition and drying of a drop of the powder dispersed in ethanol onto a formvar-coated 400 mesh copper grid.

Secondary ion mass spectra (SIMS) were carried out in Vilnius University, Lithuania, using a RIBER, LAS-SIA 2000 system.

X-ray photoelectron spectroscopy (XPS) measurements were carried out using LAS-3000 (RIBER, France). The residual pressure analysis chamber was 2×10^{-10} Torr. The photoelectrons were excited by Al K_{α} radiation ($h\nu = 1486.6$ eV). The photoelectrons were analysed using a MAC 2 analyser system (double-pass cylindrical mirror analyser). The calibration of analyser energy scale with the spectrometer work function was done such that Au $4f_{7/2} = 83.8$ eV. The position of C (1s) was 284.6 eV (the adsorbed surface contamination on Au). The binding energy of C (1s) = 284.6 eV was taken as the reference for all samples. Prior to individual elemental narrow scans a survey scan was made for all the samples in order to detect the elements which can be detected. An energy step width of 50 meV and dwell time of 200 ms was used for narrow scan of peaks. Typically 5 scans were accumulated for each spectrum. Fitting and deconvolution of the spectra were performed using XPSPEAK41 software.⁴ The narrow scan spectra were used for fitting and for quantitative analysis. The quantitative analysis was performed on the basis of peak area measurement from the spectra.

XPS was also carried out in Campus Lagoas-Marcosende, Spain and carried on a VG ESCALAB 250iXL spectrometer. The pressure in the analysis chamber was 8×10^{-10}

mbar. Neutralisation of the surface charge was performed by using both a low energy flood gun (electrons in the range of 1 to 14 eV) and an electrically grounded stain screen placed directly on the sample surface. The XPS measurements were carried out using monochromatic Al- K_{α} radiation ($h\nu = 1486.92$ eV). Photoelectrons were collected from a take off angle of 90° relative to the sample surface. The measurement was done in a Constant Analyser Energy mode (CAE) with a 100 eV range for survey spectra and 20 eV for high resolution spectra. Charge referencing was done by setting the lower binding energy C 1s photo peak at 285.0 eV from the surface contamination. The spectra fitting is based on "Chi-squared" algorithm⁵ used to determine the goodness of a peak fit. A Shirley-type baseline was used for all peak-fits. The assignments were carried out using different handbooks and databases.⁶

The XRD in this work was carried out using a Siemens D-500 X-ray diffractometer. X-ray patterns from powder samples were taken in the reflection mode. The crystallite size of the particles was calculated using the Debye-Scherrer equation.⁷

$$\text{Crystallite size} = \frac{0.9 \lambda}{\beta \cos \theta}$$

Where, λ is X-ray wavelength (1.54 Å), θ is Bragg angle and β is the FWHM of the peak in radians (theoretically corrected from the instrumental broadening).

The electrical conductivity was done by a four-point probe method. The technique involves passing a fixed known current between the outer probes and measuring the corresponding voltage drop across the inner probes. Geometric factors such as the probe spacing and sample thickness must be taken into consideration in order to get a reasonable estimate of resistivity. For a particular set-up, resistivity, $\rho = 4.532 (V/I) x_j$, where x_j is the wafer thickness, V is the voltage in mV and I is the current in mA. The constant 4.532 is a correction factor to allow for the fact that current does not flow in a straight line between the outer probes but rather in an arc-like path.

7.2 Experimental for Chapter II

7.2.1 Electrochemical etching of silicon using 7 vol% HF in H₂O

Silicon (100) wafers of resistivity, $\rho = 10 \text{ } \Omega \text{ cm}$ have been used in this experiment. Galvanostatic anodic etching was performed under a current density of 23.5 mA/cm^2 for 3 hours and the electrolyte used for the etching process was 7 vol% HF in water. Porous silicon samples were also fabricated by etching in this electrolyte for 3 hours using low current density of 0.39 mA/cm^2 . The silicon samples of $10 \text{ } \Omega \text{ cm}$ also were etched using the same electrolyte and current density of 23.5 mA/cm^2 for 6 hours.

7.2.2 Electrochemical etching of silicon using 1: 1: 1 HF: C₂H₅OH: H₂O + 10^{-3} M CTAC

An aluminium thin film was deposited on the backside of the wafer prior to etching. Silicon (100) wafers of resistivity, $\rho = 17 \text{ } \Omega \text{ cm}$ were etched with a galvanostatic anodic etching, using an initial current density of 35 mA/cm^2 in a 1: 1: 1 HF: C₂H₅OH: H₂O + 10^{-3} M CTAC electrolyte solution for one hour. CTAC is used as a pore wall modifier and also as a surfactant to reduce the surface tension between the electrolyte–silicon interface.⁸ The silicon samples of resistivity $17 \text{ } \Omega \text{ cm}$ were etched with current densities of $j = 32 \text{ mA/cm}^2$ for 3.5 hours and $j = 40.6 \text{ mA/cm}^2$ for 5 hours using the same electrolyte. The etching current density of the samples was reduced by 3 mA/cm^2 every hour interval to prevent the lift off of the material.

In the second set of experiments using 1: 1: 1 HF: C₂H₅OH: H₂O + 10^{-3} M CTAC electrolyte in order to determine the influence of etching time on porosity and pore depth silicon samples of low resistivity, $\rho = 0.02 \text{ } \Omega \text{ cm}$ was used with different etching times of 30, 120 and 180 minutes by keeping the constant average current density of 34.49 mA/cm^2 through out the experiments. The influence of silicon resistivity on pore depth and morphology of the samples were determined by using silicon samples of resistivities 0.021, 5.69, 14.85 and $17.01 \text{ } \Omega \text{ cm}$ with an average current density of 10.01 mA/cm^2 and an etching time of one hour.

7.2.3 Electrochemical etching of silicon using 1: 1 HF: C₂H₅OH

The electrochemical etching using 1: 1 HF: C₂H₅OH electrolyte solution was performed on silicon (100) samples with resistivities, $\rho = 0.021, 3.49$ and $17.01 \text{ } \Omega \text{ cm}$ using an average current density (20.02 mA/cm^2) and an etching time of 60 minutes. The photoluminescence dependence on the silicon resistivity was determined using the same electrolyte and samples of resistivities $\rho = 0.021, 3.49, 5.69, 14.84$ and $17.01 \text{ } \Omega \text{ cm}$ using an average current density (20.02 mA/cm^2) and an etching time of 60 minutes.

