Photoluminescence of nanostructured silicon

This item was submitted to Loughborough University's Institutional Repository by the/an author.

Additional Information:

• A Doctoral Thesis. Submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy at Loughborough University.

Metadata Record: https://dspace.lboro.ac.uk/2134/20999

Publisher: © Adwan Nayef Hameed Al-Ajili

Rights: This work is made available according to the conditions of the Creative Commons Attribution-NonCommercial-NoDerivatives 2.5 Generic (CC BY-NC-ND 2.5) licence. Full details of this licence are available at: http://creativecommons.org/licenses/by-nc-nd/2.5/

Please cite the published version.
This item was submitted to Loughborough University as a PhD thesis by the author and is made available in the Institutional Repository (https://dspace.lboro.ac.uk/) under the following Creative Commons Licence conditions.

You are free:
- to copy, distribute, display, and perform the work

Under the following conditions:

**Attribution.** You must attribute the work in the manner specified by the author or licensor.

**Noncommercial.** You may not use this work for commercial purposes.

**No Derivative Works.** You may not alter, transform, or build upon this work.

- For any reuse or distribution, you must make clear to others the license terms of this work.
- Any of these conditions can be waived if you get permission from the copyright holder.

Your fair use and other rights are in no way affected by the above.

This is a human-readable summary of the Legal Code (the full license).

For the full text of this licence, please go to:
http://creativecommons.org/licenses/by-nc-nd/2.5/
PHOTOLUMINESCENCE OF NANOSTRUCTURED SILICON

By

Adwan Nayef Hameed Al-Ajili

A Doctoral Thesis submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of Loughborough University

4th November 1996

© by Adwan Nayef Hameed Al-Ajili 1996
Abstract

The photoluminescence (PL) emitted by porous silicon has been investigated under different conditions of excitation using a pulsed nitrogen laser source, and the continuous tunable UV synchrotron source at Daresbury Laboratory. The project involved sample preparation, and PL measurements using a custom-built optical laser-based system for lifetime measurements. This in itself necessitated software and hardware development to enable interfacing and datalogging using an IBM-compatible PC. The equipment development formed a major part of the project.

A group of porous silicon sample have been studied covering a range of PL emission wavelength red to green, at temperatures 77-295 K. The PL peak is found to shift to higher frequency with decreasing temperature, but the PL decay of all porous silicon samples was intrinsically nonexponential under different laser intensities at different temperatures. The PL lifetime, defined as 1/e times the initial intensity, decreased as emission energy increased, and increased with decreasing temperature. Additionally PL lifetime measurements show two luminescence bands were emitted over the wavelength range 480 - 750 nm by green, orange and red porous silicon.

Information about the nanostructure of porous silicon have been determined from PL and EXAFS, as well as from electron microscopy. In particular the optical properties of the silicon-based nanostructured materials, obtained from PL and photoluminescence excitation (PLE) measurements, have been correlated with structural information from Si K-edge EXAFS taken at Daresbury Laboratory. Electron microscopy was used to study the relation between the nanostructure and PL of porous Si, and to investigate porous Si structure. The samples had different PL spectra and were expected to have different nanostructures. Platelet Si and Si crystallites in porous Si layers were observed in all samples. The size of crystallites ranged from 4 - 10 nm. Diffraction patterns show these porous Si samples have a crystalline structure.

In order to choose a suitable electrode material for porous Si an investigation was made of InO\textsubscript{x} and ITO\textsubscript{x} prepared by dc reactive sputtering from indium and indium-tin alloy targets respectively in an oxygen/argon atmosphere. The compositions of the InO\textsubscript{x} films, determined from EDX, have been used to show how x varies as a function of O\textsubscript{2} partial pressure in the flow to the sputtering system. Reflectance and transmittance of the InO\textsubscript{x} films and ITO\textsubscript{x} films were measured in the photon energy
range 0.5 - 6.0 eV, leading to determination of absorption coefficients as a function of \( x \). The optical band gap, which appears as \( x \) is increased, was found to increase monotonically with \( x \). The dc resistivity of \( \text{InO}_x \) films has been determined as a function of composition. Refractive index for transparent films and thickness of all \( \text{InO}_x \) and \( \text{ITO}_x \) films has been measured. The local structure of \( \text{InO}_x \) and \( \text{ITO}_x \) samples is shown by extended x-ray absorption fine structure (EXAFS) to have much configurational disorder throughout the composition range.

A wide band gap transparent conducting thin film of \( \text{ITO} \) was sputtered onto the surface of porous silicon to study the electrical and optoelectrical properties and potential for use of porous Si in devices. With positive bias applied, a yellow electroluminescence (EL) was observed with relatively wide spectrum of about 1.83 eV FWHM, and its peak centred at about 2.03 eV. No light emission was observed under reverse bias condition. EL from porous Si samples has been recorded at different applied voltages, and the PL and EL spectra have been compared. \( I-V \) characteristics of porous Si have been determined for both forward and reverse bias voltages.
Acknowledgements

I take this opportunity to offer my gratitude to those people who have made my research both possible and fulfilling.

I am grateful to Prof. K. R. A. Ziebeck for allowing, encouraging and supporting me to study in Department of Physics and to Dr. S. C. Bayliss for her kindness support and supervision throughout my studies and without them much of this work would not have been done.

I would like to express my gratitude for Prof. R. P. Howson for permitting me to make extensive use of his computing equipment and other facilities and to Dr. M. D. Crapper for his supervision of writing up my research and his assistance with the production of my thesis.

I would like to acknowledge Q. Zhang and P. Harris at the Department of Applied Physics, De Montfort University, for help with porous Si preparation and to J. S. Bates (IPTME, Loughborough University) for performing the electron microscopy. It is a pleasure to acknowledge my friend and colleague N. Al-Maliky for his computing assistance. My sincere thanks to the technical and administrative staff at Department of Physics for their cheerful cooperation.

Finally, I am grateful to the Council for the Central Laboratory of Research Councils for beamtime awards for steady-state EXAFS, photoluminescence and electroluminescence at Daresbury Laboratory Synchrotron Radiation Source, United Kingdom.

Last but not least, my special thanks to my wife and children for their generous patience and understanding whilst undertaking this work.
# Table of contents

## Chapter 1  Correlation between electronic and structural properties of semiconductors

1.1 Introduction........................................................................................................1  
1.2 Determination of the relationship between the atomic system and electronic subsystems of solids...............................................................2  
1.2.1 Atomic structure.........................................................................................3  
1.2.2 Chemical bonding......................................................................................6  
1.2.3 Electronic structure...................................................................................8  
1.3 Band structure.................................................................................................9  
1.4 Nanostructured materials (silicon and porous silicon)..............................14  
1.5 Radiative recombination in semiconductors.............................................18

## Chapter 2  Optical properties of semiconductors

2.1 Introduction.......................................................................................................22  
2.2 Density of states of non-crystalline materials............................................22  
2.3 Microscopic structure and composition of inhomogeneous solids.........28  
2.4 Interband absorption....................................................................................30  
2.5 Absorption and reflection spectra...............................................................32  
2.6 The absorption edge.....................................................................................33

## Chapter 3  Photoluminescence and electroluminescence

3.1 Photoluminescence emission.........................................................................36  
3.2 Photoluminescence in amorphous silicon...................................................39  
3.3 Photoluminescence in porous silicon...........................................................42  
3.4 Photoluminescence excitation spectra in porous silicon..........................45  
3.5 Photoluminescence lifetimes in porous silicon..........................................46  
3.6 Photoluminescence temperature dependence in porous silicon.............48  
3.7 Electroluminescence in porous silicon.........................................................50
Chapter 4 Methods of determining structure of disordered or inhomogeneous media

4.1 Introduction.................................................................53
4.2 X-ray absorption spectroscopy ........................................54
4.3 EXAFS and porous Si.....................................................60
4.4 Characterisation by electron microscopy..............................61
4.5 Energy dispersive analysis of X-rays (EDAX).......................62

Chapter 5 Design and development of photoluminescence lifetime system

5.1 Introduction.................................................................64
5.2 Photoluminescence lifetime system.....................................65
5.3 Apparatus........................................................................66
5.3.1 Excitation source.........................................................66
5.3.2 Low temperature equipment.........................................67
  A. Vacuum system..............................................................67
  B. Cryostat..............................................................67
  C. Sample holder..............................................................68
  D. Temperature controller................................................68
5.3.3 Optics........................................................................70
  A. Collecting lens..............................................................70
  B. Monochromator............................................................70
  C. Filters............................................................................71
    1. Bandpass interference filters........................................71
    2. Neutral density filters................................................72
    3. Cut-off filters..............................................................72
5.3.4 Detectors.....................................................................73
  A. Photomultiplier tube......................................................73
  B. Silicon detector............................................................74
  C. InGaAs detector............................................................74
5.3.5 Amplifier.....................................................................75
5.3.6 Instrumentation..........................................................75
  A. Oscilloscope.................................................................75
  B. Data acquisition...........................................................76
5.4 Calibration of PL lifetime system.........................................76
Chapter 6 Sample preparation techniques

6.1 Methods of porous silicon preparation.......................................................... 78
  6.1.1 Porous Si samples for photoluminescence and EXAFS investigation .......................................................... 79
  6.1.2 Porous Si samples for electroluminescence investigation......................... 79

6.2 Methods of thin film preparation.................................................................... 80
  6.2.1 Preparation of InO\textsubscript{x} and ITO\textsubscript{x} thin films on PET ............ 81
  6.2.2 Preparation of ITO thin film on porous Si................................................. 82

Chapter 7 Steady-state photoluminescence and structural properties of porous Si

7.1 Introduction.................................................................................................. 83
  7.2 Steady-state photoluminescence.................................................................. 84
  7.3 Structural properties of porous Si............................................................... 88
    7.3.1 Extended X-ray absorption fine structure.............................................. 88
    7.3.2 Electron microscopy for porous Si......................................................... 92

Chapter 8 Investigation of photoluminescence lifetime in porous Si

8.1 Introduction.................................................................................................. 96
  8.2 General features of photoluminescence....................................................... 96
  8.3 Photoluminescence lifetime measurements............................................... 99
  8.4 Evolution of lifetime................................................................................... 104
  8.5 Photoluminescence lifetime for red-green emitting porous Si............... 109
  8.6 Photoluminescence at different excitation intensities............................. 112
  8.7 Temperature dependence of PL decay and integrated PL intensity...116

Chapter 9 Investigation of optical, electrical and structural properties of reactive sputtered InO\textsubscript{x} and ITO\textsubscript{x} thin films

9.1 Introduction................................................................................................ 119
  9.2 Determination of composition of InO\textsubscript{x} and ITO\textsubscript{x} thin films......... 120
  9.3 Determination of optical properties of InO\textsubscript{x} and ITO\textsubscript{x} thin films....121
Table of contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.3.1</td>
<td>The dual-beam spectrometer</td>
<td>121</td>
</tr>
<tr>
<td>9.3.2</td>
<td>Reflectance and transmittance spectra</td>
<td>123</td>
</tr>
<tr>
<td>9.4</td>
<td>Film thickness determination</td>
<td>124</td>
</tr>
<tr>
<td>9.4.1</td>
<td>Thickness determination using SEM</td>
<td>127</td>
</tr>
<tr>
<td>9.4.2</td>
<td>Thickness determination using interference fringes in reflection</td>
<td>128</td>
</tr>
<tr>
<td>9.4.3</td>
<td>Thickness determination using ellipsometry</td>
<td>130</td>
</tr>
<tr>
<td>9.5</td>
<td>Absorption coefficients and refractive indices of InO_x and ITO_x films</td>
<td>133</td>
</tr>
<tr>
<td>9.6</td>
<td>Local structure</td>
<td>136</td>
</tr>
<tr>
<td>9.7</td>
<td>Electrical properties of InO and ITO films</td>
<td>140</td>
</tr>
<tr>
<td>10</td>
<td>Electroluminescence in porous Si</td>
<td></td>
</tr>
<tr>
<td>10.1</td>
<td>Introduction</td>
<td>141</td>
</tr>
<tr>
<td>10.2</td>
<td>Investigation of electroluminescence in porous Si</td>
<td>141</td>
</tr>
<tr>
<td>10.3</td>
<td>Comparison between photoluminescence and electroluminescence</td>
<td>146</td>
</tr>
<tr>
<td>10.4</td>
<td>I-V characteristics of porous Si</td>
<td>159</td>
</tr>
<tr>
<td>11</td>
<td>Discussion, conclusion and suggestions for further work</td>
<td></td>
</tr>
<tr>
<td>11.1</td>
<td>Discussion</td>
<td>151</td>
</tr>
<tr>
<td>11.1.1</td>
<td>Porous Si samples</td>
<td>151</td>
</tr>
<tr>
<td>11.1.2</td>
<td>Steady-state PL</td>
<td>151</td>
</tr>
<tr>
<td>11.1.3</td>
<td>EXAFS of porous Si</td>
<td>152</td>
</tr>
<tr>
<td>11.1.4</td>
<td>Electron microscopy for porous Si</td>
<td>153</td>
</tr>
<tr>
<td>11.1.5</td>
<td>PL lifetime</td>
<td>154</td>
</tr>
<tr>
<td>11.1.6</td>
<td>InO and ITO thin films</td>
<td>155</td>
</tr>
<tr>
<td>11.1.7</td>
<td>EL</td>
<td>156</td>
</tr>
<tr>
<td>11.2</td>
<td>Conclusions</td>
<td>157</td>
</tr>
<tr>
<td>11.3</td>
<td>Suggestion for further work</td>
<td>159</td>
</tr>
<tr>
<td></td>
<td>References</td>
<td>160</td>
</tr>
</tbody>
</table>

Appendix: List of blications                                                  175
Chapter 1

Correlation between electronic and structural properties of semiconductors

1.1 Introduction

The study of solids is a rich scientific area, which depends on a great variety of experimental probes. The techniques using electromagnetic radiation are among the most fruitful of these. The very short wavelengths of x-rays are valuable, even essential, in examining the atomic lattices that define crystalline solids. Wavelengths from the ultraviolet through to the visible and infrared to millimetre range have enormous power for examining all aspects of solids. For semiconductors, radiation can be of use to determine many features; the crystal lattice, including the band gap, where light is absorbed; free electrons and holes, which also absorb light as they move; impurities and defects, which interact with light through their own vibrations in the lattice, or by ionisation processes. When semiconductors are formed into the microstructures that increasingly find use in devices, electromagnetic radiation also measures the dimensions and explores the interfaces of these artificial systems.

Therefore, most of the properties of semiconductors and their structures can be examined by light; alternatively to know how a semiconductor reacts to light, its basic properties must be understood. Of equal importance is the ability of optical analysis to contribute to applications of semiconductors. Such analysis can measure those properties which determine whether a semiconductor will serve well in a specific use, that is, optical methods can characterise semiconductors.

The very qualities that make semiconductors interesting and useful make it difficult to determine their intrinsic and extrinsic characteristics. The flexibility to choose design parameters, by selecting from the large family of semiconducting materials or creating new ones, requires equal flexibility in characterisation methods. The sensitivity to small amounts of impurities which makes semiconductors essential to the electronic and photonic industries means that small inadvertent changes or minute contamination during growth, for instance, have large effects. The performance of semiconductor...
Correlation between electronic and structural properties of semiconductors

The material must have a reasonably large energy gap between adjacent energy levels if it is to emit luminescence. Consequently it is luminescent found that solids are either large band gap semiconductors or insulators, since both of these are characterised by a filled electron band separated by a sufficiently large gap from an adjacent unfilled electron band [Azároff and Brophy (1963) and Pankove (1971)]. In the case of an insulator, the band gap corresponds to the energy of an ultraviolet photon, and visible luminescence is not expected from the pure material. Impurity atoms and defects, however, are always present, and these may possess electronic levels separated by a gap which corresponds to a photon of visible light [Azároff and Brophy (1963), Imbusch (1978) and Elliott (1990)].

1.2 Determination of the relationship between the atomic system and electronic subsystem of solids

The main feature which distinguishes amorphous from crystalline materials is the disorder of the atomic structure. It is of particular significance in semiconductors because the periodicity of the atomic structure is central to the theory of crystalline semiconductors. Bloch's theorem is a direct consequence of the periodicity and describes the electrons and holes by wavefunctions which are extended in space with quantum states defined by momentum. The theory of lattice vibrations has a similar
basis in the lattice symmetry. The absence of an ordered atomic structure in amorphous semiconductors necessitates a different theoretical approach. The description of these materials is developed instead from the chemical bonding between the atoms, with emphasis on the short range order bonding interactions rather than the long range order.

The structural disorder influences the electronic properties in several different ways which are summarised in Fig. 1.1. The similarity of the covalent silicon bonds in crystalline and amorphous silicon leads to a similar overall electronic structure—amorphous and crystalline phases of the same material tend to have comparable band gap. The disorder represented by the deviations in the bond lengths and bond angles broadens the electron distribution of states and causes electron and hole localisation as well as strong scattering of the carriers. Structural defects such as broken bonds have corresponding electronic states which lie in the band gap. There are also new phenomena which follow from the emphasis on the local chemical bonds rather than the long range transitional symmetry. The possibility of alternative bonding configurations of each atom leads to a strong interaction between the electronic and structural states and causes the phenomenon of metastability [Lannin (1988) and Street (1991)].

<table>
<thead>
<tr>
<th>STRUCTURE</th>
<th>ELECTRONIC PROPERTIES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bonding disorder</td>
<td>Band tail, localisation, scattering</td>
</tr>
<tr>
<td>Structural defects</td>
<td>Electronic states in the band gap</td>
</tr>
<tr>
<td>Alternative bonding configurations</td>
<td>Electronically induced metastable states</td>
</tr>
</tbody>
</table>

Fig. 1.1 The correspondence between features of the atomic structure and the resulting electronic properties [After Street (1991)].

1.2.1 Atomic structure

Amorphous semiconductors are not completely disordered. The covalent bonds between the silicon atoms are much the same as in crystalline silicon, with the same number of neighbours and the same average bond lengths and angles. The disorder is represented by the atom pair distribution function, which is the probability of finding an atom at distance $R$ from another atom. Schematic pair distribution functions for
crystalline, amorphous (or liquid) and gaseous phases are illustrated in Fig. 1.2. The relative positions of atoms in a dilute gas are random (except at very close spacings), whereas a perfect crystal is completed ordered to large pair distances [Street (1991)]. The amorphous material has the same short range order as the crystal but lacks the long range order. The first few nearest neighbour distances are separately distinguished, but the correlation between atom pairs loses structure after a few interatomic spacings. The material properties of amorphous semiconductors are similar to their crystalline counterparts because they share the same local order. In contrast, there is often little connection between the properties of gaseous and condensed phases.

![Fig. 1.2 Schematic diagram of the atom pair distribution functions for a crystalline and amorphous solid and a gas, scaled to the average separation of nearest neighbour atoms, $R_{av}$, showing the different degree of structural order [After Street (1991)].](image)

The short range order and long range disorder lead to the model of the continuous random network, introduced by Zachariasen (1932) to describe glasses such as silica. The periodic crystalline structure is replaced by a random network in which each atom has a specific number of bonds to its immediate neighbours (the coordination). Fig. 1.3 is a two-dimensional illustration of such a network, containing atoms of different coordination (4, 3 and 1). The random network has the property of easily
incorporating atoms of different coordination, even in small concentration. This is in marked contrast to the crystalline lattice in which impurities are generally constrained to have the coordination of the host because of the long range ordering of the lattice.

Fig. 1.3. An example of a continuous random network containing atom of different bonding coordination, as indicated.

A real crystal contains defects such as vacancies, interstitials and dislocations. The continuous random network may also contain defects, but the definition of a defect has to be modified. Any atom which is out of place in a crystal is the simplest defect such defects are vacancies and interstitials. The only specific structural feature of a random network is the coordination of an atom to its neighbour. Thus the elementary defect of an amorphous semiconductor is the coordination defect, when an atom has too many or too few bonds. The ability of the disordered network to adapt to any atomic coordination allows an isolated coordination defect, which is not possible in a crystal. The different defects are illustrated in Fig. 1.4 [Street (1991)].
1.2.2 Chemical bonding

The local chemical bonding of atoms is emphasised by the continuous random network model. Most amorphous semiconductors including a-Si:H are covalently bonded, with well-defined bonding geometries and coordination. Fig. 1.5. illustrate the molecular orbital model for silicon. The electrons of an isolated silicon atom occupy two 3s and two 3p states, in addition to the deeper core states which are not involved in the bonding. When the atoms combine to form a solid, the electron interaction splits the valence states into bonding and anti-bonding levels, as in Fig. 1.5. Chemical bonding occurs because the bonding state has a lower energy than the isolated atomic levels and the material has the lowest total energy when the maximum number of electrons occupy bonding states. Their number is constrained by the Pauli exclusion principle which prevents more than two electrons occupying one state. To optimise the number of bonding states, the atomic wavefunctions combine to form hybrid molecular orbitals, described by:

\[ \Phi_{hyb} = a\Phi(3s) + b\Phi(3p) \]  

where \( a \) and \( b \) are constants. The four silicon valence electrons combine to give four \( sp^3 \) orbitals. Each orbital comprises \( 1/4 \) of an s state and \( 3/4 \) of one of the three equivalent p states. These four orbitals form bonds to adjacent atoms and since silicon has four valence electrons, all the bonds are occupied by two electrons, one
from each atom forming the bond. The hybridisation minimises the total energy by arranging as many electrons as possible in bonding orbitals [Street (1991)].

It is not always possible to arrange all the valence electrons in the bonding orbitals, because four is the maximum number of orbitals which can be made from s to p states. Similar diagrams can be constructed for other elements. For example, group V elements bond in p³ configurations, with s electrons forming the non-bonding pairs [Mott (1969) and Mott (1993)]. The different rules of the local chemistry in the amorphous and crystalline networks are highlighted by considering the bonding of an impurity atom. Since every atomic site in a crystal is defined by the lattice, the impurity either substitutes for the host, adapting itself to the chemistry of the host or occupies a position which is not a lattice site, forming a defect. A substitutional impurity such as phosphorus is four-fold coordinated and acts as a donor because one of its electrons is not involved in the bonding and is released into the conduction band [Spear and Le Comber (1975)]. An amorphous material has no rigidly defined array of lattice sites, so that an impurity can adapt the local environment to optimise its own bonding configuration, while also remaining a part of the host atomic network.