7.2.4 Electrochemical etching of silicon using 5: 9: 26 HF: C₃H₈O: H₂O

The electrochemical etching of the silicon (100) samples with resistivity $10 \text{ } \Omega \text{ cm}$ using 5: 9: 26 HF: C₃H₈O: H₂O electrolyte for 3 hours using current density (31.5 mA/cm^2) was performed. The dependence of anodisation time with respect to the morphology was studied by using this aqueous electrolyte with silicon samples of resistivity $\rho = 5.69 \text{ } \Omega \text{ cm}$ using an average current density of 11.19 mA/cm^2 and an etching times of 90 and 180 minutes. Then the electrochemical etching was carried out with the silicon sample of resistivity $\rho = 17.01 \text{ } \Omega \text{ cm}$ with an average current density of 10.01 mA/cm^2 and an etching time of 60 minutes to study the morphology of the pores using the same electrolyte.

7.2.5 Electrochemical etching of silicon with different percentages of HF in H₂O

The electrochemical etching of the silicon (100) sample with resistivity $0.02 \text{ } \Omega \text{ cm}$ was carried out using different percentages of HF in water. The electrochemical etching was performed for one hour at a low current density of 2 mA/cm^2 . The porosity change and the pore depth variation with respect to the pH were determined. The dependence of PL with respect to different percentages of HF in water was also studied.

7.3 Experimental for Chapter III

7.3.1 Electrochemical etching of silicon samples without pre-patterning

7.3.1.1 Electrochemical etching of silicon samples using 4% HF in DMF

Silicon (100) wafers of resistivity, $\rho = 10 \Omega \text{ cm}$ was etched with galvanostatic anodic etching conditions using a low current density of 0.4 mA/cm^2 for 4 hours with an electrolyte solution of 4% HF in DMF. The electrochemical etching was also performed in silicon sample of resistivity, $\rho = 5.69 \Omega \text{ cm}$ using a high current density of 10 mA/cm^2 for 120 minutes using the same electrolyte.

The influence of etching time on the porous layer formation was studied with 4% HF in DMF electrolyte using silicon samples of resistivity, $\rho = 10 \Omega \text{ cm}$ with a low current density of 0.4 mA/cm^2 and etching times of 60, 90, 120, 180, 240, 300 and 360 minutes. The porosity and growth rate dependence on etch time in 4% HF in DMF solution were also studied. The effect of etching current density on the porous silicon layer formation was studied using two different etching times (1 hour and 3 hours) with four different current densities (3.2 mA/cm^2 , 2.17 mA/cm^2 , 1.28 mA/cm^2 and 0.51 mA/cm^2) using 4% HF in DMF electrolyte solution with silicon samples of resistivity, $\rho = 10 \Omega \text{ cm}$.

7.3.1.2 Electrochemical etching of silicon samples using 15% HF in DMF + 0.11M TBAP

The electrochemical etching using 15% HF in DMF + 0.11M TBAP (Tetrabutylammonium perchlorate) electrolyte solution was performed on silicon (100) samples with resistivities, $\rho = 0.021, 5.69, 14.84$ and $17.01 \Omega \text{ cm}$ using an average current density (40 mA/cm^2) and an etching time of 60 minutes. Silicon samples with different resistivities were studied to find the correlation between silicon resistivity and porosity of the sample by using this electrolyte.

7.3.1.3 Electrochemical etching of silicon samples using 4% HF in FA

The electrochemical etching of silicon (100) samples of resistivity, $\rho = 10 \Omega \text{ cm}$ in formamide solution was performed similarly above using current density of 25.19

mA/cm^2 and an etching time of 6 hours. The photoluminescence characteristics of these porous silicon samples have been studied by PL spectroscopy.

7.3.1.4 Electrochemical etching of silicon samples using 10% HF in MeCN

The effect of etching current density on the porosity of the samples was determined by using silicon samples of resistivity, $\rho = 0.02 \text{ } \Omega \text{ cm}$ with an average current densities of 2.03, 10.86 (figure 3.14), 20.01 and $40.08 \text{ mA}/\text{cm}^2$ and an etching time of 60 minutes. The effect of silicon resistivity with respect to the porosity was determined by using 10% HF in MeCN electrolyte solution by silicon samples of resistivities, $\rho = 0.021, 3.49, 5.69, 14.84$ and $17.01 \text{ } \Omega \text{ cm}$ with an average current density of $20.04 \text{ mA}/\text{cm}^2$ and an etching time of 60 minutes.

7.3.2 Electrochemical etching of pre-patterned silicon samples

The starting material was Cz boron-doped silicon with resistivity ranging from $2 \text{ } \Omega \text{ cm}$ to $20 \text{ } \Omega \text{ cm}$. $300\text{--}400 \text{ } \mu\text{m}$ thick wafers of (100) orientation were used. To form the nucleation pits two photo-masks were used. The masks had round holes arranged in a triangular 'lattice'. One of them had a lattice period of $12 \text{ } \mu\text{m}$, and another of lattice period $4 \text{ } \mu\text{m}$. The pattern was imaged onto the surface of oxidized (100) Si by a standard photolithographic process. Pits, in the shape of inverted pyramids, were subsequently etched in a hot solution of KOH through the oxide mask. The oxide layer was removed (using BOE) before anodization.

Etching was conducted in a standard electrochemical cell using a platinum contra-electrode. Anodic voltage was applied to the backside of the sample using a pressed metal contact. The etching process was performed in the galvanostatic regime for a current density ranging from a few tenths to a few units of mA cm^{-2} . The main focus of this work was etching in organic electrolyte solutions. This is because in aqueous solutions macropores could be obtained only on *p*-type Si with resistivity higher than $20 \text{ } \Omega \text{ cm}$. The organic electrolyte contained 4 vol% aqueous HF in DMSO or DMF. In some cases water (1/4 of volume) was added to the solution. The resistivity of organic electrolytes used are a few orders higher than that of the aqueous ones. This is caused by the lower dissociation of HF due to the lower values of the dielectric constants of the

solvents ($\epsilon = 45$ for DMSO and $\epsilon = 36.7$ for DMF). The resistivity values for the 4% HF solutions used in this work are listed in table 7.3.

Table 7.3 Resistivity values for the 4% HF solutions used.

4% HF in	$\rho, \Omega \text{ cm}$ (At room temperature)
H ₂ O	21.5
DMSO	14×10^3
DMF	7.4×10^3

SEM was done on both the top view and the cross section. In order to obtain the cross section the samples were cleaved. For a rough surface, to make the picture of the top view more distinct, a thin layer (1–2 μm) was removed by polishing.

7.3.2.1 Electrochemical etching of silicon samples using 4% HF in DMF

The silicon samples with resistivities $\rho = 7.5 \Omega \text{ cm}$ and $20 \Omega \text{ cm}$ prepatterned with pits of lattice period (a) = 12 μm were etched using 4% HF in DMF with a current density of 1.6 mA/cm^2 for a 25 hours and 2 mA/cm^2 for 4 hours respectively.

7.3.2.2 Electrochemical etching of silicon samples using 4% HF in DMSO

The silicon samples with resistivities $\rho = 20 \Omega \text{ cm}$ prepatterned with pits of lattice period of $a = 12 \mu\text{m}$ were etched using 4% HF in DMSO with a current density of 2 mA/cm^2 for a 3 hours. The etching of silicon samples with resistivity, $\rho = 7.5 \Omega \text{ cm}$, prepatterned with pits of lattice period, $a = 4 \mu\text{m}$ was performed under a current density of 1.6 and 1.77 mA/cm^2 for 2 hours. The experiments were also carried out on silicon samples ($\rho = 7.5 \Omega \text{ cm}$) prepatterned by pits of lattice period 4 μm by adding water to DMSO electrolyte solution in a ratio of (4 vol% HF in DMSO: H₂O = 4: 1 v/v) and with a current density of 2 mA/cm^2 . A porous silicon membrane was fabricated from silicon sample of resistivity, $\rho = 7.5 \Omega \text{ cm}$ using 4% HF in DMSO electrolyte solution using a current density of 3 mA/cm^2 and an etching time of 3 hours.

7.4 Experimental for Chapter IV

All preparation and handling of starting materials and subsequent products were carried out under vacuum or argon by using Schlenk techniques. Solvents were dried over sodium-potassium alloy and distilled under argon prior to use and then condensed into a reaction flask under vacuum shortly before use. The starting materials NaOBu^t and FeBr₂ (ferrous bromide) were purchased from Aldrich. Ferric chloride and ferrous chloride which were used in the second part of the experiment were obtained from BDH (British Drug House) chemicals and Merck respectively.

7.4.1 Preparation of iron oxide layers on porous silicon using a metallorganic precursor

The solution [Fe(OBu^t)₂(THF)]₂ precursor in THF has been prepared according to published procedure.⁹ Briefly, solution of NaOBu^t (0.68 g, 7.08 mmol) was added to FeBr₂ (0.76 g, 3.54 mmol) in dry degassed THF (100 ml) at *ca.* 0 °C under argon. The mixture was stirred for 24 h at ambient temperature, filtered and the filtrate then was used in further experiments for the functionalisation of PS samples. The 25 ml of the filtrate was added to the hydroxyl functionalised macroporous silicon samples (1x1cm²) under argon. The mixture was sonicated for one hour. PS samples were washed under argon with dry hexane (3 × 15 ml) and then twice with wet diethyl ether (2 × 15 ml). The argon was removed and the PS samples were heated at 100°C under vacuum for 12 hours using an oil bath.

7.4.2 Preparation of magnetite-porous silicon composite

The porous silicon samples used in the present studies were both *n*-type and *p*-type silicon. The *n*-type macroporous silicon used in this study has a system of regular cylindrical pores of micrometer diameter and high aspect ratio.¹⁰ The starting material was single-crystal (100)-oriented Czochralski-grown *n*-type silicon with resistivity $\rho = 15 \Omega \text{ cm}$. A standard photolithographic process was employed to form pits spaced 12 μm apart on the polished surface of the silicon wafer. Deep pores were etched electrochemically in a 2.5% (v/v) aqueous-ethanol solution of HF for 300 to 450 min under backside illumination¹⁰ at a voltage of 5V and a constant current density of $j = 3$

mA/cm^2 . The pore depth was 200-250 μm and pore diameter $d = 3 - 4.5 \mu\text{m}$. The *p*-type silicon samples used for the present investigations were prepared by electrochemical etching in 4% HF in DMF electrolyte solution at a current density of 7.7 mA/cm^2 and an etching time of 6 hours. The *n*-type and *p*-type porous silicon samples were first etched with HF (2 wt%) and then functionalised with hydroxyl groups, as reported earlier.¹¹ The magnetite nanoparticles were prepared according to published procedure¹² with slight modifications. In brief, FeCl_2 and FeCl_3 were weighed by maintaining the stoichiometry of $\text{Fe}^{3+}/\text{Fe}^{2+} = 2$. Both were dissolved in 100 ml of 1.0 M NaCl aqueous solution (deoxygenated water) under argon. Sodium chloride was used to adjust the ionic strength of the iron solutions. The above solution was placed in a water-bath preheated to 25°C with ultra-sonicating. Concentrated ammonia solution was added drop-wise until the pH reached 9. The hydroxyl functionalised silicon samples were introduced to this magnetite solution. The dark precipitate together with the porous silicon samples were washed with deoxygenated water for three times followed by solvents using one solvent each time for one study. The solvents used for washing were ethanol, tetrahydrofuran (THF), chloroform and diethyl ether. The composite samples after washing with solvents were dried under vacuum for 9-10 hours. The PS-magnetic composites were further annealed under high vacuum (10^{-5} Torr) at a temperature of 350°C and 450°C for three hours.

7.5 Experimental for Chapter V

All alkoxides (TEOS, aluminium iso-propoxide, europium isopropoxide and erbium isopropoxide) and europium chloride were obtained from Aldrich. The micro-channel glass samples were provided by State Optical Institute, St. Petersburg. The channel glasses were having pore size of 8-9 μm and a thickness of about 0.05cm.

7.5.1 Preparation of rare earth doped aluminosilicate xerogel/glass-porous silicon composite

The precursor for rare earth doped sol-gel glass was prepared as reported earlier.¹³ The preparation of PS-glass composites is schematically presented in the figure 5.1 of chapter

V. Erbium iso-propoxide and europium isopropoxide/chloride have been used as precursors for Er- and Eu- doped samples respectively.

The preparation of Eu^{3+} doped $\text{Al}_2\text{O}_3\text{-SiO}_2$ sol was carried out as previously described by Nogami et al.¹³ In brief, the $\text{Si}(\text{OC}_2\text{H}_5)_4$, TEOS (4.5 g, 0.021 moles), was first hydrolysed for 1 h at room temperature with a solution of H_2O , $\text{C}_2\text{H}_5\text{OH}$ and HCl in the molar ratios 1: 1: 0.0027 per mole of $\text{Si}(\text{OC}_2\text{H}_5)_4$. $\text{Al}(i\text{-OC}_3\text{H}_7)_3$ (2.08 g, 0.01 moles) was added to this solution, followed by stirring for 15 min at 70°C . After cooling at room temperature, $(\text{Er}(\text{OPr}^i)_3)$ (0.1 g, 0.29 mmoles) was added and stirred for 1 h. The resultant homogenous solution was hydrolysed by adding the mixed solution of H_2O , $\text{C}_2\text{H}_5\text{OH}$ and HCl . In this second reaction, the molar ratio was maintained at 4: 1: 0.011 per mole of alkoxide. We have optimised that the conversion of this sol to gel takes place within 30 minutes of final stirring. For the preparation of Eu^{3+} doped alumino-silicate sol, 2wt% of europium isopropoxide/chloride was added to the aluminosilicate sol in place of erbium isopropoxide in the above procedure followed by hydrolysatation and further gelation.