Fig. 1.5 Illustration of the bonding configuration of silicon atoms constructed from hybridised molecular orbitals. The position of the Fermi energy, \( E_F \), is indicated [After Street (1991)].
1.2.3 Electronic structure

The presence of a band gap separating the occupied valence band from the empty conduction band states is one of the most important properties of semiconductors. The band gap can be considered to be a consequence of the periodicity of the crystalline lattice [Elliott (1990) and Street (1999)]. In the past, there was considerable debate over the reason why amorphous semiconductors had a band gap at all, let alone one that is similar to that in the corresponding crystal. Subsequent work explained that the band gap is equivalently described by the splitting into the bonding (or lone pair) and anti-bonding states of the covalent bond (Fig. 1.5). The bands are most strongly influenced by the short range order, which is the same in amorphous and crystalline silicon and the absence of periodicity is a small perturbation [Lannin (1988) and Mott (1993)].

These results were most clearly stated by Weaire and Thorpe [Weaire (1971) and Thorpe and Weaire (1971)], they described the bonding by a tight binding Hamiltonian of the form:

$$H = V_1 \sum_{ij} \left| \Phi_{ij} \right> \left< \Phi_{ij} \right| + V_2 \sum_{i \neq j} \left| \Phi_{ij} \right> \left< \Phi_{ij} \right|$$

(1.2)

The wavefunctions, $\Phi$, are the sp³ hybrid orbitals of the tetrahedral silicon bonding. The first term in eqn (1.1) is a sum over interactions for which the two wavefunctions $\Phi_{ij}$ belong to the same atom and the second term sums pairs of orbitals that belong to the same bond. This Hamiltonian describes the short range bonding information, but contains no information about the long range order, and so applies equally to amorphous and crystalline silicon. Weaire and Thorpe showed that there are ranges of the interaction strength $V_1 / V_2$ for which the conduction and valance bands are separated by a band gap irrespective of long range structure; $V_1$ the bonding interaction which is responsible for the width of the bands and $V_2$ the bonding interaction which is responsible for the separation of bonding and anti-bonding bands [Elliott (1990) and Street (1991)].

The three principal features of the structure of amorphous semiconductors are the short range order of the ideal network, the long range disorder and the coordination defects. The preservation of the short range order results in a similar overall electronic structure of an amorphous material compared to the equivalent crystal. Thus, silicon dioxide is an insulator in both its crystalline and amorphous forms and silicon is a semiconductor in both forms. The abrupt band edges of a crystal are
replaced by a broadened tail of states extending into the forbidden gap, which originates from the deviations of the bond length and angle arising from the long range structural disorder. The band tails are most important despite their relatively small concentration, because electronic transport occurs at the band edge. Electronic states deep within the band gap arises from departures from the ideal network, such as coordination defects. These defects determine many electronic properties by controlling trapping and recombination. The electronic structure of an amorphous semiconductor comprises the bands, the band tails and the defect states in the gap and the correspondence between the structure and the electronic properties is summarised in Fig. 1.1 [Street (1991)].

### 1.3 Band structure

The basic property of a semiconductor is that it has an energy gap which separates the filled valence band from the empty conduction band. The energy bands are known in detail for most simple semiconductors by a combination of semiempirical band structure calculations and optical experiments [Rice (1977)]. The band structure of a material is intimately dependent on several factors, including band structure, lattice constant, chemical species, bonding and bond length, electronegativity, stiffness and elasticity [Iyer and Xie (1995)]. Conventionally, the band structure of a semiconductor is represented by a dispersion relation \( E(k) \) where \( E \) is the energy of an electron (or hole) at the band edge and with a wavevector \( k \) in the first Brillouin zone. This is shown in Figs. 1.7 and 1.8 for Si and GaAs [Chelikowsky and Cohen (1976)].

A semiconductor can be changed from insulator-like to metal-like: it is the extent of the energy gap and relative availability of electrons that determine whether a solid is a metal, a semiconductor, or an insulator. In a semiconductor the energy gap usually extends over less than about 3 eV and the density of electrons in the upper band (or of the holes in the lower band) is usually less than \( 10^{20} \) cm\(^{-3} \). By contrast, in a metal the upper band is populated with electrons far above the energy gap and the electron concentration is of order of \( 10^{23} \) cm\(^{-3} \). Insulators, on the other hand, have a large energy gap, usually greater than 3 eV, and have a negligible electron concentration in the upper band (and practically no holes in the lower band). This enormous variation can be caused by adding impurities to the material, or by changing its temperature. Both effects are a direct manifestation of a semiconductor's most characteristic feature, its band gap [Pankove (1971) and Perkowitz (1993)]. The gap comes from the quantum physics of the crystalline semiconductor. A schematic representation of
the conduction and valence bands with large band gap, and a quadratic relationship of electrons and holes and Fermi levels are shown in Fig. 1.6.

![Diagram of conduction and valence bands](image1)

![Energy vs. wavevector diagram](image2)

Fig. 1.6 (a) Representation of the conduction and valence bands in a semiconductor showing the band gap, and the impurity level in the gap. (b) Energy versus wavevector diagram showing the quadratic relationship for electrons and holes, the Fermi energy $E_f$, and multiple hole bands [After Perkowitz (1983)].

Full quantum calculations give a complex picture of valence and conduction band energy $E$ as a function of electron momentum $p$, or electron wavevector $k$, defined by the de Broglie relation $p = \hbar k$. Fig. 1.7 and 1.8 show the $E$ versus $k$ diagram for Si and GaAs, respectively. Both illustrate the directional character of electronic band structure, due to the change in lattice properties along different crystalline axes. The figures show, for instance, different bands along the (100) and (111) directions. The directional character means that the band gap, the smallest energy between a valence band state and a conduction band state, may not occur at the point of minimum momentum $(k_x,k_y,k_z) = (0,0,0)$. Note that the valance band structure for most semiconductors is similar especially at $k = 0$, the zone centre. Semiconductors can be divided into two classes. Those in which the conduction band minimum and valence band maximum occur at the same value of the wavevector are known as direct gap semiconductors, while those in which they are separated in $k$ space are known as
indirect gap semiconductors. Fig. 1.8 demonstrates that GaAs is a direct band gap semiconductor, with its conduction minimum directly above the valence band maximum, while Fig. 1.7 shows that the Si has an indirect gap, with the lowest minimum in the conduction band displaced from (0,0,0). Here, an electron moving from valence to conduction band must undergo a change in wavevector. In indirect gap semiconductors optical absorption is allowed only with the emission or absorption of a phonon to conserve crystal momentum and is a much weaker process than in direct gap materials [Ioffe (1960), Moss (1961), Rice (1977) and Perkowitz (1993)].

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{energy_wavevector_diagram.png}
\caption{Energy versus wavevector diagram for silicon. The arrow shows the indirect gap of 1.1 eV (at 300 K), the smallest energy spacing between the valence band and the conduction band. It is located away from the \textit{\Gamma} point, where the wavevector $k = 0$ [After Chelikowsky and Cohen(1976)].}
\end{figure}

The band properties profoundly affect the optical behaviour of semiconductors. An electron can be elevated from the valence band to the conduction band if it absorbs a photon whose energy is at least equal to the gap value. The reverse process since momentum must also be conserved, absorptive and photoluminescence processes near the gap are strongly affected by whether it is direct or indirect [Pankove (1971) and Iyer and Xie (1995)].
Correlation between electronic and structural properties of semiconductors

Fig. 1.8 Energy versus wavevector diagram for GaAs. The arrow shows the direct gap of 1.4 eV (at 300 K), the smallest energy spacing between the valence band and the conduction band. It is located at the Γ point, where the wavevector \( k = 0 \) [After Chelikowsky and Cohen (1976)].

The electrons which do reach the conduction band are free to move. In vacuum, ordinary free electrons of mass \( m_o \) have an energy-momentum relationship:

\[
E = \frac{p^2}{2m_o}
\]  

(1.3)

Near the bottom of the band, mobile electrons in a semiconductor crystal obey a similar quadratic law, except that their interaction with the atomic cross gives them an effective electronic mass \( m^* \) rather than \( m_o \). Their energy-wavevector relationship is:

\[
E = \frac{p^2}{2m^*}
\]  

(1.4)

From quantum mechanics we have the following expression:

\[
p = k\hbar
\]  

(1.5)
where \( \hbar \) is Dirac's constant = \( h/2\pi \), \( h \) being Plank's constant; and \( k \) is the wavevector. Because of the relations (1.4 - 1.5), and to couple better to classical intuition, \( k \) is called the 'momentum vector'. If the crystal is conceived as a square well potential with an infinite barrier and a bottom of width \( L \), or \( k \) can have a discrete values \( k = n(2\pi/L) \), where \( n \) is any non zero integer. Note that \( L \) is an integer number \( N \) of unit lattice cells having a periodicity, \( a \). Therefore, \( a \) is the smallest potential well one could construct. Hence \( n = N, k = \pi/a \) is the maximum significant value of \( k \). This maximum value occurs at the edge of the Brillouin zone. A Brillouin zone is the volume of \( k \)-space containing all the values of \( k \) up to \( \pi/a \), where \( a \) varies with direction [Pankove (1971) and Elise (1973)]. Larger values of the momentum vector \( k' \) just move the system into the next Brillouin zone, which is identical to the first zone and, therefore, the system can be treated as having a momentum vector \( k = k' \cdot \pi/a \). The kinetic energy of the electron can be expressed as:

\[
E = \frac{k^2\hbar^2}{2m^2} \tag{1.6}
\]

If the whole crystal, a cubic whose sides have a length \( L \), is the potential well, the allowed energies are:

\[
E = \frac{\hbar^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2) \tag{1.7}
\]

Although \( E \) varies in discrete steps, since the quantum numbers \( n \) are integers, the steps are so small (=10^{-18} \text{ eV for a 1 cm}^3 \text{ crystal}) that \( E \) appears as a quasi-continuum. This quadratic relationship is illustrated in Fig. 1.6(b). In addition to their effective mass, electrons in the conduction band are described by their concentration \( n \), their scattering time \( \tau \), the mean time between collisions, and their mobility \( \mu \), defined as the velocity produced per unit electric field. From the simple Drude model for electronic behaviour, the d.c. mobility

\[
\mu = \frac{e\tau}{m^*} \tag{1.8}
\]

where \( e \) is the electronic charge. These parameters all come together in the resistivity \( \rho \) which characterises the of a semiconductor, or its inverse, the conductivity \( \sigma \). In the Drude model, and in the d.c. limit, these are related by:

\[
\sigma = \frac{1}{\rho} = ne\mu = \frac{ne^2\tau}{m^*} \tag{1.9}
\]
The motion of the charged particles is not confined to the conduction band; holes in the valence band can also conduct. Electrons and holes generally have different effective masses, with holes having larger values. This shown in Fig. 1.6(b) by different curvatures of the electron and the hole $E$-$k$ parabolas [Street (1991) and Perkowitz (1993)].

1.4 Nanostructured materials (silicon and porous silicon)

Although bulk Si is intrinsically inefficient at radiative recombination Si can however be produced in nanostructured forms which produce efficient photoluminescence (PL). The first report on porous Si was about 40 years ago by Uhlir (1956) during his electropolishing of silicon in aqueous hydrofluoric acid. Since that time the basic formation mechanism of this new material have been studied extensively by a large number of scientists [Turner (1958), Gee (1960), Memming and Schwartz (1966), Theunissen (1972), Watanable et al. (1975), Labunov et al. (1979), Unagami (1980), Parkhutik et al. (1983), Beale et al. (1985) and Bomchil et al. (1989)]. One form of porous Si, produced when the surface of bulk silicon is etched to leave nanoscale features in a surface layer. The optical properties of porous Si are drastically different from those of bulk crystalline Si. Porous Si exhibit PL at an energy that is large compare to band gap of crystalline Si [Canham (1990), Cullis and Canham (1991), Föll (1991), Lehmann and Gösele (1991), Buda et al. (1992), Herino et al. (1992), Kalkhoran et al. (1992), Koshida and Koyama (1992), Lehmann et al. (1992), Ohno et al. (1992), Read et al. (1992), Sanders and Chang (1992), Lee and Peng (1993), Qin and Jia (1993), Gavartin and Matthai (1995), Motohiro et al. (1995) and Ünal and Bayliss (1996)]. The absorption edge is shifted to higher energies by about 1.5 eV compared to bulk crystalline Si, which has an infrared band gap of 1.1 eV as shown in Fig. 1.9, and there is efficient room temperature PL in the visible range. The reasons suggested for this increase in band gap and emission energy have include the quantum confinement effect, whereby carriers are confined in one or more dimensions. Other possible mechanisms which could be responsible include the existence of luminescent molecules such as siloxene on the surface of the cores, or the presence of a disordered phase on luminescent surface states. The data on porous Si obtained so far appear to support in general the quantum confinement mechanism i.e. the thinner the wires the greater the band gap and hence the band-to-band PL emission energy. Thus a band gap of 2.6 eV corresponds to a quantum core of approximately 4 nm in diameter.
1 - Correlation between electronic and structural properties of semiconductors

Fig. 1.9 Measured transmission for monochromatic light of porous Si samples grown on a nondegenerate p-type substrate (square), on a degenerate p-type Si substrate (circles) and of a silicon single-crystal reference sample (crosses) [After Lehmann and Gösele (1991)].

The increased band gap decreases the concentration of mobile charges within the remaining silicon structure and creates a depletion layer [Smith and Collins (1992)]. These results were quickly and easily reproduced by workers in several laboratories around the world and kindled intense investigations into this phenomenon. Porous Si is itself fabricated by an anodic dissolution process, usually in hydrofluoric acid (HF)-based electrolyte. While the microscopic details of pore formation are complex and as yet incompletely understood, a labyrinth of interconnected Si skeleton is created. The microstructure of porous Si depends on the composition of the electrolyte, the type and resistivity of the starting Si substrate, the current density during anodisation, and the post anodisation treatment [Halimaoui et al. (1991), Brandt et al. (1992), Herino et al. (1992) and Qin and Jia (1993)]. Under the right conditions, a large pore structure is created, wherein as much as 85-90% of the silicon is etched off leaving filaments as thin as a few nm across. In highly porous films, very small silicon structures are formed and it has been suggested that these very small dimensions (on a scale of nanometers) are the origin of carrier confinement which increases the energy gap so that the recombination can occur in the visible range [Herino et al. (1992) and Zhang et al. (1992)]. The principal feature of porous Si is extremely fine structure either wires or dots, which are small enough to exhibit some quantum confinement effects. Structural analysis of this aptly called ‘Quantum Sponge’ [Gösele et. al. (1992), Gösele and Lehmann (1995) and Wang (1995)] is quite difficult but several workers
Correlation between electronic and structural properties of semiconductors

using electron microscopy, X-ray diffraction and Raman spectroscopy have confirmed that the filaments are crystalline [Cullis and Canham (1991) and Iyer and Xie (1995)]. In contrast, the formation of porous Si appears to be a self-adjusting or self-limiting process in which the quantum confinement effect, the desired final result, also governs the formation process. The resulting structure which is schematically shown in Fig. 1.10 may be considered as a system of interconnected quantum wells. The material is fragile and by nature exhibits a very high surface area. Immediately after anodisation, this surface is usually hydrogen passivated with little evidence for oxygen or other impurities. The pores can be widened, or equivalently the filaments made thinner, by leaching in HF solution, or oxidising the sample using rapid thermal oxidation [Petrova-Koch et al. (1992)]. The resulting structure luminescence from red to blue when pumped with broad band UV radiation at room temperature.

![Fig. 1.10 Schematic structure of porous Si layer (1) on crystalline bulk Si (2), [After Gösele and Lehmann (1995)].](image)

The diameters of electrochemically etched pores in silicon cover three orders of magnitude depending on type and density of doping. They are designated by the pore diameter: microporous Si (width <2 nm), mesoporous Si (2-50 nm width) and macroporous Si (width >50 nm), [Cullis et al. (1992) and Gösele and Lehmann (1995)]. The material of greatest interest is microporous Si, because of its luminescent properties. In principle, microporous Si is found on all samples independently of doping, but only on moderately doped p-type material can pure microporous Si be found. On p+ and n+-doped samples the porous Si structure is a mixture of microporous Si and mesoporous Si and for low doped n-type Si,
Microporous Si is found to cover the walls of macropores. In addition, mesopores due to breakdown of the space charge region may be found on n-type electrodes. Inhomogenous doping of the electrode makes things even more complicated [Gösele and Lehmann (1995)].

The formation of microporous Si can be understood in term of hole depletion in porous structure due to its quantum size dimensions [Lehmann and Gösele (1991)]. It is one of the prediciations of this model that under higher formation bias (and therefore current density) the skeleton of microporous Si will become smaller and mechanically less stable. A microporous Si layer of high porosity cracks while drying and the pieces shrink considerably in size, like mud in a drying lake. This is probably due to a collapse of the pores under the attractive (Van-der-Waals) forces between the hydrogen surface atoms. Microporous silicon formed at current densities below 100 mA/cm² was found to dry without cracking for a layer thickness up to 10 μm, which may be due to a more stable silicon skeleton formed at low current densities [Lockwood (1992) and Gösele and Lehmann (1995)].

The photon energies of the PL from porous Si fall mainly between 1.6 - 2.2 eV. The band gap widened by quantum size effect must be at least larger than this. The relationship between the band gap widening and the size of the Si nanocrystallities has been calculated by many researchers. The crystallite size distribution is generally not accurately known, but according to different experimental studies typical sizes range between a few nm and 10 nm [Muller et al. (1993), Noguchi and Suemune (1993) and Bayliss et al. (1994)]. Fig. 1.11 shows the dimensions and morphology of typical, [001] oriented crystalline silicon structure present within the highly porous Si layers [Cullis and Canham (1991)]. The columns in Fig. 1.11(a) indicated a cross-sectional diameter of < 5 nm, which is direct evidence for a crystalline silicon quantum wire array. Fig. 1.11(b) shows similar isolated structures with width down to < 3 nm, measured from an other porous Si sample. Some calculated size ranges of the Si nanocrystallites which correspond to the above photon energy rang of 1.6 - 2.2 eV [Motohiro et al. (1995)] have been made. For example Sanders and Chang (1992) give the wire thickness of 1.5 - 3.0 nm for the fundamental band gap and 1.5 - 2.7 nm for the lowest excitation transition energy. Other calculations by Buda et al. (1992) gives a range of the wire thickness between 0.83 - 1.45 nm, whereas 2.5 - 4.5 nm is given in Proot et al. (1992) and Delenue et al. (1995). Steigmeier et al. (1992) gave the diameters of 3.7 - 8.4 nm. From the study of Lookwood and Wang (1994), it was found that the nanoparticle diameters of porous Si are between 2.6 - 3.1 nm and 3.0 - 3.2 nm at 295 K and 4.2 K, respectively.
Although there is some divergence of the calculated values depending on the methods and researchers, it's obvious that the calculated values for Si nanowire model are too small to be consistent with the experimentally observed Si nanocrystalline size.

Fig. 1.11 Transmission electron images of thin porous Si layers showing irregular matrix structures and narrow silicon columns. The magnification of (b) is the same as that of (a), [After Cullis and Canham (1991)].

1.5 Radiative recombination in semiconductors

In semiconductors has been the subject of an enormous number of experimental and theoretical investigations which have proven very fruitful for the development of semiconductor physics. These fundamental studies have given rise to interesting applications in light emitting diodes and semiconductor lasers. Radiative recombination is the inverse of the optical absorption. In the simplest case electrons in the conduction band recombine with the holes in the valence band, giving up energy, which approximately corresponds to the energy gap, as electromagnetic radiation which may be emitted from the semiconductor. Similarly, recombination via impurity or defect states may occur radiatively, the emitted photons then having an energy less than the energy gap [Ellis (1973) and Street (1991)].

In the electronic excitations of a semiconductor which result in nonequilibrium, or excited, state of the semiconductor, radiative recombination represents one of the processes that can achieve a relaxation to the semiconductor ground state. Typically, excitation may be by photon absorption, current injection, or electron beam excitation, which the initial excited state corresponding to any accessible point in the Brillouin Zone. Subsequent interactions typically result in the relaxation of carriers to the states at or near the minimum of the conduction band for electrons, and the maximum of the valence bands for holes. The mechanism responsible for this relaxation, and the
resultant distribution of carriers, depends to a large extent on the relative efficiency with which the injected carriers interact with themselves, the other carriers already present in the sample, or with the crystal lattice. It is most often the case that a quasi-equilibrium is established and the usual statistical distribution of the carriers temperature, can be applied for determination of recombination kinetics [Moss (1961) and Voos (1980)].

The starting point for consideration of radiative recombination typically correspond to the carriers occupying states illustrated in Fig. 1.12(a) for the case of direct and indirect band structures. As indicated in Fig. 1.12(a), impurity states are localised and carriers trapped at these sites can recombine through interactions with either free carriers (e-A, D-h) or carriers bound to other impurities (D-A). Total momentum must be conserved for the recombination event. Since the momentum of a photon, \( h/\lambda \) (\( \lambda \) is the wavelength of light, thousands of angstroms), is very small compared to the crystal momentum \( h/a \) (\( a \) is the lattice constant, a few angstroms), the photon recombination process should conserve the momentum of the electron [Pankove (1971), Calcott et al. (1993) and Nash et al. (1994)]. Radiative recombination in indirect gap materials requires that the considerable crystal momentum associated with the carrier at the zone edge, be transferred to the lattice. Carriers occupying states in the band are free and can move freely through the lattice with little or no correlation of their respective motion. However the Coulomb interaction between free electrons and holes cannot be ignored. This interaction can result in the formation of a positronium-like bound state. Considerable part of the energy of formation of electron-hole pair consists of separating the pair against their Coulomb attraction. If the free hole and electron move in the crystal under an electric field as if they were particles, each with its appropriate effective mass, we see that a hole and electron could form a system with energy levels, and could move as a unit through the crystal lattice. Such a system is called an exciton [Smith (1978) and Voos et. al. (1980)]. For the free excitons the motions of the paired electron and hole are completely correlated, and the energy of this state is reduced relative to that of the uncorrelated free carrier state by an amount corresponding to the excitation binding energy. With increasing excitation density more complex pairings of carriers can occur such as trions, or excitonic molecules. The energy of these states is reduced even further relative to the bands. For sufficient density, and low temperatures, excitons can condense to form an electron-hole liquid [see, for example, Voos and Benoit à la Guillaume (1976) and Rice (1977)].
As described in Fig. 1.12(b) carriers can relax, or be trapped, in these states either individually or as complexes. For moderately to heavily doped materials these impurity-related states trap the majority of injected carriers at low temperatures and the recombination from these states can then dominate the PL spectrum. Even at high temperatures impurity states can play a very significant role in the recombination kinetics. Radiative recombination can be further complicated by the simultaneous emission, or absorption, of one or more phonons or the Auger excitation of other carriers, or carrier complexes, into higher energy states. Each of these processes can modify the energy of the emitted photon. It is not uncommon that in a given experimental situation the injected carriers relax through more than one of these various states, so that a variety of recombination channels may contribute to the luminescence. As a result the radiative recombination spectrum can be rich in detail and contain a good deal of information about the fundamental processes and interactions influencing carriers in a semiconductor. Nonradiative recombination invariably involve the conversion of excitation energy into phonons. Nonradiative processes can also contribute significantly to the recombination processes, competing with the radiative channels and severely limiting the intensity of light, emitted at a given injection level [Voos et al. (1980), Street (1991) and Delerue et al. (1993)].

To calculate the radiative recombination rate for transitions from a given level in detail, one must consider the usual quantum mechanical matrix element, using the appropriate wavefunctions describing the initial and final electronic states of the semiconductor [Ziman (1965) and Barry Bebb and Williams (1972)]. The intensity and line shape of luminescence arising from a particular transition depends on this matrix element, on the density of states appropriate to the initial and final states involved, and on the occupation of these states determined by the appropriate statistics describing the distribution of the injected carriers among the available states.

The properties of porous Si are most easily explained by a radiative recombination mechanism which is essentially the same as in bulk crystalline Si ['t Hooft et al. (1992)]. A model for electron-hole recombination inside nanoscale units of porous Si has been proposed by Qin and Jia (1993). The radiative recombination of carriers is ascribed to an indirect band gap transition. The creation of an electron-hole pair by photoexcitation, where the energy of the pair is much larger than the band gap of the bulk Si (1.12 eV at room temperature), and both electron and hole recombine to emit visible light: (I) through various luminescence centres (point defects or impurities), which are located at the Si/SiO₂ interfaces and/or in the thin SiO₂ layers and/or on its outer surface; these are for the case where the surface region is covered with SiO₂
layers, which is shown schematically in Fig. 1.13. (II) In the second case, supposing the surface is not covered with SiO2, the luminescence centres (most probably complexes of Si with O, H or F) are located on the surface of nanoscale units.

**Fig. 1.12(a)** Schematic of radiative recombination for direct and indirect band gap materials. (b) A schematic of recombination via various channels [After Voos et. al. (1980)].

**Fig. 1.13** Schematic illustration of electron-hole pairs recombining to emit visible light through luminescence centres which are located in the SiO2 layers [After Qin and Jia (1993)]
Chapter 2

Optical properties of semiconductors

2.1 Introduction

For a long time optical spectroscopy has been a very powerful tool to study the electronic levels of atoms and molecules. However for solids, and especially for semiconductors, it was only around 1960 that it was realised that the same kind of information could be obtained, in spite of the lifetime broadening and the overlapping of the bands. A large proportion of knowledge of the energy levels of semiconductors comes from a theoretical analysis of the energy dependence of the reflectivity (or the absorption) between the energy gap ($E_g$) and 25 - 30 eV; this means that the photon used to probe the crystal mostly induces transitions between the filled valence bands and the empty conduction bands [Petroff (1980)].

Optical absorption in solid or liquids can occur by several different mechanisms, all of which involve coupling of the electric vector of the incident radiation to the dipole moments in the material and a consequent transfer of energy. Analysis of optical absorption spectra, with the variable incident photon energy provides essential information on phonon and electron states in the materials whether this is crystalline, amorphous or liquid [Davis (1973), Ellis (1973), Jackson (1987) and Elliott (1990)].

2.2 Density of states of non-crystalline materials

The concept which is remains a valid concept for non-crystalline as for crystalline materials is density of electron states, because solutions to the Schrödinger equation with a random potential must still exist, and its form can be determined by various experimental methods [Mott and Davis (1979) and Piggins (1988)]. Several factors that determine the density of states for a given material consist of, among others, the coordination number, the interatomic distance and the type of chemical bonding [Madan and Shaw (1988)]. In general, the available evidence suggests that the form of the density of states in liquid or non-crystalline materials does not differ greatly from the corresponding form in the crystal, except that the finer features may be
smeared out, and some localised states may appear in the forbidden energy range in semiconductors. In contrast, the description of individual electron states used for electrons in crystalline materials is not always appropriate for the non-crystalline case. In crystalline materials, assuming a perfect crystal and neglecting the effect of phonons, the electron states in this case can be written as 'Bloch waves' extending through the crystal:

\[ \psi = u(x,y,z) \exp(ik.r) \]  \hspace{1cm} (2.1)

where the function \( u(x,y,z) \) has the periodicity of lattice and \( \exp(ik.r) \) represents a plane wave [Mott and Davis (1979) and Elliott (1990)]. The wavevector \( k \) is a quantum number for the electron. In non-crystalline materials the wave function \( \psi_E(x,y,z) \) does not necessarily have this form (i.e. 2.1). Nevertheless, a solution of the Schrödinger equation must exist, and therefore the first concept that can be carried over from the theory of crystal to the theory of non-crystalline materials is the density of states \( N(E) \), defined so that \( N(E)dE \) is the number of eigen-states in unit volume for an electron in the system with given spin direction and with energy between \( E \) and \( E+dE \). Then at a temperature \( T \) the number of electrons in the energy range \( dE \) is, for each spin direction,

\[ N(E)f(E)dE \]

where \( f(E) \) is the Fermi distribution function

\[ f(E) = \frac{1}{\exp\left[(E-E_F)/kT\right]+1} \]  \hspace{1cm} (2.2)

The Fermi energy \( E_F \) is a function of \( T \) and tends to a limiting value as \( T \to 0 \), \( E_F \) then separating occupied from non-occupied states [Mott and Davis (1979)].

The allowed energies of the electrons can be represented by means of a ‘band structure’ in k-space [Imbusch (1978) and Elliott (1990)]. A free electron has an energy:

\[ E = \hbar^2 k^2 / 2m^* \]  \hspace{1cm} (2.3)

where \( m^* \) is the effective mass. \( N(E) \) can be calculated from the free electron approximation which is good one if the electrons are not strongly scattered. In this
case the Fermi surface is spherical, and the density of states for the electrons is given for each spin direction by the free-electron formula:

\[
N(E) = \frac{4\pi k^2}{8\pi^3} \left| \frac{dE}{dk} \right| = \frac{km^*}{2\pi^2 h^2} = \frac{(Em^*/2)^{3/2}}{\pi^3 h^2}
\]  

(2.4)

In crystalline materials the interaction with the field of the lattice can lead to large deviations from eqn (2.3), because the energy depends on the direction of \( k \) and also because of the formation of band gaps [Mott and Davis (1979)].

Because of phonons or impurities, electron scattering take place, and a mean free path \( L \) is introduced; for instance, if there are \( N \) impurities per unit volume each with a differential scattering cross-section \( I(\theta) \), the mean free path is given by:

\[
\frac{1}{L} = N \int_0^\pi I(\theta)(1 - \cos\theta)2\pi \sin\theta d\theta
\]  

(2.5)

The formula assumes that the Fermi surface is spherical, so that \( I(\theta) \) is independent of the initial direction of motion of electrons, but it is, of course, characteristic of the conduction and valence bands of many crystalline solids in that the energy \( E(k) \) corresponding to the wavefunction (2.1) does depend on the direction of \( k \). Unless, however, \( L \) is small \( (kL \sim 1) \) the changes in the density of states are not large. In non-crystalline materials, however, the disorder is responsible both for the finite mean free path and for deviations from the eqn (2.4) for the density of states, and large deviations will occur if the scattering is strong. Nonetheless, the most striking fact about many non-crystalline materials is that they are transparent, either in the infrared or in the visible: \( SiO_2 \), borosilicate glasses, and chalcogenide glasses are examples. These transparency properties are frequently determined by the form of the density of near band-edges [Pierce and Spicer (1972) and Mott and Davis (1979)]. The following situations for non-crystalline materials may therefore arise:

(I) The scattering by each atom is weak. The wavevector \( k \) is then a good quantum number, the uncertainty \( \Delta k/k \ll 1 \), the surface of constant energy is spherical and eqns (2.3) and (2.4) are valid. This is the case for most liquid metals for values of \( E \) near the Fermi energy.

(II) The scattering by each atom is strong, so that \( \Delta k/k \sim 1 \). In this case \( k \) is not a good quantum number for describing the eigenstates, and the concept of Fermi surface (for
metals) is no longer valid. Ioffe and Regel (1960) pointed out that under these conditions the mean free path is of the order $\sim 1/k$, and cannot be shorter than this. When $\Delta k/k \sim 1$, considerable deviation from (2.4) can occur for the density of states.

(III) If the interaction becomes yet stronger, a new phenomenon occurs which is absent in crystalline materials, namely that for a given energy $E$ all the wavefunctions $\psi_E$ are localised. This means that each wavefunction $\psi_E$ is confined to a small region of space.

Thus, since the short-range order present in the crystalline phase is essentially unchanged (i.e. similar bond length, bond angles, and local coordination) the gross features of the crystalline density of states are preserved, though there are differences.

The question of 'states in the gap', whether of intrinsic or extrinsic nature, is of considerable importance. The considerations of Anderson's work of 1958, that conduction and valence bands and a gap exist, that in the conduction bands the disorder produces a tail of localised states, and that somewhere within this tail there is a mobility edge. In hydrogenated amorphous silicon the range $\Delta E$ of the energies where states are localised is thought to be about $0.1 \text{ eV}$, though if an exponential tail exist, as now seems probable and was first predicated by Halperin and Lax (1966), the bottom of the band is rather ill-defined.

There are also deep states in the gap. A model by, Mott and Davis (1979) for amorphous silicon is that most of these are caused by dangling bonds. Normally a simple dangling bonds contains an electrically neutral electron; which is amphoteric (being able to donate or accept an electron). Fig. 2.1 illustrate the dangling bonds in amorphous silicon. It occurs when a silicon atom is so placed that it can form only three bonds with neighbours. If the fourth s-p orbital is singly occupied, as will be the case for a neutral centre, it will give an electron spin resonance signal, and such a signal is observed with $g = 2.0055$; where $g$ is the so-called g-factor determining the observed moment [Elliott (1990) and Mott (1993)]. The dangling bonds in silicon produced abundant traps with levels near both the conduction and valence bands [Koshida et al. (1992) and Ünal and Bayliss (1996)].
Cohen, Fritzsche, and Ovshinsky (1969) supposed that the non-crystalline structure would lead to overlapping band tails of localised states as in Fig. 2.2(a). Those derived from the conduction band would be neutral when empty and those from the valence band neutral when full. In the overlap region they would be charged, leading to centres with unpaired spins. Such overlapping states would pin the Fermi energy. The other principal feature of this model was the existence of 'mobility edges' at energies in the band tails. These are identified with the critical energies separating localised from extended states, [Mott (1966)], so that the model is sometimes called the Mott-CFO (Cohen-Fritzsche-Ovshinsky) model. The difference between the energies of the mobility edges in the valence and conduction bands is called the 'mobility gap' [Mott and Davis (1979) and Street (1991)]. Although there is considerable evidence for the concept of mobility edges, the proposal of overlapping tails is now considered unlikely to apply to amorphous semiconductors and insulators that are transparent in the visible or infrared. An ideal amorphous semiconductor in which all bonds are saturated and in which there are no long-range order fluctuations should have a density of states as in Fig. 2.3(b) with a true band gap.
Real non-crystalline materials, however, are thought to contain imperfections, such as impurities, or dangling bonds at point defects or microvoids, and these, just as in crystals, may lead to levels within the band gap. Nonetheless amorphous semiconductors are not normally 'intrinsic', in the sense that the valence and conduction bands control the Fermi energy. The evidence is summarised for instance by Fritzsche (1973, 1974); the continuation of a straight plot of log $\sigma$ versus $1/T$ down to low temperatures, in addition to thermopower and field-effect measurements, all point to a Fermi energy pinned in some way near mid-gap.

![Diagram of density of states in amorphous semiconductors](image)

**Fig. 2.2** Various forms proposed for the density of states in amorphous semiconductors. Localised states are shown shaded. (a) Overlapping conduction and valence band tails as proposed by Cohen et al. (1969), the CFO model; (b) a real gap in the density of states, suggested here as being appropriate for a continuous random network without defects; (c) the same as (b) but with a partially compensated band of defect levels; (d) the same as (b) but with overlapping bands of donor ($E_D$) and acceptor ($E_A$) levels arising from the same defect [After Mott and Davis (1979)].

Alternative suggestions to the CFO model for states in the gap are shown in Fig. 2.2(c) and (d). In Fig. 2.2(c) a band of deep acceptors is partially occupied by electrons originating from a weaker band of donors. The role of donors and acceptors can of course be reversed. This simple model, proposed by Davis and Mott (1970), was based on several experimental results which implied a finite density of states at $E_F$. As long as the total density of states in the gap is not large, the model allowed optical transparency without the need for assumptions about the magnitude of the matrix elements; however, no explanation was offered as to why the controlling states should lie near mid-gap. Mott (1972b) suggested that if the states arose from a defect centre, e.g. a dangling bond, then they could act both as deep donors ($E_D$) and acceptors ($E_A$), single and double occupancy conditions leading to two bands separated by an appropriate correlation energy or Hubbard $U$ (see Fig. 2.2(d)) with $E_F$
pinned between them [Mott and Davis (1979), Jackson (1987) and Madan (1988)]. The correlation energy composed of two terms:

\[ U = U_c + U_r \]  

where \( U_c > 0 \), represents the coloumbic repulsion between the two electrons. This is given by:

\[ U_c = \frac{e^2}{4\pi\varepsilon_0\varepsilon r_{12}} \]  

and \( r_{12} \) is the separation between the electrons [Jackson(1987) and Elliott (1990)]. \( U_r \) in eqn 2.6 represents a negative term due to electron-lattice coupling (relaxation). If this is large enough, it can make the correlation energy, \( U \), negative overall. It is found that the value of \( U \) is 0.4 eV for Si [Stutzman and Stuke (1983)]. An experimental determination by Vardeny and Tauc (1985) gave 0.5 eV for a-Si:H.

### 2.3 Microscopic structure and composition of inhomogeneous solids

Determination of the structure of a crystalline solid is made straightforwardly by the need only to solve the structure within the 'unit cell', containing relatively few atoms in most cases and the fundamental 'building unit' of the structure; the structure of the crystal as a whole is then generated by replacing in a periodic fashion the position of the unit cell in space. Such a procedure is impossible for a non-periodic amorphous solid, for which the unit cell may be regarded as being infinite in extent. The operational definition of an amorphous solid, however, is merely that the structure is non-periodic (i.e. non-crystalline), not that it is necessarily truly random in a statistical sense. In many cases the structure of many amorphous solids is in fact non-random, at least on certain length scales, e.g. there may be a considerable degree of local ordering despite the overall lack of periodicity. It is widely believed that the bulk atomic structure of amorphous silicon is such that on the average a silicon atom has four other around it at the same distance (as in the crystal) forming a tetrahedron. For example the Si-O-Si angle is 144° in \( \alpha \)-quartz, and has mean value of 153° in vitreous material, though it may vary from side to side [Mott (1993)]. According to a model of a continuous random network by Bell and Dean (1968), most bond angles lie between 140° and 170°, though tails in their histogram extend to 120° to 180°. Further, each of these atoms in turn has three more neighbours, similarly arranged, giving rise to a well defined second shell of 12 atoms, none of which is a neighbour to any other. The structural data show that the resemblance of amorphous silicon to crystalline silicon
ceases beyond the second shell [(Madan (1988)]. For example, the structure of silica and silicates in the glassy state was anticipated as being composed of SiO$_4$ tetrahedra connected together in some random manner. The presence of discrete SiO$_4$ tetrahedra, identifiable by a number of techniques, certainly signifies the lack of complete randomness in the structure; a similar occurrence of local order is to be found whenever chemical bonding takes place between atoms in the solid, whether formally as covalent bonds or as weaker components in addition to non-directional forces, such as those involved in metallic or ionic systems [Madan (1988) and Elliott (1990)].

Therefore the arbitrarily defined length scale which separates microscopic structure from macroscopic structure is taken to be in the region of 100 Å. Conventional X-ray diffraction is only sensitive to structural variations of the order of a few Å, i.e. in the microscopic region, whereas optical microscopy, say, is only useful for direction for structural inhomogeneities on the scale of thousands of Å or more, which are in the macroscopic domain. It was also found convenient to subdivide the section on microscopic structure into two parts, one dealing with 'short-range order' (of the order of a few Å) and the other dealing with 'medium-range order' (on length scales of the order of 5 to 20 Å); there is no 'long-range order' of an amorphous solid by definition, [Elliott (1990)].

For non-crystalline semiconductors we must distinguish between materials that can be formed by rapid cooling from the melt, such as vitreous SiO$_2$ and certain types of chalcogenide glasses, and those that cannot, such as amorphous silicon and germanium. In the latter, the coordination number is the same as that in the crystal, namely four, but in the melt it is larger, and the liquids are metallic, with properties similar to those in liquid lead. Amorphous silicon and germanium can therefore be prepared only by deposition from some gaseous phase, for instance in a glow discharge, or by bombarding the crystals with fast ions [Mott (1993)].

There are several techniques which can be used to obtain structural information on solids, such as X-ray diffraction, electron and neutron diffraction, extended X-ray absorption fine structure, infra-red and Raman spectra, nuclear magnetic resonance (NMR), and Mössbauer spectroscopy [Madan (1988), Elliott (1990) and Mott (1993)]. The radial distribution function for amorphous germanium determined by electron diffraction [Moss and Gracyzk (1970)] is shown in Fig. 2.3. In general it is found in elements that the coordination number is the same as in the crystal. In glasses with two or more components, such as As$_x$Se$_{1-x}$ with varying composition, it is
normally the case that each As atom (for example) has three neighbours and each Se atom has two, Ge or Si if present 4. This has been called the 8-\(N\) rule, meaning that the number of neighbours of each atom is equal to the number of bonds that it can form [Mott (1993)].

A brief description on extended X-ray absorption fine structure will given in Chapter 4.

![Graph](image)

Fig. 2.3 Radial distribution function of amorphous (evaporated) and crystalline silicon determined by electron diffraction [After Moss and Graczyk (1970)].

### 2.4 Interband absorption

One of the most important differences between crystalline and non-crystalline materials, which has a direct bearing on the absorption data, is the relaxation of the \(k\)-conservation rule [see § 2.2(I and II)]. Therefore 'indirect' transitions (as opposed to 'direct' in crystals) take place in these materials without the requirement of phonon emission or absorption processes to conserve momentum. The resulting differences in the optical data are clearly evident in Fig. 2.4 for silicon, [Pierce and Spicer, (1972)].
Here the imaginary part of the dielectric constant, $\varepsilon_2$, is plotted as a function of the photon energy, $h\nu$. The absorption coefficient, $\alpha$, is related to this quantity by the expression $\varepsilon_2 = \alpha n c/\omega$, when $n$ is the refractive index. The gross features of the two curves are similar in that they both peak between 3 - 4 eV. This similarity is due to the persistence of short-range order in the amorphous phase. However, the lack of long-range-order in the amorphous material is reflected in the absence of any sharp spectral features seen in the curve of crystalline silicon.

The relaxation of the $k$-selection rule in (unhydrogenated) amorphous silicon is evident in the difference between the two curves in the region 1 - 3 eV. Although both materials have a similar gap near ~ 1 eV, crystalline silicon is an indirect-gap material. Only indirect transitions involving phonons can take place at energies between 1 - 3 eV, and are much weaker than direct transitions. These cannot take place until ~ 3 eV, resulting in the sharp rise of $\varepsilon_2$ seen in Fig. 2.4. The relaxation of the $k$-selection rule in amorphous silicon allows stronger absorption to take place over this energy range. Technologically this is very important, since the higher absorption of amorphous silicon in the visible region from 2 - 3 eV gives it a distinct advantage over its crystalline counter-part in solar cell applications [Jackson (1987)].

![Fig. 2.4 Comparison of the $\varepsilon_2$ spectra of crystalline and amorphous silicon](image-url)
2.5 Absorption and reflection spectra

In semiconductors both bound and free electrons produce significant absorption. Ellis (1973), considered the electrons into four types of states:

(a) Valence-band electrons.
(b) Inner-shell electrons.
(c) Free carriers—including, of course, holes as well as electrons.
(d) Electrons bound to localised impurity centres or defects of some type.

The absorption process of greatest importance in the study of semiconductors involves transitions from states of the first type and arises from the optical excitation of electrons across a forbidden gap $E_g$ into the conduction band. In an ideal semiconductor at zero temperature the valence band would be completely full, so that an electron could not be excited to a higher energy state within the band. The only possible absorption process is that due to there being sufficient energy to excite the electrons across the forbidden gap into the empty conduction band, leaving holes in the valence band [Azároff (1960), Azároff and Brophy (1963), Ellis (1973) and Smith (1978)]. In practice the resulting absorption spectrum is a continuum of intense absorption at an absorption edge (at $\hbar \omega = E_g$) beyond which the material is relatively transparent. For most semiconductors this edge occurs in the infrared part of the spectrum and the absorption can result from ‘direct’ or ‘indirect’ optical transitions, depending on the energy band structure of semiconductor [Moss (1961) and Ellis 1973)].