The porous silicon samples used in the present studies were both *n*-type and *p*-type silicon. A set of porous silicon samples has been fabricated through the electrochemical etching in HF based electrolyte. Single crystal (100)-oriented, Cz-grown, *p*-type Si wafers of resistivity, $\rho = 10 \Omega \text{ cm}$ have been used for this experiment. The *n*-type macroporous silicon used in this study has a system of regular cylindrical pores of micrometer diameter and high aspect ratio.¹⁰ The starting material was single-crystal (100)-oriented Czochralski-grown *n*-type silicon with resistivity $\rho = 15 \Omega \text{ cm}$. A standard photolithographic process was employed to form pits spaced $12 \mu\text{m}$ apart on the polished surface of the silicon wafer. Deep pores were etched electrochemically in a 2.5% aqueous-ethanol solution of HF for 300 to 450 min under backside illumination¹⁰ at a voltage of 5V and a constant current density of $j = 3 \text{ mA/cm}^2$. The pore depth was 200-250 μm and pore diameter $d = 3\text{-}4.5 \mu\text{m}$. The *n*-type and *p*-type porous silicon samples were first etched with HF (2 wt%) and then functionalised with hydroxyl groups, as reported earlier.¹¹

The porous silicon samples ($1 \times 1 \text{ cm}^2$) functionalised with hydroxyl groups were introduced into the rare earth doped sol prior to the second addition of acid – ethanol mixture and kept for slow drying under room temperature. The dried samples were heat

treated at different temperatures. The sintering was done by placing the green samples on alumina plate in a Nabertherm furnace. The as-prepared rare earth doped aluminosilicate glass-porous silicon samples were used for further studies.

The microchannel glass-rare earths doped aluminosilicate xerogel samples were prepared using the same procedure as described for porous silicon.

7.5.2 Preparation of rare earth doped xerogel-porous silicon composite material by vacuum infiltration method

The synthesis of aluminosilicate sol was performed analogously as it described in the section 7.5.1 above.

The porous silicon sample was placed in the chamber and vacuum (29-30 mbar) was slowly applied to the sample. The "sol", just before its gelation point was poured onto these porous silicon samples and vacuum assisted filtration was used to pull the sol through the pores to form fibres. The pouring of sol before its gelation point is important as this defines the viscosity of the sol and its amount passing through the matrix.

7.5.3 Preparation of rare earth doped xerogel-microchannel glass composite material by vacuum filtration method

The micro-channel glasses were cleaned by using acetone and dried. A set-up for the fabrication of microtubes is presented in figure 5.18 of the chapter V. The method of preparation of fibres, is similar to one above for the fibres prepared using porous silicon membranes. In brief, the micro-channel glass samples were placed in the chamber and applied vacuum (29-30 mbar) slowly during the initial stage. The "sol", just before its gelation point was poured onto these micro-channel glass samples. The vacuum assisted filtration resulted in the formation of xerogel microtubes inside the micro-channel glass matrix. The composite is dried at room temperature and further annealed at 500°C for 2 hours heating time. The microcapillaries can be extracted from the matrix by a simple cut on the micro-channel glass template.

7.6 Experimental for Chapter VI

All experiments were carried out using the Schlenk techniques under argon.

The mesoporous silicon was prepared using a standard procedure of anodic etching of *p*-type Si(100) wafer with 1: 1 48% HF(aqueous)/EtOH in a Teflon cell. The macroporous silicon samples were prepared by electrochemical etching in 4% HF in DMF with silicon sample of resistivity 10 Ω cm.

The porous silicon samples were first etched by a HF: NH₄F (4:1) mixture for 10 minutes followed by rinsing with de-ionised water (Millipore, 18.2 M Ω) taking less than one minute. These etching conditions produce a mono-hydride porous silicon surface.¹⁴ The samples were then dried under argon gas.

To generate -OH functionalities on the silicon surface we followed a procedure as reported earlier¹¹ with slight modifications. The silicon samples were cleaned for 1 h in a H₂SO₄/H₂O₂ (7:3 v/v) mixture at $\sim$ 80°C and then cooled to room temperature. The cleaned substrates were rinsed with de-ionised water then treated further with a H₂O/H₂O₂/NH₃ (5:1:1 v/v/v) mixture and dried under vacuum. A hydrophilic surface condition has been related to the presence of a high density of silanol groups (Si-OH) or to a thin interfacial oxide film.¹

7.6.1 Chemical binding of ferrocene functionality

Two different procedures *via* spacer and direct bonding have been used in this work for the chemical binding of ferrocene to the silicon surface.

7.6.1.1 Bonding of ferrocene *via* a spacer

Hydroxylated porous silicon substrates were immersed in a 1:50 (v/v) solution of (3-chloropropyl)triethoxysilane (1 ml) and triethylamine (0.5 ml) in *n*-hexane (50 ml). The samples were then treated in ultrasonic bath for 20 minutes. Washings were done with hexane and then dried by the flow of argon gas. The samples were then treated with lithiated ferrocene in dry THF, place in an ultrasonic bath for 30 minutes and allowed to settle over night. Similar procedures were performed using (3-bromopropyl) trichlorosilane as a spacer but without using triethylamine as a catalyst.

7.6.1.2 Direct bonding of ferrocene

The H- terminated porous silicon wafers were irradiated under UV light in quartz Schlenk vessel for one hour in presence of Cl_2 gas. The resulting Cl-capped porous silicon was treated with lithiated ferrocene in dry THF, place in an ultrasonic bath for 30 minutes and allowed to settle over night. The procedure for the preparation of monolithiated ferrocene is described elsewhere.¹⁵

7.6. 2 Chemical bonding of cyclopentadienyl functionality

A solution of Sodium cyclopentadienide (CpNa) in THF was prepared according to published procedure.¹⁶

7.6.2.1 Bonding of Cp *via* a spacer

Hydroxylated porous silicon substrates were immersed in a 1:50 (v/v) solution of (3-chloropropyl)triethoxysilane (1 ml) and triethylamine (0.5 ml) in n-hexane (50 ml). The samples were then treated in ultrasonic bath for 20 minutes. Then the samples were washed with dry hexane and diethyl ether and dried under argon gas. The samples were then treated with the solution of CpNa (0.002 mol) in dry THF (20 ml), sonicated for 30 minutes and kept over night. Then the solution was decanted, the samples were washed 3 times with dry degassed THF and dried in vacuum for 12 hours at room temperature.