For semiconductors in which the limits of the energy band occur at the same value of the wavevector $k$, the onset of absorption will be at $\hbar \omega = E_g$ as a result of direct transitions. As discussed earlier in this and the previous chapter indirect transitions occur with a lower probability, and give rise to an absorption edge which is less steep than for direct transitions. Two possible phonon interactions can occur in the optical absorption process, dependent upon whether the phonon is absorbed or emitted. Thus the photon energy required for excitation of an electron across the energy gap is

$$\hbar \omega \geq E_g + E_p$$

for emission of phonon of energy $E_p$

and

$$\hbar \omega \geq E_g - E_p$$

for phonon absorption.
Absorption coefficient data can be derived readily from transmission and reflection measurements for photon energies up to and just in excess of a direct energy gap, and can be used to determine the energy gap of a semiconductor [Pankove (1971), Davis (1973), Ellis (1973) and Mott and Davis (1979)]. Typically with a sample 5 μm thick one can measure the absorption coefficient up to $\approx 2 \times 10^4 \text{cm}^{-1}$, but the measurement of higher absorption levels becomes increasingly difficult due to the requirement for thinner specimens. It is for this reason that most optical data in the UV part of the spectrum have been derived from the measurement of normal-incidence reflectivity.

An important parameter which determines the magnitude of the absorption coefficient for a particular photon energy, and which thus in turn influences the reflectivity is the 'joint density of electron states'. This is, in effect, the density of energy-level pairs which are available for optical transitions, each pair having one level in each of two bands with an energy separation $\hbar \omega = E_c - E_v$ [Azároff (1960) and Ellis (1973)]. The joint density of states may be shown to vary rapidly with energy near to the Van Hove singularities [Van Hove (1953)] which occur at symmetry points where

$$\nabla_k E_c(k) = \nabla_k E_v(k) = 0$$

(2.8)

and at point of lower symmetry where

$$\nabla_k E_c(k) = \nabla_k E_v(k) \neq 0$$

(2.9)

2.6 The absorption edge

So far, the optical absorption properties of amorphous semiconductors have been discussed in general terms over a range of photon energies extending well beyond the gap. Since many of the properties of these materials are determined by the nature of the density of states at the band edge, it is now important to focus attention on the optical properties at energies less than or equal to the band gap [Jackson (1987)]. The vicinity of the absorption edge can provide information on the optical gap as well the density of states within the gap [Davis (1973) and Madan and Shaw (1988)].

In crystalline semiconductors emission at the absorption edge has a sharp peak and is well defined, owing to the sharp electronic band structure of these materials. On the other hand, in amorphous semiconductors the bands do not have sharp edges, but tail off into the gap (see Fig. 2.2) with the extent of the tails being dependent on disorder [Ellis (1973), Jackson (1987) and Piggins (1988)]. Consequently the absorption edge
is quite broad and sensitive to preparation conditions. This makes the concept of an optical gap difficult to define experimentally. Despite this sensitivity, the general form of the absorption edge is very similar for a wide variety of amorphous semiconductors. This has been generalised by, [Tauc (1970) and Abeles (1980)] and is illustrated in Fig. 2.5. For each material the absorption edge can be divided into three regions:

(a) a power law region,
(b) an exponential absorption edge, often referred to as the ‘Urbach edge’, and
(c) a low-energy shoulder which extends into the gap.

In region (a) of Fig. 2.5 the absorption data of many amorphous semiconductors is well described by the relation:

\[ \alpha \hbar \omega \propto (\hbar \omega - E_r)^2 \]  

(2.10)

This relation has been derived by Tauc (1970) on the assumptions that the density of states just beyond the mobility edge is parabolic and that the k-selection rule is completely relaxed. The energy \( E_r \) can be used to define an optical gap, which is often known as the Tauc gap. Although most amorphous semiconductors obey equation 2.10, there are some exceptions. Amorphous selenium (a-Se), for example, exhibits a linear, rather than a quadratic dependence on \( \hbar \omega \) [Jackson (1987)].

For values of \( \alpha \) between \( 10^3 \) cm\(^{-1} \) - \( 10^4 \) cm\(^{-1} \) there is usually a transition from the power law behaviour of region (a) to the exponential behaviour of region (b) (see Fig. 2.5). This is a general feature of amorphous semiconductors and can be described by:

\[ \alpha = \alpha_0 \exp \left[ -\gamma(E_o - \hbar \omega) \right] \]  

(2.11)

where \( E_o \) is comparable to the mobility gap and \( \gamma \) is a constant representing the slope of the edge, with values ranging from 10 - 25 eV\(^{-1} \). Similar exponential edges have been observed in crystalline solids, such as alkali halides, CdS and trigonal Se, and this region is referred to as the ‘Urbach Edge’ [Urbach (1953)]. This term can has been carried over for use in the amorphous case also. Unlike amorphous solids, however, the Urbach edge in crystals is temperature dependent, with a slope varying as \( \gamma/kT \) down to some critical temperature, \( T_o \), below which it remain constant [Mott and Davis (1979) and Jackson (1987)]. The current interpretation of the Urbach region is that it is associated with absorption involving the band tail.
The low energy absorption tail seen in region (c) of Fig. 2.5 is attributed to absorption due to defect states deep in the gap. This tail usually occurs for values of $\alpha$ below $\sim 10^{-1}\,\text{cm}^{-1}$, but this depends on the conditions of sample preparation [Jackson (1987), Madan and Shaw (1988) and Piggins (1988)].

The absorption coefficient has quadratic dependence on photon energy and has two branches. In direct semiconductors, no phonon assistance is needed and $\alpha$ shows a parabolic dependence with incident photon energy. The net result is that when band-to-band absorption occurs in direct semiconductors, the incident radiation is absorbed in a much shallower depth than in an indirect semiconductor. A state in the forbidden gap can also mediate electron-hole recombination. In an indirect semiconductor, phonon assistance may still be required making gap state mediate radiative recombination potentially less efficient than a direct transition [Iyer and Xie (1995)].

Fig. 2.5 The idealised absorption edge of an amorphous semiconductor [Tauc (1970)].
Chapter 3

Photoluminescence and electroluminescence

13.1 Photoluminescence emission

Photoluminescence and electroluminescence

Photoluminescence and electroluminescence

13.1 Photoluminescence emission

The interaction of light with semiconductors occurs across the energy spectral range 0.001 to 12 eV. The energy range in the near-infrared/visible/near-ultraviolet region is 0.24 to 4 eV, and the dominant effect in this range is absorption at the gap and by impurities. Under certain conditions, this leads to photoluminescence (PL).

Absorption occurs when the photon raises an electron from a neutral donor to the conduction band, or from the valence band to a neutral acceptor. It is also possible to induce absorptive transitions from the valence band to an ionised donor, or from an ionised acceptor to the conduction band. These processes are fruitful probes of semiconductor bands and impurities. They also lead to the more sensitive probe of PL, which occurs when the electron returns from the excited state to the initial state [Jackson (1987) and Perkowitz (1993)].

PL is defined as the optical radiation emitted at different wavelengths by a physical system resulting from excitation to a nonequilibrium state by irradiation with light [Barry Bebb and Williams (1972) and Djebbar (1989)]. PL experiment provide a particularly sensitive technique which is widely used for studying the localised states within the band gap of a semiconductor [Mott and Davis (1979) Street (1981) Kozlowski and Lang (1992)]. PL emission involves radiative transitions between electronic energy levels of material, and emission is characteristic of material. The transition originates on some excited electronic level, and after the emission of a photon a lower electronic level is occupied [Imbusch (1978)]. Excitonic behaviour can be important in PL, and is an indicator of sample quality. If the semiconductor is very pure, the Coulomb attraction between the generated electron and hole can bind them into the quasi-hydrogenic exciton and may in addition be either free or bound to impurities. If the sample is not very pure, Coulomb forces from donor, acceptor, or neutral impurities attract free excitons to form bound excitons [Perkowitz (1993) and Iyer and Xie (1995)]. High doping reduces the probability of exciton formation because the free charges tend to screen out the Coulomb interaction. The exciton can move as a whole through the crystal, but with net charge of zero, it carries no current.
Excitons form when photon absorption occurs at any of the critical points in the band structure which obey the relation:

$$\nabla_k [E_{\text{conduction}}] = \nabla_k [E_{\text{valence}}]$$  \hspace{1cm} (3.1)

since this condition ensure the electron and hole have equal group velocities and hence are likely to be bound by electrostatic force. When excitons decay radiatively light is emitted. Excitonic luminescence is good indicator of material quality, but unfortunately, in general, excitations have lifetimes that are too short at room temperature to be significant [Iyer and Xie (1995)]. In the coming sections various aspects of the PL properties of porous Si will be reviewed, to provide sufficient background information to supplement the experimental work and discussion in chapters 7, 8 and 10. In the case of rapidly emerging technologies, it should be noted that the keynote textbooks and, to a lesser extent scientific references, do not become available to the worker undertaking a study of the field until perhaps several years afterwards.

The mechanism of PL can be divided into three stages, the first of which is the excitation of electron-hole pairs. This occurs by photon absorption with energies close to the band gap energy. Secondly, the excited carriers thermalise (i.e. relax) rapidly down to the band edges by emitting phonons, until they are captured into localised states. Finally, the carriers can recombine either radiatively to give PL or non-radiatively [Barry Bebb and Williams (1972), Wallis and Sébenne (1980) and Jackson (1987)]. Since the exciting light is absorbed in creating electron-hole pairs, the greatest excitation of the sample is near the surface; the resulting carrier distribution is both inhomogeneous and nonequilibrium. In attempting to regain homogeneity and equilibrium, the excess carriers will diffuse away from the surface while being depleted by both radiative and nonradiative recombination processes. Most of the excitation of the crystal is thereby restricted to a region within a diffusion length (or absorption length) of the illuminated surface. Since the recombination radiation is subjected to self-absorption, it will not propagate far from this region. It follows that recombination radiation most readily escape through the nearby illuminated surface. Consequently, the vast majority of PL experiments are arranged to examine the light emitted from the irradiated side of the sample. This often called front surface PL. In thin samples with relatively low absorption of recombination light, the back surface or transmission PL can also be examined.
Fig. 3.1 illustrates of these three stages in a simple schematic diagram, and also highlights some of the non-radiative processes that can have an influence on the properties of the PL (note that only the behaviour of electrons is shown for simplicity, although holes also undergo equivalent thermalisation and capture processes) [Jackson (1987)]. Thermalisation can result in a carrier being captured by a radiative or a nonradiative centre, depending on the capture cross-section $\sigma_r$ and $\sigma_n$ respectively. In the latter case recombination takes place nonradiatively and does not directly influence the PL properties. On the other hand, three competing processes can occur at radiative centres. Recombination can either take place radiatively with a rate $P_r$, resulting in the emission of a photon of energy $\hbar\omega$, or via a directly competing nonradiative pathway with a rate $P_n$. In addition, thermal ionisation of the carriers to the band edge can occur with a rate $P_{nt}$, at sufficiently high temperatures [Jackson (1987), Madan and Shaw (1988), Elliott (1990) and Street (1991)].

Alternatively it was found by Imbusch (1978) that if the gap between an excited level and the adjacent lower level is small, the material in the excited state tends to decay non-radiatively by phonon emission releasing the energy as heat to the material. Radiative decay, that is, the transition from a higher to a lower electronic level which is accompanied by the emission of a photon, only occurs when the gap to the adjacent lower level is above a critical value.

![Schematic Diagram](image)

Fig. 3.1 A schematic diagram showing the radiative and non-radiative processes that influence the PL processes, as described in the text [After Jackson (1987)].
3.2 Photoluminescence in amorphous silicon

In amorphous semiconductors, radiation can be emitted either by the relaxation of an excited defect or by an electron-hole pair bound together by their Coulomb attraction (an exciton). Extensive work using the PL technique has led to the conclusion that in chalcogenide glasses PL occurs via charged defects since the luminescent efficiency falls off rapidly with temperature. The electron (or hole) escapes from the neutral excited centre and find a non-radiative recombination channel. The emitted radiation shows a Stokes shift, which we shall discuss later [Madan and Shaw (1988)].

It must be stressed at the outset that the phenomenon of luminescence is not solely associated with the presence of structural defects: the luminescence can result from intraionic electronic transitions of transition metal (3d) or rare earth (4d) atoms in amorphous matrices. Often, however, PL spectra are observed at energies considerably lower than the energy of the exciting photons, and electron states in the gap are often involved. These states can be band-tail states, but are more often associated with structural defects (dangling bonds); moreover the deeper into the gap a level lies, the stronger will be the electron-phonon coupling and this will greatly influence the luminescence process. Extensive reviews on PL in amorphous semiconductors has been given by Street (1976), for chalogenides, and by Fischer(1979) Street (1981) and Jackson (1987) for a-Si:H.

Various mechanisms for radiative recombination which give rise to photons emitted at significantly lower energies than those of the exciting radiation are illustrated in Fig. 3.2. One possibility is that an electron excited from the valence band into the conduction band will recombine with defect states deep in the gap Fig. 3.2.(a); another is that a similarly excited electron will thermalise down in energy through deep-lying localised tail states (e.g. in the Cohen-Fritzsche-Ovshinsky model) until recombination occurs with a hole trapped at a comparably deep valence band-tail state Fig. 3.2.(b). Both these mechanisms assume negligible electron-lattice coupling. Alternatively, this coupling may be strong, and the energy of the level changes with its electron occupation, with the consequence that if an electron is excited to the conduction band from a defect gap state (at Y in Fig. 3.2.(c)), relaxation at the centre takes place after excitation and radiative recombination at the same centre (X) will occur at different energy; the difference in excitation and luminescence energies (in this case only) is termed the 'Stokes shift'. In particular, note that in principle the optical absorption can take place at the same energy for mechanisms (a) and (b), but not for mechanism (c) and this is the test for the true Stokes shift.
Fig. 3.2 Possible radiative recombination channels which give rise to a luminescent energy much less than the excitation energy: (a) and (b) assume negligible electron-phonon coupling, whereas (c) assumes strong electron-phonon coupling [After Street (1976)].

Fig. 3.3 gives a description of electron-phonon interaction by a configurational coordinate diagram. Here the potential energies of the ground and excited states are plotted against a coordinate \( q \) which represents the distortion of the lattice. As seen from the above figure the excited state has a minimum energy \( E_e = E_x - W \), where \( W \) is the polaron energy, and \( E_x \) and \( E_g \) are the ground and the excited energies respectively. The linear deformation potential \( B \) represents the strength of the electron-phonon interaction. The system may lose energy nonradiatively by phonon emission when it transfers from the excited state to ground state configuration by passage over the small potential barrier separating them [Jackson (1987), Street (1976), Elliott (1990) and Street (1991)].

To compare between steady-state (c.w.) PL and photoluminescence excitation (PLE), Fig. 3.4 show the experimental result of PL and PLE for SiO\(_2\). The PLE spectrum is defined as the change of PL intensity as a function of excitation energy, generally measured at fixed emission energy. The PL and PLE spectra have identical gaussian line shapes with their peaks separated by \( 2W \) (i.e., the PL shifted to lower energies by \( 2W \)). As the strength of the electron-phonon coupling increases, the Stokes shift and the line width increases [Elliott (1990) and Street (1991)].
3 - Photoluminescence and electroluminescence

Eq. 3.3 Configuration coordinate diagram in a system representing optical absorption and emission with strong phonon coupling [After Street (1991)].

Fig. 3.4 Schematic illustration of PL and PLE spectra in SiO₂. The PL is Stokes-shifted by energy 2W. α represents the absorption edge [After Elliott (1990)].
3.3 Photoluminescence in porous silicon

Since the discovery of the strong visible PL in anodically etched porous Si by Canham (1990) numerous experimental and theoretical investigations have tried to identify the origin of this PL. However, the mechanism of the strong visible PL from porous Si is still unclear: the difficulty of this problem arises mainly from a large surface-to-volume ratio in nanostructures and the surface effects become more enhanced on decreasing the nanostructure size. The surface of luminescent porous Si is usually covered by silicon oxyhydrides or silicon dioxide, which cause the electronic properties of the near-surface region to differ from those of the crystalline Si core, [Kanemitsu et al. (1994)]. Two main categories of mechanisms have been invoked to explain this PL: the origin could be either of an extrinsic nature with different Si-based complexes located at the surface, [Brandt et al. (1992), Fuchs et al. (1992), Stutzmann et al. (1992 and 1993), Fuchs et al. (1993) and Koch et al. (1993)], or of an intrinsic nature as a result of quantum confinement effects in small size silicon particles in the porous layer, [Canham (1990), Cullis and Canham (1990), Lehmann and Gosele (1991), Tsu et al. (1992), Kanemitsu et al. (1993), Muller et al. (1993), Amato et al. (1994), Filippov et al. (1994), Francia et al. (1994), Lockwood Wang (1994), Delerue et al. (1995), Wang (1995) and Zhang et al. (1995)]. The first explanation concludes that the entity causing the PL in porous silicon layers is identical to that in the molecular compound siloxene (Si₆O₃H₆). Fig. 3.5 shows the structural models for siloxene proposed by Brandt et al. (1992). In Fig. 3.5(a) the layers formed by hexagonal silicon rings separated from each other by oxygen bridges, and the remaining silicon dangling bonds are terminated by hydrogen. Alternative structures with the same composition are shown in Fig. 3.5 (b and c), here the structure units are linear silicon chains interconnected by oxygen or pure silicon layers with alternating OH or H bond terminators. In particular they found a full agreement between vibrational properties and the behaviour of the PL (lifetimes, intensities, positions, shifts) in both materials. Also they conclude the visible light emission from porous Si layers is not an intrinsic property of crystalline silicon (quantum confinement effects) but depends on specific chemical reactions of silicon with hydrogen and oxygen, and the long lifetimes would be difficult to understand if the luminescence was from small quantum wells. This explanation was strongly contested by Petrova-Koch et al. (1992), Friedman et al. (1993) and Koch et al. (1993).
The second explanation seems to be now more favoured [Wang et al. (1993)], because most works agree that the quantum size effect in the spongelike porous silicon skeleton might play a key role in its optical properties as suggested originally by Canham (1990). In addition, the surface states or surface related species are found also to be responsible for the PL process [Vial et al. (1992)]. Many experiment have been devoted to seeking evidence to support the quantum size effect model. In the model of Qin and Jia (1993) the PL originates from electron-hole recombination inside nanoscale Si units and PL photon energies much larger than the band gap of the bulk Si can be explained by the quantum confinement effect. The most convincing fact is the relation between the blue shift of the PL peak and the porosity which really represents the average size of Si nanostructures. Theoretically the quantum size effect model is the model for which most calculations have been made, although no unambiguous proof of that nature exists yet. Another model proposed by Read et al. (1992) which supports the quantum confinement effect is illustrated in Fig. 3.6. This model considered the porous Si as wires of rectangular cross section with the wire axis along the [001] direction, and wire surfaces which correspond to [110] surfaces of the bulk Si. Each surface dangling bond is saturated by a H atom. In this wire
there are twenty Si atoms per unit cell. The thickness of the wire in this model is comparable in width to the thinnest of wires observed by the transmission electron microscopy studies of porous Si by Cullis and Canham (1991).

Fig. 3.6 Cross-sectional view of the 5 x 4 wire structure. Hydrogen atoms we denoted by H. The directions of the arrows indicate bond which project out of the plane of the paper [After Read et al. (1992)].

In the quantum confinement hypothesis, the visible PL of porous Si is expected to be due to radiative recombination of electron-hole pairs from the lowest excitation states whose binding energies are enhanced compared to bulk silicon (obviously, this does not apply to the infrared PL which is mostly below the band gap energy of bulk silicon) [Delerue et al. (1993) and Qin and Jia (1993)]. If the gap widening is an obvious consequence of the confinement, it is more difficult to predict its influence on the efficiency of radiative processes compared to nonradiative ones. In bulk silicon, because of its indirect band gap, the emission of light is only possible with the assistance of phonons to supply momentum in second-order processes [Hybertsen (1992) and Calcott et al. (1993)]. Therefore the PL of bulk silicon is weak as nonradiative recombinations become more efficient. The confinement of the electron-hole pair in real space leads to a spread of the wave functions in reciprocal space and then radiative recombination can occur in a first-order process [Hybertsen (1992)].

To compare the surface complex model with Canham's quantum confinement model, the most critical argument is whether the PL comes from the radiative recombination of quantum confined electrons and holes (or excitons) in crystalline Si nanostructures, or from so far unspecified localised states. To confirm or deny the above models, one must provide further experimental evidence to answer the following questions: (1)
Does the direct recombination of carriers or excitons confined in the crystalline Si cores occur in the PL process? If so, what is the radiative lifetime of the excited electron-hole pairs (excitons)? (2) What are the carrier or exciton excitation and de-excitation dynamics in the light emission process?

The relaxation dynamics of photon-excited carriers in a nanoscale structure of a semiconductor is governed by the scattering, thermalisation and recombination processes. If the nanostructure size is comparable with the Bohr radii of excitons in the corresponding bulk material, it is expected that the interaction between the excited carriers and the surrounding fields, such as surfaces, phonons etc., is rather strong, and the carrier dynamical processes are very fast. Thus it is necessary to use ultrafast time-resolved PL spectroscopy to investigate the carrier dynamics and recombination behaviour. A resolution better than several ns is necessary to reveal the initial stage of the PL process [Wang et al. (1994)].

3.4 Photoluminescence excitation spectra in porous silicon

For about the last twenty years, optical absorption and photoluminescence excitation (PLE) spectroscopy experiments have proven very fruitful in low-dimensional semiconductor structures to determine the origin of the observed optical transitions and also provide evidence for the reduced dimensionally as in the case, for instance, of GaAs-AlGaAs quantum well heterostructures. Compared to optical absorption, PLE experiments, which under certain circumstances give the same kind of information as absorption measurements, offer an important advantage since it is not necessary to remove the bulk Si substrate which is highly absorbing in the visible. PLE measurements performed on porous Si whose data are discussed in terms of quantum confinement in Si wires, are reported by Voos et al. (1995). The results are in fact in qualitative agreement with a quantum size effect and indicate that it would be helpful to obtain information on the carrier relaxation processes and on the size distribution of the Si wires or nanostructures which can be involved in the PL of porous Si. When the porosity becomes larger, the transverse size of the Si filaments gets smaller and the carrier confinement energy increases in a quantum confinement model. When the detecting energy is increased, the corresponding confinement energy is also increased and the size of the Si wires involved in the luminescence becomes smaller. This should lead to a shift of the PLE spectra towards high energies when the detecting energy increases. To proceed further, one can first evaluate the confinement energy \( E_c \) corresponding to the maximum of the PL lines. This energy is equal to \( h\nu-E_g \),
where $h\nu$ is the energy of the corresponding photon and $E_g$ the band gap of bulk Si which is equal to 1.12 eV at 300K [Herino et al. (1992)]. It is clear from electron microscopy measurements by Cullis and Canham (1991) that Si wires are not isolated and that there are connections between wires with different sizes, which implies that carriers can move from a wire to another one. In a PLE measurement, one detects the PL signal at a given energy corresponding to a wire size $L$. Free electrons and holes created by the excitation source at an energy $h\nu'$ relax and then recombine radiatively, yielding photons with energy $h\nu$. For isolated wires, such a process should give PLE data close to one of the absorption spectra, if the relaxation of the carriers is faster than their nonradiative recombination. However, since wires with different sizes are not necessarily isolated and can communicate, carriers excited in wires with sizes $L_1 < L < L_2$ can move into wires with a size $L$ while they relax. In this case, the PL signal observed at energy $h\nu$ is due to the recombination of carriers excited not only in wires with size $L$ but also in wires with sizes different from $L$, and the PLE experiments are thus likely to involve wires with different sizes. A better understanding of the PLE measurements would at least require a good knowledge of the carrier relaxation and of the wire size distribution, [Voos et al. (1994)].

PLE provides an alternative technique to probe the electronic structure. Sinha et al. (1994) have made a detailed investigation of the PLE at different temperatures for various PL emission energies. The results provide strong evidence of disorder-related processes in the excitation and emission of porous Si.

3.5 Photoluminescence lifetimes in porous silicon

The measurement of excited state lifetimes has become a pervasive and invaluable tool in the realms of experimental and theoretical spectroscopy, solution kinetics, solid state physics, energy transfer, laser and solar energy technology, analytical chemistry, and biology. Lifetimes are used to evaluate solid state energy transfer parameters, and also find application in evaluating laser dyes, developing analytical methods, and determining static and dynamic conformational information about macromolecules and monolayers. The result of lifetime measurements are reported in journals of physics, biology, chemistry, spectroscopy, and analysis. In short, photoluminescence lifetime measurements have become an indispensable tool in the physics and biological sciences.
Measurements of the decay of the total PL emission after pulse excitation can yield important information on the mechanisms involved, as different processes have different recombination rates. Many studies of this kind have been carried out on porous Si [Laiho et al. (1993), Wang et al. (1993), Gaponenko et al. (1994), Takahiro et al. (1994), Kovalev et al. (1994) and Takazawa et al. (1994)]. It is generally agreed that there exists a wide distribution of radiative lifetimes extending from a few ns to several tens of μs. The spread of lifetimes is usually interpreted in terms of the size distribution of Si microcrystals. The nonexponential decay suggest that several trapping mechanisms are involved [Andrianov et al. (1993) and Tsuboi et al. (1995)]. Lifetime measurements were performed on high efficiency porous Si material and so the lifetime distributions of visible are assumed to be representative of the radiative lifetime only: it is strongly temperature dependent, the increase of the temperature changing the behaviour of the PL decay [Fuchs et al. (1992), 't Hooft et al. (1992), Pavesi et al. (1993), Mauckner et al. (1993), Calcott, et al.(1993), Wang et al. (1994), Ookubo et al. (1994), Harris et al. (1994), Finkbeiner and Weber (1995) and Tsuboi et al. (1995)]. Fig. 3.7 shows how PL decay curves change with temperature at PL emission energy 1.914 eV. In general, the PL intensity follows a nonexponential decay, which can be described by two exponential processes, i.e., a faster decay followed by slower decay, both those decays being strongly temperature dependent. PL decay patterns are intrinsically nonexponential in porous Si, because they are independent of the intensity of the excitation source. PL lifetime, defined as (initial intensity) /Ie, are found to decrease as PL emission energy is increased, as shown in Fig. 3.8 where the PL decay curves decreases with increasing PL emission energies at 293 K. There may be two mechanisms governing the nonexponential decay in porous Si, one assuming a distribution of recombination rates, the other assuming independent recombination paths. The PL decay rate is well fitted by two exponential PL decay components, suggesting that the fundamental PL mechanism of porous Si is mainly due to radiative recombination processes via luminescence centres [Wang et al. and Takazawa et al. (1994), and Ventura et al. (1995)].

The observations of a broad PL spectrum and nonexponential behaviour in PL decays suggest that these processes are related to random distributions in size and spatial distance of nanocrystallites, and/or random terminations of surface silicones on nanocrystallites. Alternatively, an amorphous layer alone has been said to explain the observed PL behaviours [Ookubo et al. (1994)].
3.6 Photoluminescence temperature dependence in porous silicon

The discovery of room temperature efficient visible PL by Canham (1990), has generated an enormous interest in this material in view of possible optoelectronics applications of fully integrated silicon structures. The efficient light emission in anodically etched silicon samples contrasts with the behaviour of bulk crystalline Si,
which emits in the near-infrared luminescence with very low efficiency [Read et al. (1992)].

Although some consensus of opinion has emerged during the last five years, the word ‘anomalous’ is too often used in the porous Si literature. The main anomalies concern the temperature dependencies of the PL intensity and differing accounts of the temporal behaviour, but porous Si is obtained as a result of a more or less poorly controlled electrochemical reaction. It is therefore true to say that samples differ from one laboratory to another. Ventura et al. (1995) found quite different temperature dependencies in their samples. It is clearly possible that the balance between these processes and nonradiative recombination change from one sample to another.

Change in the PL emission band, i.e., green to red, and in the PL spectrum width have been reported for various samples, suggesting the light emitting objects are distributed differently in different samples. This implies that the PL spectrum is inhomogeneously broadened, in accordance with the observation that the spectrum width is weakly dependent on temperature [Zhang et al. (1992) and Suemoto et al. (1993)]. Upon cooling down from room temperature, the integrated PL intensity is known to increase [Naylor, et al. (1992), Ookubo and Sawada (1995) and Tsuboi et al. (1995)]; and the energy of the spectrum peak shifts to the high-energy side (blue shift), and its width broadens [Malý et al. (1994)], as shown in Fig. 3.9, which gives a steady-state PL spectra excited by a Hg lamp (365 nm) at various temperatures between 180 - 305 K. But the changes in the spectrum peak and width with temperature have been reported to be sample dependent [Ookubo and Sawada (1995)]. Under resonant excitation at low temperature, the PL spectrum is reported to have no resonant component and the structure is presumably due to phonon satellites. The variation in the PL lifetime with temperature has been explained by changes in the relative population of carriers in triplet and singlet states, without assuming nonradiative processes [Calcott et al. (1993)].

In spite of the great deal of effort so far devoted to this phenomenon, the mechanism for the efficient light emission in porous Si is still unclear. There is quite a general agreement about the values of PL decay time, in spite of the different analysed samples and of the experimental set-ups. Most authors [Mochizuki et al (1992), Finkbeiner et al. (1993), Laiho et al. (1993) and Wang et al. (1994)] report rather long PL decay times (10-100 μs) at room temperature. When the temperature is decreased, the PL decay time further increases, and measurements of PL decay times of different samples at constant emission PL energy show that the decay gets remarkably slower.
Photoluminescence and electroluminescence with decreasing temperature, [Vial et al. (1992), Mauckner et al. (1993), Kanemitsu (1993), Ookubo et al. (1994), Amato et al. (1995) and Ookubo and Sawada (1995)]. The PL decay time does not greatly depend on the porous Si sample (i.e., it depends strongly on the temperature and on the emission energy: it is faster and more dispersive for higher PL emission energy). The increase in the PL lifetime by cooling the sample has thus been ascribed to the suppression of carrier transitions to nonradiative paths, [Vial et al. (1992)]. The reason for the distribution of the PL decay rates in these models, however, has not yet been sufficiently described, [Ookubo and Sawada (1995)].

Luminescence decay rates as long as hundreds of μs show that both radiative and nonradiative processes have low efficiencies at room temperature. This should mean that the confinement of carriers into nanometer-sized crystallites strongly restricts the different paths for nonradiative de-excitation, [Amato (1994)].

![Fig. 3.9 Steady-state PL spectra of porous Si, taken at various temperatures, excitation wavelength 365 nm [After Malý et al. (1994)].](image)

### 3.7 Electroluminescence in porous silicon

Electroluminescence (EL) occurs when electrons of materials, such as semiconductors are excited by the application of an electric field to the material, resulting in an
electric current passing through it. The electrons recombine with holes to emit light as a function of applied voltage [Azároff (1960) and Djebbar (1989)]. Most practical solid state devices for visible injection EL used III-V compounds, principally alloys of GaAs, CdS and GaP. This is because this series of materials produces high efficiency LEDs due to their direct energy gap and also allow the efficient injection of the minority carriers which then radiatively recombine [Halimaoui et al. (1991) and Kalkhoran et al. (1992)].

Since the discovery of highly efficient visible PL from porous Si by Canham (1990), the production of efficient visible EL from porous Si has become a goal of extreme practical importance, motivated by the potential application in optoelectronics devices [Halimaoui et al. (1991), Koshida and Koyama (1992), Riess et al. (1994), Takasuka and Kamei (1994), Bsiesy et al. (1995), Koshida et al. (1995) and Steiner et al. (1995)]. This EL has been observed with either dry contacts obtained by metallisation (e.g., semitransparent metal) of the sample surface [Koshida and Koyama (1992) and Koyama et al. (1993)] or wet contacts resulting from immersion of the porous Si layer in a liquid electrolyte [Halimaoui et al. (1991)]. Solid state EL has been induced by injection of a sufficient number of electrons and/or holes into the porous layer (where the radiative recombination occurs inside nanocrystallites) [Koshida and Koyama (1992), Propst et al. (1994), Astrova et al (1995) and Steiner et al. (1995)]. Tsybeskov et al. (1995) has ascribed the EL to the possibility of a direct tunnelling across the energy barrier between the metal (Au in his study) and porous Si, with stronger applied electric fields. This results in an EL component at shorter wavelength involving carriers in shallow states. This component explained the observed shoulder in EL spectrum observed with a large bias voltage. Fig. 3.10 gives a comparison between radiative recombination in partially oxidised porous Si, taking place in the interface region of SiO-silicon nanocrystallites [Tsybeskov et al. (1995)]. In consideration of EL there are two types of emitting crystallites, the first electrically ‘disconnected’ from the substrate. These crystallites will only shine under optical excitation, and they will not contribute to EL because it is not possible to inject charge carriers in them by polarisation the Si substrate. The second kind of crystallites are still electrically ‘connected’ to the substrate, and charge carriers can be injected according to substrate polarisation. For this latter population the emission excitation can be either optical or electrical, so that it can contribute to both PL and EL. Just as the PL can be analysed in the framework of the quantum confinement model, EL can also be analysed in this way [Kozlowski and Lang (1992), Muller et al. (1993) and Bsiesy et al. (1995)]. Short-lived EL has been observed during anodic oxidation of p-type porous Si [Halimaoui et al (1991)]. Highly efficient EL has also been observed
on $n$-type porous Si [Canham et al. (1992), Bsiesy et al. (1993) and Astrova et al (1995)].

![Diagram of band structures for weak and strong fields](image)

Fig. 3.10 Schematic band diagram for EL in partially oxidised porous Si with relatively weak and strong electric fields [After Tsybeskov et al. (1995)].

Solid state EL has been obtained from porous Si by making Schottky diodes containing $p$-type porous Si with Au or ITO. Diodes made by evaporation of Au or ITO however showed a very low efficiency because the evaporated contact does not penetrate into the nanometer porous Si structure and involves high applied bias voltage [Bsiesy et al. (1995)]. Using ITO as the top electrode in LEDs instead of a metal, has several advantages. These advantages include potentially better contacts and less light absorption, and the efficiency of LEDs using ITO is consistently higher than of LEDs using metals such as Au or Ag [Fauchet (1995)]. In addition, in a film with tin electrodes the electrical contact between the electrode and the specimen film does not change with time [Varghese et al. (1983)].
Chapter 4

Methods of determining structure and composition of disordered or inhomogeneous media

4.1 Introduction

It is essential to know the structural arrangement of atoms of a solid substance for a detailed understanding of its physical or chemical properties, and this is true for crystalline materials as for amorphous solids. As is well known the structure of the crystalline state is obtained by generating in a periodic fashion the unit cell in space. This procedure is impossible for a non-periodic amorphous solid, in which the unit cell is absent, and the structure is random and chaotic and hence structural information, if any, can only be obtained in the form of a statistical average. The structures of amorphous solids in many cases are in fact non-random. Semiconductor properties such as the optical absorption edge and activated electrical conductivity can be directly determined from the short range order [Piggins (1988)]. The physical properties of amorphous materials can often be varied continuously simple by varying the composition. The intrinsic optical properties, namely the optical band gap of amorphous semiconductor alloys, can be varied systematically by changing the composition of the alloy system [Elliot (1990)].

In this chapter will be given a description of the techniques employed to obtain structural and composition information for disordered or inhomogenous media which extend over a few Å. The development of synchrotron radiation in the last two decades has allowed one to go beyond simple reflectivity measurements. During the same time, additional band structure information (valence bandwidth, density of states) was obtained by photocemission spectroscopy (UV and X-rays). High resolution scanning (transmission) electron microscopy were used to study the surface morphology, films thickness and nanostructural dimension.
4.2 X-ray absorption spectroscopy

X-ray absorption spectroscopy (XAS) is, like anomalous scattering, an atom-specific structural probe; that is, the local structure of a given type of atom can be probed. It is atom-specific for exactly the same reason as is anomalous X-ray scattering, namely an energy-dispersive spectrum is measured close to an X-ray absorption edge of a particular atom, and such edges are separated in energy for different elements. XAS is particularly well suited to this purpose. In general, an X-ray absorption spectrum can be separated into three regions in energy: the pre-edge region generally consists of a featureless monotonic decrease of X-ray absorption coefficient $\mu_x(E)$ with photon energy $E$ (although occasionally certain peaks may be observed, giving rise to so-called 'pre-edge structure'); the absorption edge itself is characterised by a discontinuous increase in $\mu_x(E)$ at an energy $E$ corresponding to the absorption threshold $E_0$ (i.e. the difference in energy between the core-level electron being excited, usually a 1s electron at the $K$-edge and the vacuum level); in the post-edge region $\mu_x(E)$ is again a featureless, monotonic decreasing function of energy for isolated (gas-phase) atoms but for atoms in any form of condensed state (including gas-phase molecular species) $\mu_x(E)$ exhibits small oscillations on the high-$E$ side of the absorption edge. These oscillations are known as 'extended X-ray absorption fine structure' (EXAFS) for energies ~ 100 eV beyond the edge. The pre-edge and post-edge structures have different physical origins and carry different types of structural information.

Pre-edge structure arises when core-level electrons are photoexcited into low-lying bound states of ionised atoms (or into resonant states in the continuum). This form of XAS is particularly useful with transition-metal (or rare-earth) atoms incorporated into glassy matrices, since the number and type of ligands around such atoms affects the relative occupancy and energy splitting of levels in the d (or f) manifold; XAS can be particularly sensitive to such local structurally induced changes. In certain favourable cases, XAS is a sensitive probe of the local coordination of atoms. In particular, it can distinguish between tetrahedral and octahedral coordinations, although some other structural information (e.g. of bond lengths) it cannot reveal. In this sense, pre-edge XAS is able to provide a type of local, atom-specific structural information.

The post-edge fine structure (EXAFS), is a technique for studying structural arrangements which involves measurement of the energy dependence of the absorption coefficient beyond an X-ray absorption edge, i.e. EXAFS arises not from direct absorption processes, as does the pre-edge structure discussed above, but from
what can be viewed as an 'internal diffraction' phenomenon. Consider what happens when a photon of energy slightly higher than threshold is absorbed by an atom, and a photo-electron is ejected from a deep electronic state (e.g. the K-shell) of a particular atom. The photo-electron wave propagates outwards to infinity if the absorbing atom is isolated (e.g. in a rare gas); in this case the absorption coefficient decreases smoothly from the absorption edge. However, if other atoms surround the absorbing atom, as in a gaseous molecule or in a condensed phase, the outgoing photo-electron wave will be back-scattered (diffracted), and the back-scattered waves will interfere with the outgoing waves, Fig. 4.1. This in turn influences the matrix elements for the absorption process itself. Since, as the X-ray photon energy is increased above threshold, the energy of the photo-electron also increases and consequently the electron wavelength decreases, constructive (destructive) interference occurs when the interatomic spacing is an integral (half-integral) number of wavelengths. Thus one expects to observe a periodic oscillation of the X-ray absorption above the absorption edge—the fine structure.

The photo-electric absorption processes can be treated semi-classically by regarding the photon as a classical electromagnetic field but treating the electron quantum-mechanically. In the dipole approximation, where the wavelength of the photon is large compared with the spatial extent of the excited core state, the absorption can be treated to first order in perturbation theory and Fermi’s golden rule then yields for the absorption coefficient:

\[ \mu_x = 4N_0\pi^2e^2 \frac{\omega}{c} \left| \langle f | \hat{\mathbf{P}} | i \rangle \right|^2 \rho(E^F) \]  

where \( |i\rangle \) and \( |f\rangle \) are the initial core state and final photo-electron wavefunction, respectively, \( \omega \) is the X-ray frequency, \( \rho(E^F) \) is the density of final states and \( N_0 \) is the number of atoms of one type in the sample. Since in the dipole approximation the photon field can be regarded as being spatially uniform, it can be approximated by a scalar potential proportional to the distance \( z \) if the X-ray polarisation is in the \( z \)-direction. Hence, only the matrix element or the density of states in eqn (4.1) could give rise to oscillatory behaviour of \( \mu_x \). For photon energies well above threshold, \( \rho(E^F) \) varies monotonically since it is well described by the free electron value. Therefore, the matrix element alone must be responsible for the oscillatory behaviour, and this is because the final state wavefunction \( |f\rangle \) is made up of contributions from both the outgoing wave and the back-scattered wave, and interference between the two modulates the matrix element and hence \( \mu_x \), [Stern (1978)], see Fig. 4.1
EXAFS is conventionally measured using a transmission geometry in which the incident ($I_i$) and transmitted ($I$) X-ray intensities passing through a thin foil of thickness $d$ are measured as a function of photon energy (Fig. 4.2(a)); they are related to the absorption coefficient $\mu_x$ by $I = I_i \exp(-\mu_x d)$. Two sources of broad-band X-rays may be used: either the bremsstrahlung spectrum from a conventional X-ray tube or radiation emitted by synchrotrons. For the work in this thesis synchrotron radiation was used. Synchrotron radiation offers the advantage of a factor of $\sim 10^4$ increase in photon flux and concomitant radiation in counting time; in both cases the beam is monochromatised by a crystal. For dilute samples, the desired EXAFS is swamped by the background intensity in transmission mode, and the more sensitive technique of fluorescence detection must be employed. In this, the $K$-shell hole left by the photo-electron is filled by a p-electron from the L-shell, emitting an X-ray photon of
characteristic energy less than that of the exciting X-ray (Fig. 4.2(b)). Thus by measuring the fluorescent X-ray emission, only those atoms which are excited are monitored, with a consequent dramatic increase in intensity. Radiative (fluorescent) recombination is the predominant recombination pathway for heavy elements. For lighter elements, Auger (secondary) electron emission is the preferred recombination mechanism (Fig. 4.2(b)), and monitoring of the Auger electron emission can also be used as a measure of $\mu_x(E)$. Since the mean free path of the emitted Auger electrons is so short ($\sim 20 \text{ Å}$), this technique is particularly surface-sensitive. Although X-rays are usually used for photo-excitation, high-energy ($\sim 100 \text{ keV}$) electrons can also be used to excite indirectly the core electrons.

Fig. 4.2. (a) Schematic illustration of the experimental arrangement used for performing X-ray absorption spectroscopy measurements in both transmission and fluorescence modes. (b) Electronic transitions in (i) the initial X-ray absorption and (ii) subsequent fluorescent radiative recombination or (iii) Auger non-radiative recombination processes.
The magnitude of the EXAFS signal is obtained from the measured value of \( \mu_x(E) \) by subtracting the background \( \mu_o \) and normalising:

\[
\chi(E) = \frac{\mu_x(E) - \mu_o}{\mu_o}
\]  

(4.2)

\( E \) is the photo-electron energy which, however, is not known exactly since the threshold energy (i.e. the zero of energy \( E_o \)) cannot be ascertained precisely; instead it is left as an adjustable parameter. The background absorption \( \mu_o \) is also difficult to measure, and it is usually fitted by means of a polynomial.