7.6.2.2 Direct bonding of Cp- to silicon surface

The H- terminated porous silicon wafers were irradiated under UV light in presence of Cl_2 gas. The resulting Cl-capped porous silicon was treated with metallated Cp, place in an ultrasonic bath for 30 minutes and kept over night. Then the solution was decanted, the samples were washed 3 times with dry degassed THF and dried in vacuum for 12 hours at room temperature.

7. 7 References

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VIII

Conclusions and Future Work

8.1 Thesis Conclusions

This thesis was focussed on the fabrication of porous silicon and the development of porous silicon based composite materials for the materials science applications. This work is resulted in the development of various composite materials.

Several different research areas have been developed in the thesis. These include the fabrication of porous silicon using various organic and aqueous electrolytes, preparation of magnetite-porous silicon composite, development of new rare earth doped xerogel/glass-porous silicon composites and finally the functionalisation of silicon surfaces with metallorganic groups. The possible application of porous silicon and porous silicon composite materials has been discussed.

The first part of this work was focused on the fabrication of porous silicon using different aqueous and organic electrolytes respectively. In Chapter II the etching of porous silicon using H_2O -HF electrolyte under high current density resulted in the formation of unusual *island-like* structures on (100) silicon. The islands were uniformly distributed forming a regular structure having luminescence characteristics. Porous silicon samples were fabricated using 1: 1: 1 HF: $\text{C}_2\text{H}_5\text{OH}$: H_2O + 10^{-3} M CTAC which only require a short etching time for the preparation of good macropores silicon with high aspect ratios. We have also found that for HF: $\text{C}_2\text{H}_5\text{OH}$: H_2O + 10^{-3} M CTAC electrolyte the increase in current density resulted in the formation of more branched pores. The etching of the samples in ethanol-HF electrolyte without CTAC resulted in the formation of spikes in the silicon matrix. The luminescence intensity of the samples etched using ethanol-HF electrolyte shows an increase, with respect to sample resistivity, When compared to the results obtained for the samples etched using similar electrolyte but with the addition of CTAC, the low resistivity sample showed an increase in the luminescence when compared to the high resistivity sample. It was suggested that CTAC plays a role as a surfactant influencing on the etching process kinetics. The etching of the samples using 5: 9: 26 HF: $\text{C}_3\text{H}_8\text{O}$: H_2O v/v/v demonstrated the formation of etch pits and star-shaped pores in *p*-type porous silicon samples. The pore depth decreased with increasing silicon resistivity, which is also observed in other aqueous electrolytes. The investigation of different HF percentage and pH in aqueous electrolytes showed that the porosity of the PS samples increased linearly with pH values up to 1.45, it is then stabilised at higher pH values. It was also

found that lower concentrations of HF and higher pH are favourable for the formation of luminescent microporous silicon samples.

In Chapter III porous silicon samples were prepared by etching using organic electrolytes. The patterning of silicon samples prior to etching was investigated. In the patterned samples we have found that in order to obtain regular macropores, the pattern of pits should fit the average distance between the random pores. In the absence of such a correspondence, the two types of pores were formed. The morphology of these types of pores differs drastically. The presence of pits, which act as nucleation sites, plays a crucial role in the mechanism of macro-pore formation in *p*-type (100) Si. The macropores obtained in organic electrolytes have strongly pronounced etch features, which characterize the etching process as anisotropic. It has been confirmed in our investigation on porous silicon that increasing the electrolyte water content leads to a decrease in this anisotropy. Electrochemical etching of *p*-type Si allows the formation of macroporous layers with higher porosity than for *n*-type Si. However, the stable growth of macropores is restricted by the narrow range of possible lattice periods. The preparation of porous silicon using 4% HF in DMF suggests that the best parameters to etch regular *p*-type macropores of silicon are a solution of 4% HF in DMF, with a low etching current (in order to avoid electropolishing). It has also been demonstrated that the etching current density is crucial in determining the pores depth, and an increasing of etching current increases the electrochemical reaction, so increases regularity and depth of pores.

The porous silicon samples prepared by using 15 vol% HF in DMF + 0.11M TBAP demonstrated that porous silicon samples can be etched out with higher current density by using conductive salts (here TBAP) in HF in DMF solution which otherwise would have resulted in electropolishing. Thus by the right combination of electrolytes it is possible to etch out good quality macropores. The electrochemical etching in formamide solution resulted in sponge like macroporous silicon structures but in reality composed of micropores. The photoluminescence properties of these porous structures were studied. The electrochemical etching in acetonitrile electrolyte solution put forward the dependence of porosity of the samples on various parameters like current density and the sample resistivity. The possible overview of these results could be useful in preparing porous silicon samples with controlled dimensions.

Then further work (Chapter IV) has been focused on the preparation of porous silicon-magnetite composite material. We have successfully prepared iron oxide layers on hydroxyl-terminated porous silicon using metallorganics precursors and sol-gel processing. We have demonstrated that magnetite-porous silicon composites can also be prepared by in situ co-precipitation of magnetic iron oxide nanoparticles from the mixture of iron ($\text{Fe}^{3+}/\text{Fe}^{2+}$) salts taken with ammonia solution. We have found that this process results in the self-organisation of magnetite nanoparticles into dendrite- or fractal-like magnetite structures on porous silicon samples. We believe the formation of fractal structures involves a DLA model in combination with the porous substrate effect and dipole-dipole interactions between the nanoparticles. The sintering of porous silicon magnetite composites in vacuum resulted in the formation of the micron size linear arrays of magnetite microparticles on porous silicon. The formation of these arrays most likely can be explained by the grain growth and fusion of magnetite nanoparticles. Sintered magnetite-porous silicon samples demonstrated relatively low room temperature magnetoresistance.

In Chapter V was dedicated to the development of sol-gel aluminosilicate xerogel (glass)-porous silicon composites. We have demonstrated that rare-earths (Erbium and Europium) doped aluminosilicate xerogel (glass)-porous silicon composites can be effectively prepared using standard sol-gel processing. The fabrication of rare earth doped aluminosilicate xerogel/glass fibres using porous silicon and other porous matrices was one of the highlights of the thesis. The fibres were prepared by a new vacuum filtration technique on porous matrices. The fibres, which are produced by this method, showed whispering gallery mode phenomenon, which was not reported before for aluminosilicate sol-gel materials and microcapillary optical devices. This technology and devices might have potential applications in optics field. In overall the porous silicon acts a good matrix for the preparation of different xerogel and glass composites, which can have potential applications in photonics.