The EXAFS amplitude is calculated in the form of an analytic expression which can then be used to compare with experiment, thereby providing structural information without the need for trial structures. If one assumes single scattering, and moreover that the outgoing electron wavefronts are planar at the back-scattering shells of atoms (valid for energies \( \sim 80 \) eV from the edge), then eqn (4.1) becomes

\[
\chi(k) = -\sum_j \frac{N_j}{R_j^2} \frac{|f_j(\pi)|}{k} \exp\left(-\frac{2R_j}{\lambda_x}\right) \exp(-2\sigma_j^2 k^2) \sin(2kR_j + 2\delta(k) + \eta_j(k))
\]  

(4.3)

where a sum over all shells of backscattering atoms, \( j \), is taken, each containing \( N_j \) atoms at distance \( R_j \) from the absorbing atom. The magnitude of the EXAFS is proportional to \( N_j \), inversely proportional to \( R_j^2 \) (since both the outgoing and back-scattered waves are assumed to be spherical, decreasing in amplitude as \( 1/R \)) and proportional to back-scattering amplitude \( |f_j(\pi)| \) from the atoms in the \( j \)th shell. The amplitude is attenuated because of the finite mean free path \( \lambda_x \) of the electrons in the material and by the Debye-Waller term involving r.m.s. displacements \( \sigma_j \) (static or thermal) about the equilibrium bond length along the line joining absorbing and backscattering atoms. Finally, the amplitude is sinusoidally modulated by a function involving the phase shift of electron; the additional phase shifts \( \delta(k) \) and \( \eta(k) \) arise because the photo-electron is emitted and back-scattered, respectively from atomic potentials. The wavenumber of the photo-electron, \( k \), is given by:

\[
k = \frac{2\pi}{\lambda} = \left[ \frac{2m_e(E - E_o)}{\hbar^2} \right]^{1/2}
\]  

(4.4)
where $m_e$ is the electron rest mass. Note that this is half the normal diffraction wavevector $k$ which is given by:

$$ k = \frac{4\pi \sin \theta}{\lambda} \quad (4.5) $$

The structural information available from EXAFS experiments can be seen by reference to eqn (4.3). In principle, the coordination number, $N_j$, the interatomic distance, $R_j$, and the mean square deviation, $\sigma_j^2$ for each shell, j, of atoms surrounding the central atom are obtainable; in practice, only the first and second neighbour shells are significant. Two methods of extracting the structural information are commonly employed. One approach is to treat all the structural parameters in eqn (4.3) as adjustable variables and to vary these (perhaps with crystalline values as input parameters) until the best fit between the calculated EXAFS spectrum and the experimental data is achieved.

The second method of analysis of EXAFS data is to take the Fourier transform:

$$ \phi(r) = \frac{1}{(2\pi)^{1/2}} \int_{k_{\text{min}}}^{k_{\text{max}}} \chi(k) M(k) k^n \exp(2ikr) dk \quad (4.6) $$

where $M(k)$ is a window function, and $n$ can be 1, 2 and 3, the larger values weighting the data more at high $k$-values. This procedure gives rise to a series of peaks in real space corresponding to the first, second and perhaps higher shells: since EXAFS retains phase information, in contrast to X-ray diffraction, the Fourier transform of $\chi(k)$ consists of positive and negative excursions. The peaks do not lie at the correct distances if, as in eqn (4.6), the Fourier transform is taken with respect to the argument $2ikr$ only, ignoring the phase-shift term $2\delta(k) + \eta_j(k) = \alpha_j(k)$. This is because the $k$-dependence of $\alpha_j(k)$ also contributes to the frequency of oscillation of $\chi(k)$; if $\alpha_j(k)$ is expanded in powers of $k$ as $\alpha_j(k) = \alpha_0 + (\partial \alpha / \partial k) k$, then the frequency of $\chi(k)$ would be proportional to $R_j - \partial \alpha / \partial k$ and conversely the positions of the peaks as in the simple Fourier transform, eqn (4.6), would appear at distances $R_j - \partial \alpha / \partial k$. Although interatomic spacings obtained in this fashion can be very accurate ($\pm 0.02 \text{ Å}$), the values of the coordination number are not so precise and can be $\approx 50\%$ low due to changes in the emitter potential on ejection of the photo-electron, [Elliott (1990)].
4.3 EXAFS and porous Si

Investigation of the local structure and electronic properties of porous Si using synchrotron radiation induced luminescence became an interesting subject for many researchers [Sham et al. (1992), Sham et al. (1993), Bayliss et al. (1994), Schuppler et al. (1994), Bayliss et al. (1995), Dalba et al. (1995) and Zhang and Bayliss (1996)]. The dynamic behaviour of Si in porous Si (i.e. bond length, coordination number and Debye-Waller factor), gives answers to the questions of whether or not a 13 months old porous Si samples with high porosity remains crystalline and whether or not an amorphous state exists. Also inferred is the susceptibility of porous Si to oxidation in ambient atmosphere, and whether or not this affects the UV or soft x-ray induced luminescence. It seems not; because the UV or soft x-ray induced luminescence from these samples of porous Si remains clearly visible over this long period of exposure to ambient atmosphere.

In the present study, the structural analysis of porous Si samples were carried out using EXAFS at CCLRC Daresbury Laboratory National Synchrotron Radiation Source, beamline 3.4 (SOXAFS). The beam is focused on the sample by a Cr-plated mirror. An InSb double-crystal monochromator with harmonic rejection set at 70%, is used to vary the energy of the X-ray beam incident on the sample. Al foil used to monitor the incident beam intensity.

For the EXAFS experiments the X-ray excitation beam was incident normally on the sample, and the absorption was measured as the current required to neutralise the sample due to photoelectron emission. This is called the drain current method for measuring the total electron yield [Bayliss et al. (1994) and Bayliss et al. (1995)]. Due to the requirement of a conducting path, silver-based conducting paint was used to attach the samples to the aluminium mounts, and the latter were mounted in a copper sample holder. Scans were made from 1800 to 2500 eV (k range up to 15 Å⁻¹), with 742 independent points. The k range used in the Fourier transform fitting procedures described was 3 - 12.5 Å⁻¹, with 600 independent points.

The data acquisition software on beamline 3.4 produces a signal proportional to the total absorption coefficient μ(E) as a function of photon energy E. For EXAFS analysis, the programs used are EXCALIB, EXBACK and EXCURV92 on the XRSSERV1 computer. The EXCALIB program was used for summation and averaging the EXAFS data, and for background subtraction the EXBACK program [Morrell et al.] was used to fit the data with pre- and postedge backgrounds. This produced the EXAFS function χ(E). The last part of the EXAFS data analysis used
the single-scattering curved wave theory in the EXCURV92 program [Binsted et al (1992)], for multiparameter fitting of the experimental $\chi(E)$ data. A nonlinear least-squares fit of the fast curved-wave theory to the experimental data was used, and the routine involves calculating the scattering phase shifts. The variable parameters and the energy offset $E_F$ together fix the phase and the amplitude of $\chi_j$. The Debye-Waller factors as mentioned earlier provide a description of the effects of the thermal and static disorder in the sample. The scattering phase shifts calculated within the program were checked by analysing EXAFS data for crystalline Si and SiO$_2$ taken during the same experimental shifts as the porous Si samples.

4.4 Characterisation by electron microscopy

There have been several basic methods used to study the morphological features of semiconductor layers. High resolution scanning and transmission electron microscopy [S(T)EM] are very powerful techniques which have been used to study layer morphology, film thicknesses and nanostructural dimensions, over a wide range of semiconductors materials from amorphous to crystalline, while transmission electron diffraction (TED) patterns provide very useful structural information on crystallinity. [Labunov et al. (1979), Aharoni and Durembergova (1983), Nakahara and Hebard (1983), Budhani et al (1984), Beale et al. (1986), Takagi et al. (1990), Know et al. (1991), Pearsall et al. (1992), Matsumoto et al. (1993), Mauckner et al (1993), Muranaka et al. (1993), Yeh et al. (1993), Bayliss et al. (1994), Guang-Pu et al (1994), Lin et al. (1994), Reid et al. (1994), Takasuka and kamei (1994), Kammei et al. (1995), Fathauer (1995), Parkhutik (1995) and Rauf (1995)].

The procedure for preparation of thin slices of semiconductor materials for S(T)EM measurements still remains an art available to a limited number of specialists. For TEM and TED measurements on porous Si samples presented in this thesis the porous Si was simply fractured and tilted to $\sim 45^\circ$ to obtain TEM cross sectional images of the porous/bulk interface, to obtain quantitative information about the morphology of the surface and to check whether structure sizes appropriate to quantum size effects are present. TED patterns have been obtained from the same samples to obtain further structural information. The thin film samples of indium sub-oxide and indium tin sub-oxide were examined by S(T)EM on the surface and in cross-section to determine the thickness of the film. The cross sections were produced by fracturing the film in liquid nitrogen to give a more brittle fracture. All samples in this project were examined in SEM mode on a JEOL JEM 100X TEM with scanning attachment. This
enable high resolution S(T)EM images to be obtained of magnifications up to $10^5$ times. Accelerating voltage used was 100 kV.

### 4.5 Energy dispersive analysis of X-rays (EDAX)

When a selected point on a specimen is irradiated by a focused electron beam many events can occur enabling quantitative microanalysis to be accomplished [Goldstein (1979)]. Fig. 4.3 shows schematically some of the events possible. Backscattering of primary and production of secondary electrons, the emission of Auger electrons, X-rays and light are the important events occurring in reflection, while in transmission there are unscattered, elastically and inelastically scattered electrons [Bishop (1974), Reed (1975), Chandler (1977) and Isaacson et al. (1979)]. Most of these are sources of important information: the electrons could be utilised in electron microscopy as could the light emission by cathodoluminescence, also the Auger electrons could provide chemical information. Similarly the X-rays could be used to obtain some chemical information [Bishop (1986)]. The production of the X-ray energy spectrum during the electron bombardment is characteristic of the elements so bombarded. There are a considerable number of correction factors, and these were programmed into the microprocessor controlled equipment used in this study, however these were designed for bulk samples. In general, one wants to maximise the characteristic information measured from the specimen and minimise all other signals. To carry out the compositional analysis of the In-based films it was assumed that the films were thin enough to avoid complications resulting from electron scattering, X-ray absorption and X-ray fluorescence. Furthermore, instrumental factors associated with the uncollimated fluorescence radiation and sample contamination have been assumed to be negligible [Zaluzec (1979)].
Fig. 4.3. The various types of radiation produced by an incident electron beam [After Bishop (1986)].
Chapter 5

Design and development of photoluminescence lifetime system

5.1 Introduction

The most common methods of measuring a photoluminescence (PL) lifetime of a semiconductor involve monitoring the time dependence of the sample emission while exciting it with pulsed or modulated excitation in the form of an energetically well-defined beam of photons whose energy exceeds the band gap of the materials to be examined, and whose power is sufficient to excite an adequate signal. From the sample response relative to the excitation pulse, information about the decay kinetics can be obtained [Demas (1983)]. The PL due to radiative recombination of the charge carriers must then be collected, dispersed into its component wavelengths and detected to produce an electrical signal proportional to the intensity at each wavelength [Jackson (1987)].

The most obvious advantage of PL as a property is the close connection of PL to a number of radiative devices such as semiconductor lasers, light diodes, electroluminescence panels, cathodoluminescence of CRTs, and many others. However, PL is also rapidly evolving into a major basic research tool comparable in importance to absorption measurements. Two reasons for this stand out as significant. First is the sensitivity of the technique. It often happens that features which are just discernible in absorption will completely dominate the PL spectra. The converse is also sometimes true, making PL and absorption complementary techniques. Second is the simplicity of the collection. Absorption measurements require tedious sample preparation. Samples must be cleaved or polished to the proper thickness with parallel front and back surfaces. In contrast, front surface PL measurements can be made with ease on bulk materials of thin epitaxial layers.

A disadvantage of the PL technique is the increased remoteness of the raw data from the physical phenomena of the principal interest. Sometimes considerable analysis is required to infer the spectral dependence or magnitude of the internal recombination from the radiation observed outside the sample.

This chapter gives a detailed description of apparatus and experimental techniques used to obtain the PL results presented in chapter 8. Section 5.2 presents a brief
5 - Design and development of photoluminescence lifetime system

guide of the basic experiment set-up, which is followed by a more detailed appraisal of the individual items of equipment in Section 5.3.

5.2 Photoluminescence lifetime system

A schematic diagram showing the experimental configuration is presented in Fig 5.1. The excitation source used for these experiments was a pulsed nitrogen laser. The laser output intensity could be controlled with neutral density filters and by varying the laser beam diameter by using a variable output aperture. The laser beam was focused on the sample by means of a convex lens.

The sample was mounted in a liquid nitrogen cooled cryostat. The excitation beam passed through the entrance window and the resulting PL emerged from the exit window, which was made bigger in diameter than the entrance window to allow much of the PL radiation to pass through it. The sample holder within the cryostat was angled so that the incident excitation radiation impinged on the sample at ~ 60° to the normal. The PL collection optics detected radiation emitted from the sample at ~ 30°, this prevented any directly reflected radiation emerging from the exit window and getting into the collection optics. The PL and scattered and excitation light was collected by means of a convex lens, which brought it to a focus on the entrance slit of the monochromator. Here cut-off filters were used to remove the unwanted excitation light, allowing only the PL to enter the monochromator.

In the monochromator, the wavelength selection was achieved by means of a diffraction grating, the angle of which determined the wavelength of the light appearing at the exit slit. It was possible to scan manually through the desired wavelength range. The PL at the exit slit was picked up by an appropriate photomultiplier, which had to have a high sensitivity in the spectral region of interest. The resulting signal was fed into a digital storage oscilloscope, along with a reference signal from the pulsed nitrogen laser, and then processed by a PC. The PL pulse could be displayed in tabular form on the printer and stored on floppy disk for future reference.
5.3 Apparatus

The apparatus used in PL lifetime experiment can be divided into five categories. These are:

1. Excitation source.
2. Low temperature equipment.
3. Optics.
4. Detectors.
5. Instrumentation.

5.3.1 Excitation source

The excitation source was a Molelectron Corporation Pulsed Nitrogen Laser Model UV 14 (maximum average power: 450 mW, repetition rate range 1 - 50 pulse per second, pulse energy at 20 Hz: 4 mJ, and pulse duration: 10 ns). Experimentally the highly collimated, monochromatic laser beam is far more convenient to use than high power lamps, such as xenon or high pressure mercury lamps. These latter sources pose problems in that the uncollimated beams of light, which cover a broad spectral range, must be focused down on the sample, after having been suitably filtered, or passed through a monochromator to produce the narrow band of excitation energy required...
5.3.2 Low temperature equipment

Much useful optical work can be done at room temperature; however, cooling of samples can be helpful or even necessary. The first consideration should be whether sample cooling is needed at all. This complication is to be avoided or simplified as much as possible for routine characterisation. But for exploratory work, or for research to establish the accuracy of a characterisation methods for many application which requires high resolution or an exceptional signal-to-noise ratio cooling may be essential. If so, the next decision is whether liquid nitrogen temperatures are adequate. Liquid nitrogen is inexpensive, and requires little in the way of specialised training or techniques. A sample is conveniently cooled by mounting it on a cold finger connected to a liquid nitrogen Dewar. If the assembly is held under a vacuum of 0.1 Torr, samples can be maintained to within a few degrees of 77 K.

A. Vacuum system

An Edwards pumping system capable of creating a vacuum of up to 1×10⁻⁷ Torr was used. It consists of a rotary pump (45 litres/min), a Diffstak diffusion pump (135 litres/sec). A Pirani gauge was used to measure the pressure down up to 1×10⁻³ Torr, and a Penning gauge for pressures down to 1×10⁻⁷ Torr. First the rotary pump roughed out the work chamber to a pressure of about 1×10⁻¹ Torr or less, then the chamber was isolated from the rotary pump, and the valve of the diffusion pump open to evacuate the chamber to a base pressure of below 1×10⁻⁶ Torr. The evacuation process takes about 20 to 30 min.

B. Cryostat

The cryostat used through the course of this work was made in the workshop of the Physics Department / Loughborough University, it was made of stainless steel while the sample holder was made of copper. The cryogen used was liquid nitrogen. A schematic diagram of the cryostat is shown in Fig 5.2.
The cryostat chamber is continually pumped out using the oil diffusion pump and rotary backing pump combination in order to keep the pressure below $1 \times 10^{-6}$ Torr, to prevent condensation on the sample and the windows, and also to thermally insulate the liquid nitrogen tank, cold finger, and the sample holder from atmosphere. The cryostat windows are made of Quartz-Spectrosil B, which has a good transmission of approximately 90% in the wavelength region 0.2 - 2.5 μm. The diameters of three radial windows were the same, while the fourth radial window (PL window, facing the detection system), was of bigger diameter to allow more PL radiation to collect by the lens. The f-number, (where $f$-number = distance to the sample / diameter of aperture) of this window was therefore less than the other windows: for small windows of cryostat, $f$-number = 4, while for big window it was 2.3.

The cryostat tank was filled with liquid nitrogen through a central filling tube. The heat from the sample was conducted away because it was mounted on the sample holder which is in contact with cold finger.

C. Sample holder

The sample holder was made of copper mounted on the cold finger to achieve the lowest possible temperature. A thermocouple (copper/constantan of diameter = 0.2 mm) was attached directly to this sample holder in a position very close to the sample.

A 61.73 Ω/m heater, made of 0.1 mm diameter insulated CuNi (44 SWG) wire wound around the base of the sample holder, was used to heat the sample. The end of the CuNi wire was joined to a copper wire for connection to the temperature controller used here as a power source for the heater. The power of the heater was regulated by the temperature controller to ensure a stable temperature.

D. Temperature controller

The DTC2 Oxford Instrument digital temperature controller was designed to measure the temperature of a system and to maintain this at some desired value between 77 and 295 K. The system itself may be anything from a small cryostat to a large furnace.
Fig. 5.2. A schematic diagram of the cryostat used in photoluminescence lifetime measurements.

A temperature sensor mounted within the system feeds a signal to the DTC2 which indicates the temperature on a four digit display. A wide variety of different sensors may be used according to the temperature range of interest. An interchangeable plug-in range card in the DTC2 amplifies the signal from the sensor to a level suitable for driving the display [Oxford Instruments]. The controller itself can be used as a power
feeder to the heater, regulating the power to the heater to provide optimum temperature stability. It can be used to provide up to 30 watts of output, which is sufficient for many small systems. An external output unit can be used for larger systems requiring providing higher power.

For this course of low temperature experiments the temperature control was obtained by setting the front panel switches. To obtain an accurate measurement of the temperature, one of the thermocouple junctions (the measuring junction) was attached to the sample holder, and the other (the reference junction) was held in boiling liquid nitrogen.

5.3.3 Optics

A. Collecting lens

The correct selection and careful alignment of the collection optics are a major consideration in PL experiments, especially where the laser light needs more collimation to focus on the sample. The emitted light intensities can also be very small, and losses must be kept to a minimum. For the apparatus shown in fig.(5.1), the f-numbers of the cryostat and monochromator were fixed at 2.3 and 3.9 respectively. In order to collect almost all the light emerging from the exit window of the cryostat, the convex lens must have an f-number less than 2.3, otherwise the light will not be brought to a focus. In this case the lens has a focal length of 5 cm and a large diameter of 8 cm, giving it an f-number of 0.625. By using the simple spherical lens formula:

\[ \frac{1}{f} = \frac{1}{u} + \frac{1}{v} \]  

(5.1)

where \( f \) is the focal length, the object distance \( u > f \) can be adjusted so that the image distance \( v \) is sufficient to give the correct angular spread of the light to match the f-number of the monochromator. In this way all the light entering the monochromator falls on the grating, with no overlap and no loss of signal.

B. Monochromator

A standard Mini-Chrom (Fastie-Ebert) Monochromator was used through this series of PL lifetime experiments. The device consists of entrance and exit slits, two diagonal mirrors, a plane reflective diffraction grating, a spherical collimating/
focusing mirror. Both slits are on the same axis and the slit width can be varied from 50 μm x 4 mm to 1 mm x 4 mm via fixed interchangeable slits. This monochromator has a focal length of 74 mm and f-number of 3.9. The cross-sectional area of the reflective diffraction grating is 2 cm square and the grating spacing is 1800 lines/mm, blazed at a wavelength of 500 nm, the wavelength range being 300 to 800 nm. The wavelength of the light emerging was changed by rotating the diffraction grating around its axis. The bandwidth of the light emerging at the exit slit is given by:

$$\Delta\lambda = \frac{sd}{f}$$  \hspace{1cm} (5.2)

where s is the slit width, d is the grating spacing and f is the focal length of the collimating mirror. The resolution of the monochromator varied from 0.36 to 7.41 nm depending on the slit widths.

The calibration of the monochromator was carried out by observing the well known emission of either He-Ne laser light, dye laser light or ruby emission at the exit slit.

C. Filters

Three types of optical filters were used in the PL experiments, and these were:

1. Bandpass interference filters
2. Neutral density filters
3. Cut-off filters

1. Bandpass interference filters

Interference filters operate through a complex process of constructive and destructive interference to select a narrow range of wavelengths with a maximum transmission efficiency. The transmission width of the spectral band ranges from less than 1 to many manometers. By inserting such filters into the laser beam, it is possible to remove any unwanted radiation originating in the laser plasma, whilst still transmitting the required laser line. A few filters were used to cover some lines in UV wavelengths. These filters gave a transmission of ~45% and half width of ~8 nm.
2. Neutral density filters

Neutral density filters are used to attenuate the intensity of the laser light over a broad spectral region. Although these filters are nominally 'neutral', there are variations in their transmission characteristics over the spectral region of interest. Most of the neutral density filters show an increase in transparency with increasing wavelength in the region from 700 to 800 nm, particularly in the filters with visible transmission less than 10%. As an example, the neutral density filters used in this series of PL lifetime experiments had transmissions ranging from 4% to 56% for the wavelength of 337.1 nm. Such changes in transmission would affect the intensity of the laser beam.

3. Cut-off filters

These filters were used to isolate the PL from the lower wavelength scattered excitation light at the entrance slit of the monochromator, or directly before the detector. Essentially they are long bandpass filters with rapid cut-off below a given wavelength: cut-off is specified as the wavelength at which there is 50% of the maximum transmission.

The cut-off filters used through this course of study can be divided into three categories: colour glass, UV blocking, and edge filters. The first category of these filters are made of highest quality Schott coloured glass, with uniform spectral properties over the entire aperture. However, there are two disadvantages of colour glass filters. Firstly, they function by absorbing the unwanted wavelengths. This may be a problem in high power situations, as fluorescence may be caused due to laser irradiation especially at UV wavelengths. This can be particularly troublesome where the filter fluorescence goes straight into the monochromator along with the PL. At higher excitation energy the fluorescence can be reduced to a negligible level by placing the filter at the exit slit of the monochromator, directly before the detector.

The second category of filters are the UV filters which are made of perspex. The one used in PL lifetime measurements blocks completely wavelengths below 350 nm, and its transmission is 50% at a wavelength of 375 nm, and increases until reaching a maximum value of 88% at 500 nm. The most important advantage of this filter is that it can be used without problems due to scattered laser light from PL experiments (i.e., no fluorescence has been found to originate from this type).
Finally the third category, edge filters, are commonly classified as low pass and high pass filters depending on whether they reflect or transmit at wavelengths beyond their transition wavelength. They are often further categorised as colour separation filters or 'hot' or 'cold' mirrors, depending on where in the spectrum their transition wavelength actually lies. The most important advantage of edge filters is they can be used in high power light sources without trouble from scattered laser light through PL experiments. This is because they are designed to operate through the process of reflecting the unwanted wavelengths at the coated side of the filter which faces the incoming PL and scattered radiation beams, and transmit the desired wavelengths [Melles Griot (1990)]. Edge filters are also designed to exhibit a sharp transition over a very narrow wavelength range from being highly transmitting to highly reflective or vice versa.

5.3.4 Detectors

Three kinds of photodetectors were used for PL Lifetime experiments. These were:

A. Photomultiplier tube
B. Silicon detector
C. InGaAs detector

A. Photomultiplier tube

Among the photosensitive devices in use today, the photomultiplier tube (PMT) is a versatile device that provides extremely high sensitivity and ultra fast response. The PMT used in PL lifetime experiments was a Hamamatsu, model R2949, of 28 mm diameter, side-on type, the minimum useful size of photocathode being 8 x 6 mm. The R2949 PMT features are very low dark current of order of 5 nA, extremely high quantum efficiency, high current amplification of order of $10^7$, good signal to noise ratio, and a spectral response from UV to near infrared (185 - 900 nm).

The noise equivalent power (NEP) refers to the amount of light usually in Watts producing a signal to noise ratio of unity in the output of the PMT, which is of order of $1.4 \times 10^{-16} \text{ Hz}^{-1/2}$ for this PMT. The anode pulse rise time is 2.2 ns and the electron transit time is 22 ns. Because of these features, the R2949 PMT is well suited for use in various low level photometries such as photon counting application and PL
lifetime measurements. A Thorn EMI model PM 28B stabilised power supply provided cathode to anode voltage.

B. Silicon detector

The silicon detector used was BPX 65 planar silicon PIN photodiode housed in a modified TO -18 case incorporating a plain glass flat window having no influence on the beam path of the optical system. The cathode is electrically connected to the case. Because the BPX 65 is capable of detecting wide bandwidth signals due to its excellent high frequency response, this coupled with its high sensitivity make the device ideal for PL lifetime signal detection applications.

By applying a suitable bias voltage, which for this particular detector is recommended to be 20 Volts, the typical photocurrent rise time is 0.5 ns, the dark current of the order of 1 nA, and the noise equivalent power (NEP) is $3.3 \times 10^{-14}$ WHz$^{-1/2}$. Because of these features this detector was used for detection of PL pulses.

This photodiode was actually mounted in a BNC package. This BNC package is a hermetic package, allowing convenient transmission of the output frequency for all frequencies within the operating bandwidth of the photodiode. The window at one end of the package permits the optical energy to be focused directly on the active area of the diode. The other end of the package mates with all standard BNC type plugs, thus permitting easy insertion of these devices into BNC sockets.

C. InGaAs detector

This detector is an InGaAs PIN photodiode housed in a TO -18 case incorporating a borosilicate glass window which has no influence on the beam path of the optical system. The cathode is electrically connected to the case. Because this detector covered a wide spectral range from the near infra-red through longer wavelengths (780 to 1550 nm), and has high quantum efficiency (more than 90% for infrared radiation; 95% at peak wavelength), it was useful in infrared measurement systems.

By applying a suitable bias voltage (5 Volts) typical photocurrent rise time is 2.5 ns, dark current 0.3 nA, and the NEP at peak wavelength is $4 \times 10^{-15}$ WHz$^{-1/2}$. The package of this detector was same as that of the silicon detector.
In both Si and InGaAs photodiodes the signal to noise ratio was very low and a few methods have been tried to improve it, including (I) earthing the detectors, (II) shielding the photodiodes with mu-metal and (III) cooling the photodiodes, which was achieved by the heat sink method or by liquid nitrogen using a small cryostat built up for this purpose. The signal to noise ratio however did not improve because of the pick up stray noise from the other electrical equipment. Therefore a PMT was used which was similar to that one used for steady-state PL measurements.

# 5.3.5 Amplifier

Some PL lifetime experiments give such a low light signal intensity that by using either BPX 65 or InGaAs PIN photodiodes alone, the system is unable to produce a detectable pulse. In these cases the signal needs to be amplified. In particular the PL of some semiconductor materials has a very narrow bandwidth (i.e. it decay very fast, in nanoseconds), and most amplifiers mismatch such pulse widths. Such measurements need amplifiers of special characteristics. A fast-settling operational amplifier OPA600 (Burr-Brown) was chosen for these experiments. The choice of a very large gain bandwidth up to 5 GHz, high speed and high accuracy up to 0.01% at high frequency with fast settling time, and thermally balanced design maintains this accuracy. It is also stable, has good phase margin with minimum overshoot, and allows the user to optimise the settling time for various gains.

In order to overcome the noise due to using the main voltage supply, a rechargeable battery was used as a voltage supply. To use the amplifier with a photodiode of different reverse voltages, but within the limit of amplifier voltage, a voltage regulator was added to the circuit.

# 5.3.6 Instrumentation

## A. Oscilloscope

In PL lifetime experiments involving the measurement of a fast and small signal, where the noise can be a major problem, an oscilloscope is useful with a bandwidth of at least 500 MHz, good external triggering capability, and high writing speed, to be able to observe PL pulses as well laser pulses.
A Tektronix TDS 520 digitising oscilloscope with, 500 MHz maximum analogue bandwidth (500 megasamples per second), was used in these PL lifetime experiments. In this oscilloscope the average mode lets you acquire and display a waveform record that is an averaged result of several acquisitions, thus reducing the random noise. The digitising oscilloscope display can be created as either an image or a plot depending on the output format you select. To set up remote communication, an IEEE standard 488.2 - 1987 GPIB cable was used between a GPIB connector on the oscilloscope rear panel and the GPIB port on a PC.

B. Data acquisition

The PL lifetime data presented in this thesis were collected under the control of a Viglen II PC computer, using a GPIB board and a software GPIB package supplied by National Instruments. This is read a waveform profile from the oscilloscope and stored it in a file as time and voltage value. A simple basic program has been written to translate and save the time and voltage data in a format which can be used by any spreadsheet package.

5.4 Calibration of PL lifetime system

A pulsed nitrogen gas laser was used as a monochromatic excitation source (337.1 nm) for all the PL lifetime measurements. To calibrate PL lifetime system, pyrene solution of well known fluorescence lifetime was used [Birks (1970), Kuz'min and Sadovskii (1976) Delouis et al (1979) and Bright (1988)]. A constant concentration of pyrene (4.6x10^-5 mol dm^-3) in cyclohexane was prepared and deoxygenated with nitrogen purging for 15 - 20 min prior to taking measurements. PL decay curves of this solution were recorded using the above excitation source. The cross sectional area of the laser beam at the pyrene cell was about 2 x 5 mm^2. Fig. 5.3 shows a typical fluorescence decay curve, with a lifetime of 652 ns which agrees very well with the result of 650 ns of Delouis et al. (1979), performed under the same experimental conditions (e.g., solvent, solution concentration and excitation light source). Kuz'min and Sadovskii (1976) found the lifetime of pyrene to be 480 ns. This difference between the measurements reported in this thesis and those of Kuz'min and Sadovskii might be explained by differences in the excitation and solvents used. In all of the series of PL decay measurements exactly the same system
experimental set up was used as for recording the fluorescence of the pyrene solution, except that the cross sectional area of laser beam impacting the samples was of about $3 \times 10 \text{ mm}^2$, due to the larger size of the samples.

![Fluorescence decay curve of pyrene solution used for PL lifetime system.](image)

Fig. 5.3 Fluorescence decay curve of pyrene solution used for PL lifetime system.
6.1 Methods of porous silicon preparation


The preparation of porous Si on the C-Si surface is thus a rather simple process. The thickness, structure, optical and electric properties of porous Si strongly depend on preparation conditions, such as n- or p-type starting silicon wafers, wafer resistivity, current density (or voltage) imposed, HF concentration in the electrolyte, anodising time and light illumination level, [Bomchil et al. (1989), Smith and Collins (1992), Zhang et al. (1992), Qin and Jia (1993), Lin et al. (1994) and Li and Fang (1995)]. However, it must be stressed that light-emitting porous Si can be produced over a wide range of most of these parameters [Fauchet (1995) and Koch and Petrova-Koch (1995)].

There were two groups of porous Si sample prepared in this study, the first set being used for visible PL emission measurements and the second for visible EL measurements, but both groups of the porous Si samples were prepared by the electrochemical etching of (100) p-type, boron-doped Si wafers of resistivity of 1 - 5
Sample preparation techniques

Ω cm and thickness 0.3 - 0.35 mm. The mixture of the electrolyte was initially varied until a combination was found which produced the most efficiently emitting material. The electrolytes used were a mixture of hydrofluoric acid (48%) : H₂O : ethanol, in the ratio 1 : 1 : 2, respectively, resulting in porous Si film thicknesses of >1 μm. These samples obtained showed excellent stability to laser illumination and to the environment.

6.1.1 Porous Si samples for photoluminescence and EXAFS investigation

The first group of porous Si samples used a 25 × 25 mm² platinum plate as a cathode, with silicon as anode. Current density, voltage, and time of anodisation were all varied to produce materials with different PL response. The anodising conditions for red, yellow and green emitting samples were: (i) 8 min, current density 30 mA cm⁻², (ii) 20 min, 20 mA cm⁻², + 5 min without current, (iii) 20 min, 20 mA cm⁻², + 30 min without current, respectively. All the samples were prepared at room temperature and under natural light illumination. The samples were rinsed in deionised water, dried under N₂ gas flow, and stored for about 8 months for PL lifetime measurements and 13 months for steady-state PL and EXAFS measurements in ambient conditions after preparation. The wafers for yellow and green PL were coated on the back with aluminium to provide a low resistivity electrical contact for uniform distribution of current density during anodisation and wax to prevent aluminium from making contact with HF acid solution. The purpose of this is to produce a very uniform emission area. Some other porous silicon samples used for time evolution measurement were placed in a vacuum (10⁻⁴ - 10⁻⁵ torr).

6.1.2 Porous Si samples for electroluminescence investigation

The anodisation conditions for porous Si used for EL experiment were: 10 mA cm⁻² current density, etching time 15 min and washed for 10 min in ethanol to remove the residual etched solution and also to prevent excessive exposure to oxidising agents like water and air. A porous Si sample was formed with a strong orange PL when excited by a UV lamp. The sample was exposed to the ambient conditions for a few days before ITO sputtering.
6.2 Methods of thin film preparation

Thin solid films of indium and indium tin oxides can be prepared by various techniques such as sputtering [Fan and Goodenough (1977), Madan and Shaw (1998), Kawada (1990), Shigesato et al. (1992), Shigesato et al. (1993), Fukarek and Kersten (1994), Kim et al. (1994), Kamei et al. (1995), Tsybeskov et al. (1995), Yi et al. (1995) and Danson et al. (1996)], evaporation [Lemonnier et al. (1975), Takaki et al. (1988), Shigesato et al. (1991), Korobov et al. (1994), Rauf and Brown (1994), and Abbas et al. (1995)] and chemical vapour deposition [Kane et al. (1975), Madan and Shaw (1988), Maruyama and Tabata (1990), Maruyama and Fukui (1991) and Vetrone and Chung (1991)]. These different techniques use all three phases of matter (vapour, liquid and solid) as the starting materials in producing solid films, [Elliott (1990)].

Only a brief description will be given of the dc sputtering technique, used to prepare the films used in this work. The sputtering process is rather more complicated than some other methods (for example, thermal evaporation) but enjoys the advantages of being far more flexible. In essence, it consists of a bombardment of a target by energetic ions from a low-pressure plasma, causing erosion of material, either atom by atom or as clusters of atoms, and subsequent deposition of a film on substrate. The simplest way to induce sputtering is to apply a high negative voltage to the target surface, thereby attracting positive ions from the plasma. However, this dc sputtering process is only feasible for targets composed of metals, or at least consisting of material sufficiently electrically conducting that the target can act as an electrode. An oil diffusion pump together with liquid nitrogen cooled trap (to eliminate water vapour and to a lesser extent hydrogen contamination) can produce a base pressure typically of order of $10^{-6}$ torr in the chamber. The sputtering gas, commonly an inert gas such as argon, is introduced at a higher pressure, say 1-20 mtorr. Films possessing a good degree of compositional homogeneity can be achieved for sufficiently large substrate-target distances. Usual sputtering rates for insulating target materials in an inert gas atmosphere (e.g. Ar) are in the range 1-10 Å s$^{-1}$, and perhaps a little higher for metallic targets.

A further option offered by sputtering is the use of gases other than Ar which chemically react with the target, resulting in ‘reactive’ sputtering. This can significantly increase the sputtering rate, as well as allow incorporation of chosen additives into the films. This has been used in producing hydrogenated amorphous silicon (by sputtering in an Ar:H$_2$ mixture), doped amorphous silicon films

Many factors combine to produce variability in purity and composition of the resulting films, and some are listed below:

(a) Substrate temperature.
(b) Substrate-source separation and orientation.
(c) Base gas pressure in chamber.
(d) Sputtering gas pressure.
(e) Ratio of partial pressure of reactive gas to inert gas (in reactive sputtering).
(f) Bias voltage of target or substrate.

The sputtering technique can be used to produce materials which can be either amorphous or crystalline, or both [Madan and Shaw (1988) and Elliott (1990)]. Most of the materials used in these studies have some degree of medium range order.

6.2.1 Preparation of InOx and ITOx thin films on PET

The InOx and ITOx thin films studied in this work were produced by dc reactive magnetron sputtering from indium metal and indium tin alloy targets respectively (the latter containing 10% Sn by weight) in an oxygen/argon gas mixture. This allows control of the film stoichiometry by variation of oxygen partial pressure. The substrate was 50 μm thick polyethylene teraphthalate (PET or ICI Melinex (mylar)) rolled at about 0.15 m/s under tension over a polished metal roller at room temperature. The deposition conditions were : base pressure 1 × 10⁻⁵ torr; Ar partial pressure - around 2 mtorr, O₂ partial pressure ranging between 0.1-3.8 mtorr over the composition range to above-stoichiometry, dc power up to 1 kW. A continuous series of samples was thus produced in a single deposition on a single substrate about 10 m long, the oxygen content of the films being 0 at the start of the substrate and over-stoichiometric at the end. The tin is commonly believed to provide electrons by substituting for indium and acting as a singly charged donor on an indium site [Bellingham (1991)].
6.2.2 Preparation of ITO thin film on porous Si

The \textit{np} heterojunction in porous Si was fabricated by a direct sputtering of a transparent layer of \textit{n}-type ITO onto a (\textit{p}⁺-type) porous Si surface at room temperature, using dc reactive sputtering. The ITO was sputtered in an argon/oxygen gas mixture of nearly 95\% argon and 5\% oxygen. The system preparation conditions were \textit{1 × 10}⁻⁵ torr base pressure and the dc sputtering power up to 1 kW. An alloy of indium and tin (containing 10\% Sn by weight) was used as the target to produce ITO transparent conducting thin film of about 250 nm thickness and 40 Ω/□ sheet resistivity.

To get good electrical connection, the anode was made of a Au film produced by vacuum deposition on the rear of the \textit{p}-type substrate. Thin wires were fixed onto the front and rear of the sample using silver-based conducting paint.
Chapter 7

Steady-state photoluminescence and structural properties of porous Si

7.1 Introduction

Silicon has been the subject of a great deal of investigation, both fundamental and technological. It is widely used as a basic material in modern industry applications such as microelectronics, communications and computers [Ellis (1973) and Li and Fang (1995)]. It is difficult to use it as an optoelectronic materials due to its poor optical emission efficiency and its relatively narrow and indirect band gap [Richter et al. (1991), Cullis et al. (1992), Lee and Peng (1993), Han et al. (1994) and Li and Fang (1995)]. Red photoluminescence (PL) from porous Si etched under suitable conditions was found by Canham (1990). Recently, wide attention has been paid to the phenomenon of efficient visible PL from porous Si in solid-state physics, material research and device technology because of its potential applications in silicon-based optoelectronics [Lehmann and Gösele (1991), Jang et al. (1991), Koshida and Koyama (1992), Tischler et al. (1992), Enachescu et al. (1993), Lee and Peng (1993), Koyama et al. (1993), Stevens and Glosser (1993), Ambrazevicius et al. (1994), Duan et al. (1994), Guang-Pu et al. (1994), Malý et al. (1994), Peng et al. (1994), Russell et al. (1994), Wadayama et al. (1994), Yong-dong et al. (1994), Bsieny et al. (1995) and Cruz et al. (1996)]. Therefore, intense research has been started around the world, focusing mainly on the mechanism of PL, electroluminescence (EL) and the physical structure of porous Si.

The temperature dependence of steady state PL spectra from different porous Si samples has been recorded. The PL was strong enough to be visible by the naked eye, even for low excitation power intensity. Room temperature extended X-ray absorption fine structure (EXAFS) measurements have been performed on the above samples, as EXAFS is particularly well suited technique to study the quantitative characterisation of the local structure of porous Si. The method of EXAFS is able to recognise some differences between crystalline Si and porous Si samples [Dalba et al. (1995)]. Transmission electron microscopy (TEM) has been used to investigate the
porous Si morphology and the structural information using transmission electron diffraction (TED) patterns.

7.2 Steady-state photoluminescence

The steady state PL spectra of porous Si samples used in this course of study, were measured using beamline 12.1 at the 2 GeV Synchrotron Radiation Source (SRS) at Daresbury Laboratory. The excitation wavelength was selected from broad UV synchrotron radiation using a Spex monochromator. PL from samples was analysed using a Spex (Minimate) monochromator and photomultiplier operating in photon-counting mode. To measure PL at different temperatures, the samples were mounted in a temperature-controlled Oxford Instruments cryostat which permitted the sample to be cooled to liquid nitrogen temperature.

PL emission spectra were recorded by scanning the Minimate monochromator in the wavelength range between 400 to 800 nm, using an excitation wavelength of 340 nm as this excitation gave the most efficient emission. This was comparable with the excitation wavelength (337.1 nm) used for PL lifetime measurements (see chapter 8).

The PL response of porous Si samples is shown in Figs. 7.1-2, which give typical examples in the temperature variation in the strong visible steady-state PL spectra excited with 3.65 eV. Fig. 7.1 shows PL spectra for an orange/red porous Si sample recorded at four different temperatures between 77 and 295 K, and taken nearly six months after sample preparation. A comparison will be made later of this behaviour with the temperature change of PL lifetime measurements which are measured with the same sequence of temperature variation. The spectra of Fig. 7.2 were recorded at five different temperatures on three different samples of porous Si which emit PL in green/yellow, yellow/orange and red and were prepared about 13 months prior to PL measurements and stored at the laboratory environment. This emission range covers almost all the visible PL region. As shown in Figs. 7.1-2, the PL intensity of steady-state PL spectra decreases with increasing sample temperature from 77 to 295 K [Zheng et al. (1992), Fishman et al. (1993), Amato et al. (1994), Xie et al. (1994) and Di Francia (1994)]. This in principle, is determined by radiative recombination in competition with nonradiative recombination [Qin (1995)]. These PL spectra appear to be broad bands of symmetric Gaussian shape [Kanemitsu (1993), Lebedev et al. (1993), Astrova et al. (1995), Grivickas and Linnros (1995), Li and Fang (1995) and Ookubo and Sawada (1995)], with a maximum position dependent on sample
Steady-state photoluminescence and structural properties of porous Si

presentation and the sample temperature. It was found that the PL peak positions shift to higher energies with increasing anodisation time [Lee and Chen (1994), Fauchet (1995) and Li and Fang (1995)]. Prokes et al. (1992), Prokes (1993) and Kanemitsu et al. (1993) reported that no significant blue shifting was observed on reduction of the average size of Si crystallites. The PL spectra of Figs. 7.1-2, with their broad distribution of photon energies might represent the distribution of confinement energies [Asnin et al (1993), Amato et al. (1994) and Di Fancia et al. (1994)], and be related to thermalisation of defects which have a broad band energy distribution in the band gap of porous Si [Bassous et al. (1992) and Vial et al. (1992)]. The broad spectrum width is commonly attributed to the non-uniform sizes and shapes distribution of Si nanocrystallites which are at the origin of the light emission and which contribute mainly to the spectrum widening (i.e., a broad distribution of confinement energies), [Nakagawa et al. (1992), Ohno et al. (1992), Zhang et al. (1992), Lebedev et al. (1993), Lee and Peng (1993), Wang et al. (1994), Bsiesy et al. (1995), Li and Fang (1995), Fauchet (1995) and Kux and Ben Chorin (1995)] explained the observed PL line width as due to unnatural size distribution. This implies that the broad PL peak is ascribed to the size distribution of Si wires in the porous Si sample. It was found that when the porous Si sample was cooled down from room temperature to liquid nitrogen temperature the PL intensity increases by a factor ranging between 4.5 - 5.2 for the PL spectra shown in the above figures. This observation agrees with the observation of other researchers [Mochizuki et al. (1992), vial et al. (1992) and Xu et al. (1992)]. In this work observation that the PL returned to the original intensity and position when the temperature was ramped back to 295 K, means that no permanent damage resulted to the porous Si during cooling [Tischler et al. (1992), Bassous et al. (1992), Perry et al. (1992), Lebedev et al. (1993) and Amato et al. (1994)]. As you can see from Figs. 7.1-2, the FWHM of all PL spectra are weakly dependent on temperature [Zhang et al. (1992), Suemoto et al. (1993) and Ookuba and Sawada (1995)], but it increases with the decreasing PL emission energies. On cooling down from room temperature, the PL spectra shifted toward higher energies (i.e. blue shifted) due to the increase of the band gap of Si at low temperature, [Perry et al. (1992), Zhang et al. (1992), Lebedev et al. (1993), Lee and Peng (1993), Malý et al. (1994), Astrova et al. (1995) and Tsuboi et al. (1995)]. All the steady-state PL spectra in this work were blue-shifted and increased in intensity when the temperature was decreased from 295 to 77 K. Other authors, e.g., Malý et al. (1994), had found this behaviour only in the temperature range between 305 to 180 K: below 180 K the PL spectra remained unchanged. It is straightforward to think that the blue shift of the PL peaks from the bulk silicon band gap energy is due to quantum confinement [Delerue et al. (1995) and Li and Fang (1995)]. Therefore, the
porous Si samples used here is indirect band gap [Qin (1995)]. The blue shift of the PL peak energy with decreasing average size of Si crystallites in the porous Si is considered to be strong evidence that the visible PL is caused by the quantum confinement effect in Si nanoparticles, [Malý et al. (1994), Duan et al. (1995), Li and Fang (1995) and Motohiro et al. (1995)].