In Chapter VI, we have shown that silicon both flat and porous can be effectively functionalised with ferrocene and cyclopentadienyl groups using new organometallic approaches. We have developed two methods to functionalise silicon surfaces with the ferrocene or cyclopentadiene: *via* alkylsiloxy- spacer groups and by direct bonding to the

silicon surfaces. The functionalised silicon surfaces were characterised by using various spectroscopic techniques. All these techniques have proven the formation of new species and their covalent binding to the silicon surfaces after their treatment. We also believe that new cyclopentadienyl and metallocene functionalised surfaces might find potential applications in sensing and molecular electronics.

In summary our work on porous silicon demonstrated the high potential of this material for modern science and technology. The preparation of various composite materials based on porous silicon proved to be useful in various fields such as optical, electronic and micromechanics engineering field. The emerging nanotechnology area will also be highly affected by the new materials developed using porous silicon. The molecular electronics is gaining attraction in recent years due to miniaturisation of silicon technology and the development of metallorganic chemistry on porous silicon will be leap towards the nanotechnology future. The optical fibres fabricated by using porous silicon and other porous matrices might be useful for optoelectronics, optical communications and other potential application. For example, the incorporation of biological specimens into the optical fibres can lead to the development of bio-sensing optical materials.

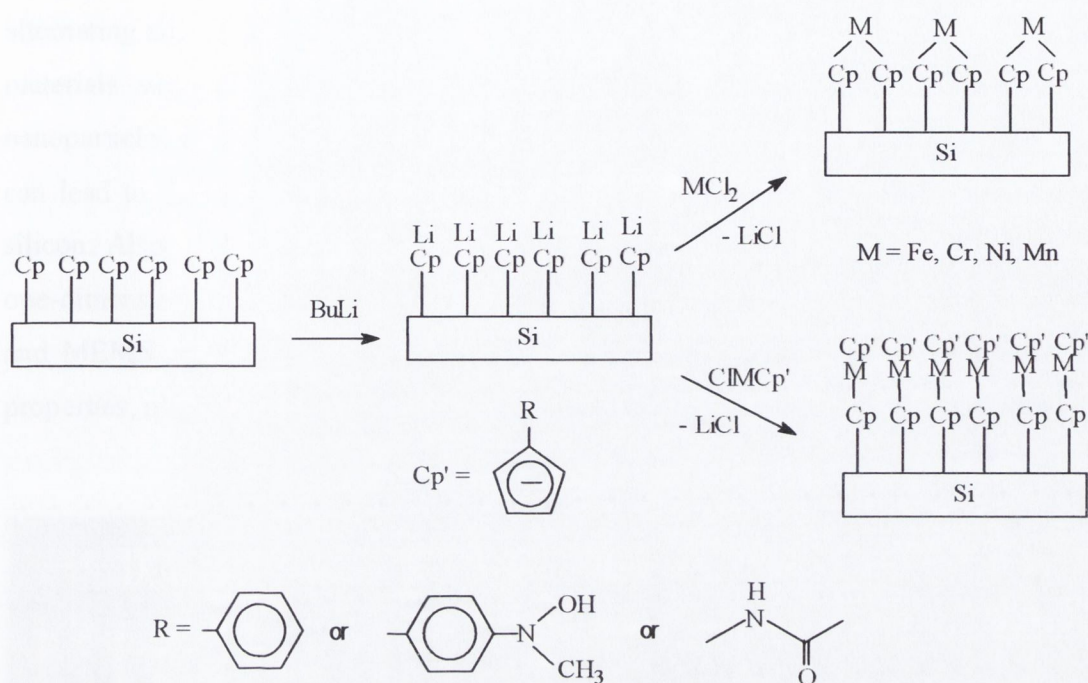
8.2 Future Work

We believe that future work could concentrate on four main areas:

- (i) Further development of metallorganic chemistry on porous silicon and flat silicon surfaces.
- (ii) Development of magnetite composite materials with nanoporous and grooved silicon.
- (iii) Fabrication of optical fibres using other porous matrices and aluminosilicate solgel materials using rare earths other than Er^{3+} and Eu^{3+} .
- (iv) Preparation of porous silicon by electrolytes that can functionalise in situ – *two in one* approach.¹

8.2.1 Further development of metallorganic chemistry on porous silicon and flat silicon surfaces

The development of Cp-modified and ferrocene modified porous silicon surfaces opens up new areas of metallorganic chemistry on silicon surfaces. The future work will be concentrated on metallate Cp-functionalised PS-surfaces using BuLi. The halogen derivatives of metals (Fe, Cr, Ni and Mn) can be reacted with the modified surface giving different metallocene on silicon surface composites (Scheme 8.1). First, the metal dichloride will be reacted with the lithiated surface giving metallocene complexes bound to Si-surface *via* both cyclopentadienyl rings. Then, the reaction of monocyclopentadienyl derivatives $\text{MCp}'\text{Cl}$ ($\text{M} = \text{Fe, Cr, Ni and Mn}$) having different substituents in the Cp-ring with lithiated Cp modified PS will give mixed Cp- Cp' (Cp' – substituted cyclopentdienyl ligand) metallocenes bound to the surface *via* one Cp-ligand. The asymmetric $\text{MCp}'\text{Cp}$ fragments might serve as molecular magnets incorporated on silicon. This might lead to the formation of new ordered nanostructured materials with variable characteristics, which might be potentially applied for spin-polarised electronics. In this case the innovative data memory can be achieved by means of magnet-semiconductor combination. The information might be stored via the magnetic polarization of the electrons in the semiconductor – i.e. the leftward or rightward spin. The metallocenes incorporated into pores could serve as molecular magnets and should have a significant effect on the properties of porous silicon. The future work looks into an investigation of the influence of electro-magnetic field and laser radiation on the properties of porous Si-magnetic composites. The surfaces will also be investigated by AFM, XPS and SIMS. Then work will be extended to react the HO-Si(surface) with different alkoxides and amide metal (Fe, Ni, Cr, Ce, Nd, Eu, Yb) complexes to get metallasiloxane species attached to Si-surface and incorporated inside the pores. Photoluminescence (PL) of the prepared composite will be studied in order to find the effect of metallorganic species on PL properties of porous silicon.



Scheme 8.1 Future work on metallocene-silicon composites (Cp' – substituted cyclopentdienyl ligand).

The chemically modified silicon surfaces will also be studied using advanced scanning tunnelling microscopy (STM) techniques and computer simulations methods. STM and other advanced techniques will give an insight into the orientation of the metallorganic moieties on the surface of silicon. Application of this technique in combination with computer simulations will help to manipulate the properties of the material.

8.2.2 Development of magnetite composite materials with nanoporous and grooved silicon

The possible incorporation of magnetite nanoparticles on porous silicon was successfully studied and it is possible to extend this area by incorporating nanoparticles to other relevant silicon matrix such as grooved silicon (Figure 8.1) The grooved silicon seems to be a very promising matrix for the incorporation of different materials giving novel composites with various exciting properties. The magnetite composite material based on grooved silicon can result in the fabrication of arrays of packed magnetite blocks made of nanoparticles with

alternating silicon walls. Further annealing of such composite could lead to new composite materials with interesting magnetic properties. The idea of incorporating magnetite nanoparticles into nanoporous silicon of pores less than 2 nm is tricky and if successful, it can lead to the uniform packaging of nanoparticles in one dimension along the walls of silicon. Also, if silicon could be selectively etched out it might lead to the fabrication of one-dimensional magnetite arrays, which will have high a potential for magnetic storage and MEMS applications. The incorporation of other magnetic materials, having similar properties, might also be addressed in the future work.

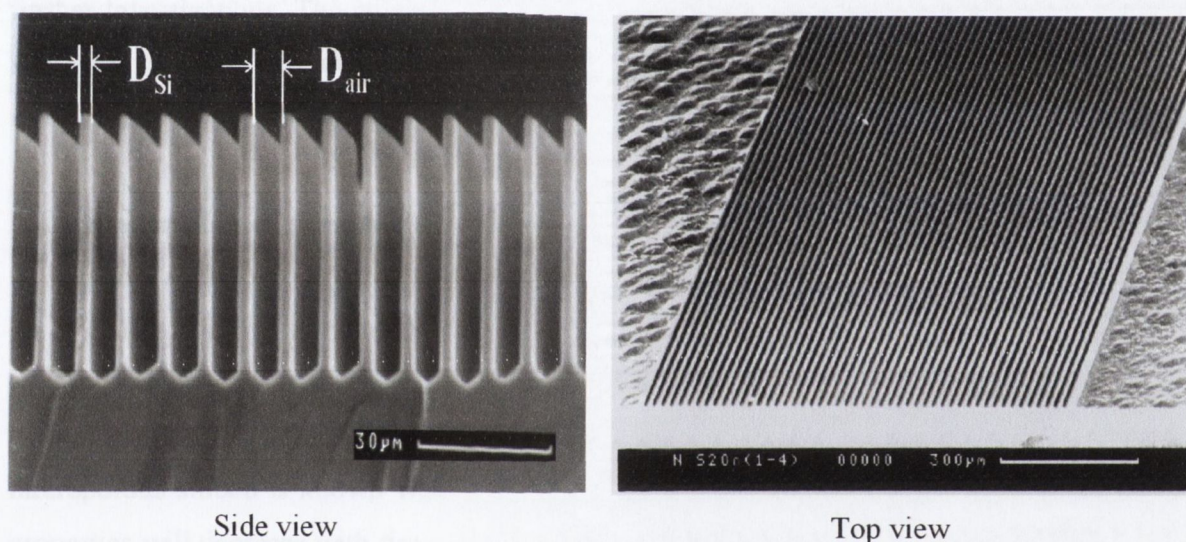


Figure 8.1 Side and top view of the grooved silicon

8.2.3 Fabrication of optical fibres using other porous matrices and aluminosilicate solgel materials doped with rare earths other than Er^{3+} and Eu^{3+}

The successful development of optical fibres described in chapter V will be applied to other substrates also. The development of fibres using alumina templates is another research area to be addressed in the future. The selective dissolution of alumina should help to make freestanding optical fibres. Also, different pore size porous matrices will be used in the future work. It may be possible to manipulate the properties of the fibre with different diameter fibres. The fabrication of new microstructures using grooved silicon is another interesting aspect. The formation of pillar like structures from aluminosilicate gel using

grooved silicon might have potential optical applications. The formation of fibres will be extended to other sol-gel materials like titania which is well known for its photocatalytic activities. Thus titania fibres and other sol-gel fibres will be the focus in future work on optical fibres.

The use of rare earths other than europium and erbium is also in focus. For example rare earths like terbium and ytterbium will be incorporated as a part of future work. The composites made out with these rare earths will be studied in detail. By using different lanthanides in porous silicon matrices will enable to elucidate the detailed mechanism of the PL of lanthanides in these types of porous structures, which in other words calls for further investigations. The stresses from the porous structures during annealing need to be studied in detail. Future research will study selected rare earth-doped porous silicon composites.

8.2.4 Preparation of porous silicon by electrolytes that can functionalise in situ – *two in one* approach

As a continuation of our work on porous silicon, the insitu functionalisation of porous silicon using organic electrolytes should be addressed in the future work. The preparation of porous silicon can be coupled with the insitu functionalisation. The PL from microporous silicon is known well but on exposure to air for long time, the luminescence properties will decrease with time. The insitu functionalisation might lead to the formation of silicon-carbon bond which are having greater stability towards oxidation and will lead to the decay in luminescence characteristics of porous silicon.¹ Normally functionalisation is done by forming the Si-C bond after the fabrication of porous silicon. So the advantage of insitu functionalisation comes here that we can functionalise the PS after the etching process thereby avoiding the extra process.

The fabrication of porous silicon using organic electrolytes, which are not mentioned in the thesis, is another area that is to be dealt with as a point of future work. The parameters, which are not addressed in thesis such as the temperature dependence on the porous silicon formation. For example the low temperature preparation of the porous silicon may result in different morphology structures. While silicon is the dominant material for electronic and micro-mechanical devices, it has only recently been used for medical and biological

applications.² Porous Silicon is advantageous for some of these applications because of its large surface area. Micro- and mesoporous silicon, for example, are found to be biocompatible materials that bond directly with healthy bone by calcification, which is an advantage if implantation in living tissue is desirable.³ Because of its biodegradability and non-toxicity, mesoporous silicon doped with trace elements has been proposed to serve as an implanted long-term delivery source.⁴ The functionalisation of porous silicon for the biological purpose is another prospective for combination of biomedical and nanotech fields. The development of biochips is already in progress so an extension to this field will be an asset for future.

8.3 References

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Appendix I

Supporting Information

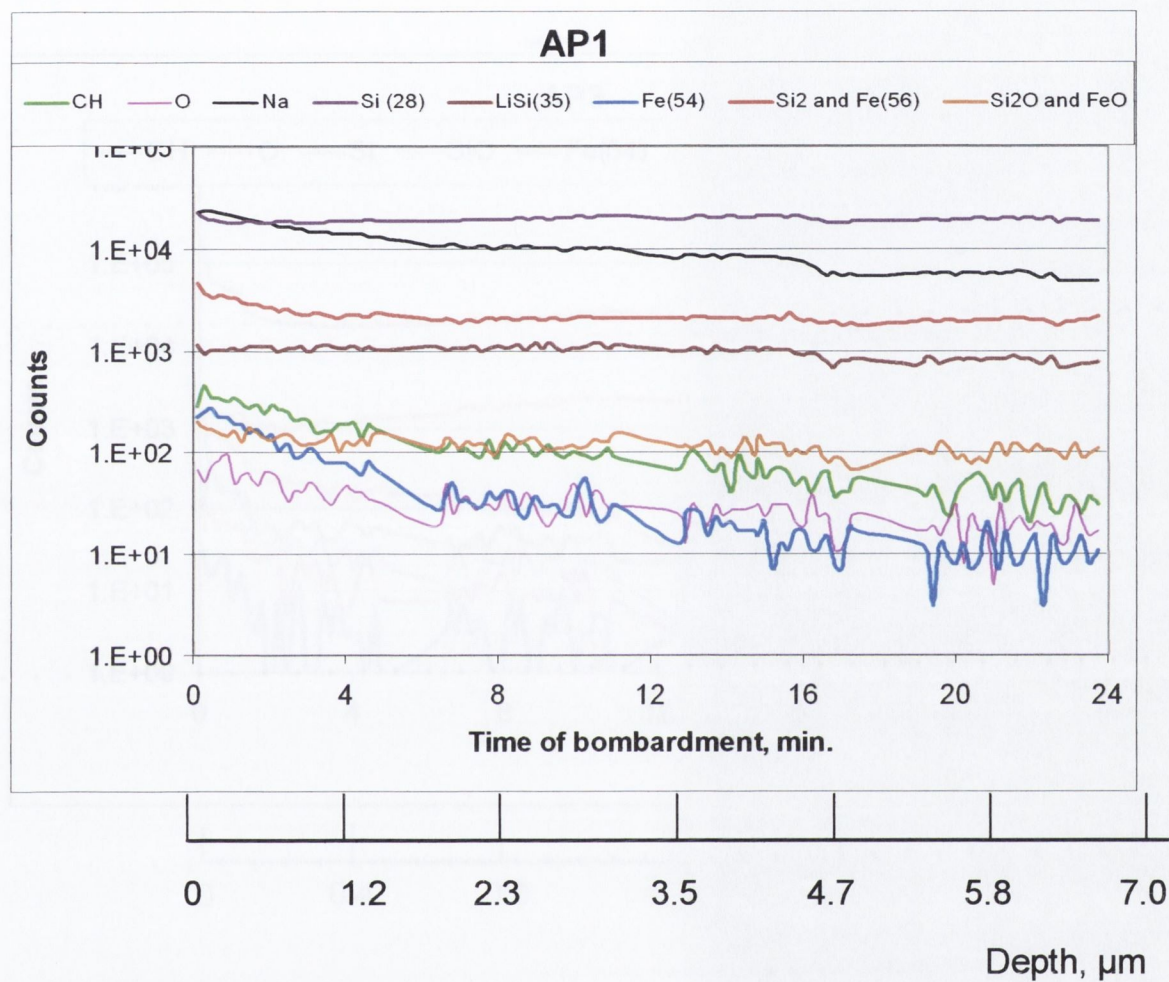


Figure 1 Depth analysis for ferrocene directly bonded to porous silicon

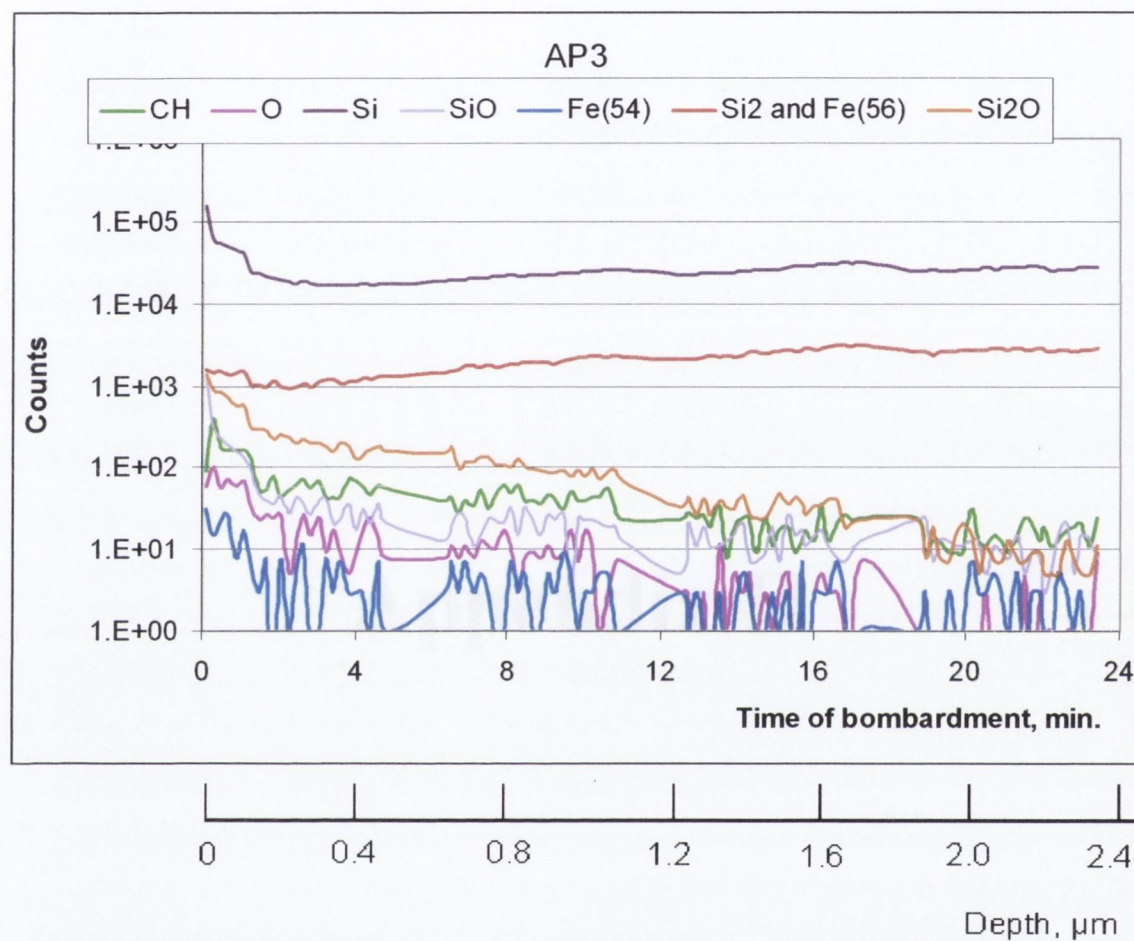


Figure 2 Depth analysis of ferrocene bonded to silicon via (3-chloropropyl triethoxy silane) spacer.

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