Fig. 7.1 PL spectra for orange porous Si sample taken at different temperatures: from top to bottom 77 K, 150 K, 220 K and 295 K.
Fig. 7.2 PL spectra for three porous Si samples: green/yellow (a), yellow/orange (b) and red (c); taken at different temperatures: from top to bottom 77 K, 130 K, 180 K, 230 K and 295 K.
7.3 Structural properties of porous Si

This section gives an explanation of the structural information for different porous Si samples which glow in the visible range from red to green and were studied with XAFS and TEM techniques. As mentioned in § 7.2 all the samples were stored in the laboratory environment for different periods of times, and exposed to different wavelengths and intensities of excitation radiation in the course of performing the steady-state and lifetime PL experiments, before taking EXAFS and TEM measurements.

7.3.1 Extended X-ray absorption fine structure

EXAFS is a suitable technique used for investigating the structural details of the effective radiative layers of porous Si. For this study the data were taken around the Si-K edge at ~ 1835 eV for 4 porous Si samples produced under different preparation conditions as described in (§ 6.1) and with different PL responses. For comparison, and to calibrate the system, EXAFS data were also taken from a crystalline silicon (c-Si) wafer.

Fig. 7.3 shows photon near-edge absorption spectra for the above samples. The measurements were conducted on beamline 3.4 (SOXAFS) at the SRS, under vacuum and at room temperature. Ring currents during data taking were between 286 and 222 mA. In Fig. 7.3 the absorption spectra are similar except the relative intensity of the peaks patterns differ from one sample to another. The absorption peaks of the features assuming to Si-Si and Si-O bonding environments are indicated at 1841.5 and 1847.5 eV respectively for c-Si and all porous Si samples. There appears to be a variation between the Si-Si features of porous Si samples, as this feature is very clear for red but decreases gradually with PL colour through the visible until it disappears for the green/yellow porous Si sample. It can be seen that the absorption behaviour of crystalline Si also shows a feature at 1847.5 eV, probably due to the presence of a surface native oxide. For data analysis using EXCURV92, the relaxed approximation was selected for the excited K-shell. Three phase-shifted files were set as Si (centred)-Si, Si-Si and O-Si, for which the amplitude and backscattering phase-shifts were calculated from EXCURV92. Figs. 7.4 - 6 show typical fits to a $k^3$ weighted $\chi(k)$ and the associated Fourier transforms {f.t.$[k^3\chi(k)]$} for the c-Si wafer and porous Si samples. Fourier transforms show the second shell in porous Si with large oxygen content are fitted well by a bridging oxygen between two silicon atoms [Bayliss et
Steady-state photoluminescence and structural properties of porous Si

al. (1995)], i.e. Si-O-Si at ~ 3.8 Å for red and orange porous Si. The disorder in Si-O bond lengths ~ 1.5 Å for all porous Si samples. The Si-O-Si Debye-Waller factor is 0.002 ± 0.002 Å². (All distances are accurate to ± 0.02 Å). This reflects the rigidity of these bonds and also provides evidence for the existence of oxygen in the bulk.

The Fourier transforms of yellow and green porous Si samples show a single peak at ~ 1.6 Å signalling the presence of a Si-O bond. There are some weak features in the 2 - 4.5 Å region. These features are probably due to the beating of backscattering waves of the Si cause and silicon oxide outer shells [Sham et al. (1992)]. It appears from these figures that these two porous Si samples are largely dominated by the surface-sensitive Si-O EXAFS signal, since the porous Si has a very large surface

Fig. 7.3 Si K-edge EXAFS spectra for c-Si, red, orange, yellow and green porous Si. Si-Si and Si-O absorption peaks are indicated.
area. On the other hand for red and orange porous Si samples the first, second and third nearest neighbour shells are clearly observed and the peak more or less in the same place in both sets of Fourier transforms, although the peak height of the theoretical fitting for the second and third shells are either a little bit lower or higher than the experimental spectrum. The first shell nearest Si-Si interatomic distances obtained by filtering and backtransforming are identical (r = 2.32 Å with an uncertainty ± 0.01 Å). Locally ordered structure in these two samples are seen from second and third neighbour shells appearing as peaks at 3.8 and 4.4 Å in the Fourier transform data; such structure is absent in a-Si [Schuppler et al. (1994)]. EXAFS shows evidence of crystalline-like structure for porous Si very similar to that of c-Si [Delba et al. (1995)].

![Fourier Transform Diagram](image)

**Fig. 7.4** $k^3$-weighted Fourier transform of SOXAFS from c-Si. 1st, 2nd and 3rd shell Si-Si and 1st shell Si-O bond are indicated.
Fig. 7.5 $k^3$-weighted Fourier transform of SOXAFS from red (a) and orange porous Si (b). 1st, 2nd and 3rd shell Si-Si and 1st shell Si-O bond are indicated.

Fig. 7.6 $k^3$-weighted Fourier transform of SOXAFS from yellow/orange (a) and green/yellow porous Si (b). 1st shell of Si-Si and Si-O bond are indicated.
7.3.2 Electron microscopy for porous Si

The structure of porous Si was investigated using TEM. Images of the surface morphology of PL porous Si are presented, and demonstrate the possibility of platelet nanometer-scale structures in these materials. Fig. 7.7 show a series of TEM images with magnification up to 160 K using Jeol JEM 100 CX. The three specimens used were from different porous Si samples, all of them prepared from p-type wafers. These images of TEM show a compact material. The surface layer of red to green porous Si consisted of mesoparticles with diameters ranging from 4 - 10 nm. The slight increase in diameter observed with emission energy increase implies a decrease in connectivity and hence a decrease in dimensionality if quantum confinement is appropriate for the PL mechanism. Unfortunately the connectivity cannot be determined from these micrographs which sample only a limited volume of potential. In general, porous Si sample of longer anodisation times produce less homogeneous surfaces [Fauchet (1995)].

Investigating TEM diffraction patterns is probably a most reliable technique to study the existence of Si microcrystallities in porous Si layers [Takazawa et al. (1994)]. Fig. 8.8 shows TEM diffraction patterns of Si microcrystallites in c-Si and porous Si layers taken from the same areas which were used for TEM images. Many edge areas of these samples were scanned with highly focused beams. The red porous Si gave a slightly sharp ring diffraction pattern with crystalline spots as shown in Fig. 7.8(b), and the orange and yellow/green porous Si gave a diffuse rings as in Fig. 7.8(c and d), which may indicate the presence of amorphous regions due to amorphous SiO₂ on the porous Si layer, formed by oxidised Si nanometer size of c-Si [Motohiro et al. (1995)]. The ‘white’ regions could show layers which are truly amorphous, or they could indicate the formation of a randomly oriented Si crystalline structure. Another possibility is that the amorphous region is primarily either SiHₓ [Pearsall et al. (1992)] or some Si nanocrystallites surrounded by SiO [Hummel et al. (1993)]. From the TEM images and the calculation of d-spacing of the TEM diffraction patterns of porous Si layer and comparing it with the c-Si d-values using Miller indices (Table 1), it is revealed that the particles are indeed crystalline Si. This is in accordance with the X-ray energy dispersive spectroscopy and diffraction pattern results on porous Si by Hummel et al. (1993). The diffraction rings are fairly broad and diffuse because of the small particle size [Zhang et al. (1992)].
Table 1 The d-spacings of diffraction pattern for porous Si samples.

<table>
<thead>
<tr>
<th>sample</th>
<th>diffraction orders/ring No.</th>
<th>r (mm)</th>
<th>d (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>c-Si</td>
<td>1</td>
<td>8.5</td>
<td>3.18</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.42</td>
<td>1.90</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.67</td>
<td>1.62</td>
</tr>
<tr>
<td>red</td>
<td>1</td>
<td>8.0</td>
<td>3.38</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>14.5</td>
<td>1.86</td>
</tr>
<tr>
<td>orange</td>
<td>1</td>
<td>7.0</td>
<td>3.86</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>21.5</td>
<td>1.26</td>
</tr>
<tr>
<td>yellow</td>
<td>1</td>
<td>7.0</td>
<td>3.86</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>22.0</td>
<td>1.23</td>
</tr>
<tr>
<td>a-SiO₂</td>
<td>1</td>
<td>7.0</td>
<td>3.86</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>22.0</td>
<td>1.23</td>
</tr>
</tbody>
</table>
Fig. 7.7 TEM micrographs of Si particles for (a) red, (b) orange and (c) green/yellow porous Si samples.
Fig. 7.8 TEM diffraction patterns of c-Si (a), red (b), yellow (c) and (d) green/yellow porous Si for the same samples used for TEM images.
Chapter 8

Investigation of photoluminescence lifetime in porous silicon

8.1 Introduction

The interest in strong visible photoluminescence (PL) from porous Si has initiated many studies on the specific recombination processes in this material. In particular, almost all the published lifetime measurements reveal a complicated nonexponential decay which varies with the detection wavelength and sample preparation [Gardelis et al. (1991), Fuchs, et al. (1992), Matsumoto et al. (1992), Calcott et al. (1993), Muller et al. (1993), Pavesi et al. (1993), Mauckner et al. (1994), Ookubo et al. (1994), Sawada et al. (1994), Takazawa et al. (1994), Finkbeiner and Weber (1995), and Kanemitsu (1995)]. Luminescence offers the possibility of a time-resolved detection after pulsed excitation, and this can be analysed to give measurements of the sum of radiative and nonradiative rates [Vial et al. (1992)]. The experimental results in most cases have been interpreted in terms of the quantum confinement model originally proposed by Canham (1990).

In this Chapter a detailed study is reported on the PL lifetime of various porous Si samples (which have also been used for steady-state PL and EXAFS measurements) as a function of PL emission energy. These are compared with each other at different temperatures and on ageing. Different regions on the samples might exhibit different PL efficiency, but the lifetimes were very reproducible.

8.2 General features of photoluminescence

The PL decay profiles of porous Si samples at different temperatures were detected following pulsed excitation from a 337.1 nm nitrogen gas laser (described in § 5.3.1). A liquid nitrogen cryostat (described in § 5.3.2.B) was used to allow variation of temperature from 77 - 295 K via a temperature controller (see § 5.3.2.D). Fig. 8.1 shows the PL decay for orange/red porous Si as a function of PL intensity for several fixed energies in the visible spectrum region. The spectra were measured at different temperatures between room temperature and liquid nitrogen temperature. The PL lifetimes for all porous Si samples, defined as 1/e times the initial intensity of PL
decay, decreased as PL emission energy increased, and increased with decreasing temperature [Xie et al. (1992) and Takazawa et al. (1994)]. The PL decay was corrected for detection efficiency. In Fig. 8.1 the axes are displaced to separate the curves. In general the main feature of all PL decay curves for all emission energies is a nonexponential response, the decay shortening rapidly with increasing sample temperatures and PL emission energies (i.e. confinement) [Ma et al. (1992), Tischler et al. (1992), Vial et al. (1992), Kanemitsu (1993), Mauckner et al. (1993), Muller et al. (1993), Tessier et al. (1993), Mauckner et al. (1994), Ookuba and Hamada (1994), Sumetoto et al. (1994), Takazawa et al. (1994), Wang et al. (1994), Li and Fang (1995), Motohiro et al. (1995) and Ookubo and Sawada (1995)], since the higher energy components decay faster than the lower energy components, that also supports the hypothesis that the distribution of crystallite sizes produces the wide PL spectrum [Fauchet (1995)]. The ultra-small size of the Si particles should confine the electrons and holes. The strong quantum confinement may enable efficient radiative recombination in these Si nanoparticles [Zhang et al. (1992)]. Clearly from Fig. 8.1, the PL decay is much slower and noisier at lower detection energies. This behaviour is similar at lower temperatures to that at room temperature although the decay times are much slower (lengthening of the PL decay is observed at lower temperatures). The increases of PL decay towards lower temperatures are a result of reduced nonradiative recombination at low temperatures [Fuchs et al. (1992), Delerue et al. (1993), Astrova et al. (1995), and Iyer and Xie (1995)]. The low nonradiative recombination rate is probably caused by surface passivation and exciton localisation by quantum confinement [Motohiro et al. (1995)]. Nonradiative channels have been introduced by oxidation of the silicon surface whereas silicon dangling bonds are likely candidates for the nonradiative centres [Tischler et al. (1992)]. Silicon dangling bonds have been identified in porous Si by several experimentalists [Brandt et al. (1992), Mao et al. (1993) and Von Bardeleben et al. (1993)]. The dangling bonds are situated either on the surface of nanoscale units or on the interface between nanoscale units and silicon oxide layer covering them [Qin (1995)].

For more details of how PL changes with temperature, see the steady-state PL spectra in Fig. 7.1 which were measured for the same sample mentioned above, over the same sequence of temperatures.
Investigation of photoluminescence lifetime in porous silicon

Fig. 8.1 PL decays of orange/red porous Si sample at 77 K (a), 150 K (b), 220 K (c) and 295 K (d) at various PL emission energies. The PL emission energies from the top to the bottom are 2.53 eV, 2.39 eV, 2.26 eV, 2.14 eV, 2.03 eV, 1.94 eV, 1.88 eV and 1.77 eV, respectively. The ordinate scale is in arbitrary units for each curve, and the zeros have been adjusted for clarity.
8.3 Photoluminescence lifetime measurements

Lifetime is used here to study the recombination process of excess electrons and holes produced by excitation in p-doped porous Si layers. The knowledge of the PL lifetime as a function of emitted photon energy can help in determining the luminescence mechanism [Tessler et al. (1993) and Qin (1995)]. The recombination lifetime is found to be a sensitive function of PL emission energy and temperature, and these dependencies give information about the nature of electronic states and the recombination mechanism. In order to investigate the recombination mechanism in the visible PL band in porous Si, the PL lifetimes of green/yellow, yellow/orange and red porous Si, have been measured. Every PL decay curve shown here is a result of summation and averaging of 16 decay pulses using a digital oscilloscope. Lifetimes were found to spread over a wide range depending on the temperature, the PL emitted wavelength and the repetition rate of the excitation source. It has been reported by several authors, that the decay lifetimes range from picoseconds to milliseconds (Table 2), correspond to a large variation of electron-hole separation [Takazawa et al. (1994) and Qin (1995)]. As explained in § 8.2 higher PL intensities and slower decays (i.e. increase in the PL lifetime) are found at low temperatures. It has been demonstrated by many researchers that at room temperature the nonradiative recombination dominates over the radiative one, and this nonradiative recombination reduced the PL efficiency [Murayama et al. (1992), 't Hooft et al. (1992), Calcott et al. (1993), Delerue et al (1993), Mauckner et al. (1993), Mihalcescu et al (1993), Di Francia et al. (1994), Iyer and Xie (1995) and Ookubo and Sawada (1995)].

In the measurements reported here nonexponential transients were observed for all PL emission energies and for all temperatures, which can interpreted as a superposition of a fast and a slow decay process, and the presence of two radiative mechanisms in the same sample of porous Si. This behaviour raises the question of the origin of nonexponential decay. It will be shown here that while the PL lifetime does not greatly depend on the porous Si sample, it depends on the temperature and on the PL emission energy.

The decay can be described by two exponential processes with two emission components of different lifetimes, i.e., a faster decay with lifetime $\tau_1$, and slower decay with lifetime $\tau_2$, and can be fitted very well using a stretched exponential, [Andrianov et al. (1992), Matsumoto et al. (1992), Boustarret et al. (1993), Laiho et al. (1993), Kanemitsu et al. (1994), Takazawa et al. (1994), Wang et al. (1994), Li and Fang (1995) and Tsuboi et al. (1995)].
where $I_1$ and $I_2$ are constant. The parameters $\tau_1$ and $\tau_2$ characterise the PL decay rate. Stretched exponentials can, for example, result from the random walk of carriers on a finite distribution of descrete sites in real space, as in amorphous silicon. Regardless of the details of the physical mechanisms, there are well-known producers to define an average or most probable lifetime and this is the lifetime that is usually quoted in the literature [Fauchet (1995)]. The PL lifetimes of the porous Si samples were determined using Origin software.

The time evolution of PL lifetimes $\tau_1$ and $\tau_2$ for orange porous Si sample are summarised in Figs. 8.2 and 8.3 respectively. In each figure, there are six groups of curves, each one corresponding to certain sample age. The PL lifetime was calculated for different temperatures between 77 - 295 K. One can observe both lifetimes, $\tau_1$ and $\tau_2$, decrease with increasing temperature and PL emission energy [Matsumoto et al. (1992), Calcott et al. (1993), Takazawa et al. (1994), Fauchet (1995) and Li and Fang (1995)]. At 295 K, $\tau_1$ is in a range of 10 - 28 $\mu$s, showing a marked decrease with increasing PL emission energy, while at the same temperature, $\tau_2$ is in a range 60 - 150 $\mu$s, and also decreases with increasing PL emission energy.

Fig 8.2 shows that $\tau_1$ for the as-prepared orange porous Si sample at 77 K decreases dramatically in the PL emission energy range 1.85 - 2.0 eV, and then increases to a peak in the PL emission energy range 2.1 - 2.4 eV. The decrease in $\tau_1$ becomes smaller with the time evolution of the porous Si sample. The presence of these features in the lifetime spectra reflects the complex nature of the emitting material [Amato et al. (1994)]. As the temperature increases, the dramatic decrease in $\tau_1$ (i.e. in the energy range 1.85 - 2.0 eV) becomes less evident and it nearly disappears at room temperature for all sample ages.

The behaviour of $\tau_2$ at 77 K in Fig. 8.3 differs from that of $\tau_1$ especially for the as-prepared sample. There are weak features for sample of ages 2 hr, 13.5 hr and 3.5 days at 2.14 eV, 2.1 eV and 2.14 eV respectively. For the other temperatures $\tau_2$ just shows a steady decrease with increasing PL emission energy, except for the as-prepared sample at 150 K, where there is a weak feature in the PL energy range 1.9 - 2.2 eV. As already stated the PL intensity consists of two decaying components, so the spectral distribution of the total PL emission results from the competition between these two components during relaxation after excitation.
Table 2 Summary review of PL decay from porous Si for different experimental conditions, and the interpretation of results. (λ wavelength, τ lifetime, ps picosecond, RR repetition rate, ns nanosecond, PW pulse width, D dimension, PL photoluminescence, Lumin luminescence, $E_{PL}$ PL energy, comp component, EX excitation, vis visible, e-h electron-hole and nano-C nanocrystallites, c confined, a amorphous, d disordered, s surface state, ch chemical, s-b slow band, f-b fast band, rec recombination, QC quantum confined).

<table>
<thead>
<tr>
<th>Who (When)</th>
<th>Lifetime (τ) value</th>
<th>Excitation source (λ nm)</th>
<th>What it is due to</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matsumoto et al. (1992)</td>
<td>RT ps to 1 μs, lower $E_{PL}$ longer τ</td>
<td>527, 40 ps, 76 MHz</td>
<td>ns PL: a (partially).</td>
</tr>
<tr>
<td>Pearssell et al. (1992)</td>
<td>47 μs</td>
<td>Ar, &lt;5 ns, 76 MHz.</td>
<td>Vis PL low D or d Si.</td>
</tr>
<tr>
<td>Trechler et al. (1992)</td>
<td>RT 10 - 70 μs lower $E_{PL}$ longer τ</td>
<td>– 360, 7, 7.</td>
<td>S, a-Si:H.</td>
</tr>
<tr>
<td>Yamada et al. (1992)</td>
<td>4.5 - 11.3 ns</td>
<td>337, 7, 7.</td>
<td>e+ ch.</td>
</tr>
<tr>
<td>Calcott et al. (1993)</td>
<td>s-b at 1.77 eV: 60 μs (287 K), 1.5 μs (12-20 K), at 2.61 eV: 10 μs (287 K), 2 μs (12 - 30 K).</td>
<td>Ar or dye, 7, 7.</td>
<td>e excitons in undulating C-Si wires.</td>
</tr>
<tr>
<td>Fuhman et al. (1993)</td>
<td>1.77 eV: higher level 22 μs and lower level 25 ns.</td>
<td>337, 7, 7.</td>
<td>e excitons in C-Si.</td>
</tr>
<tr>
<td>Kanemitsu (1993)</td>
<td>10 - 300 K: (4 - 0.2 ms).</td>
<td>355, 5 ns, 30 Hz.</td>
<td>Hopping rec in quasi-two D</td>
</tr>
<tr>
<td>Laiho et al. (1993)</td>
<td>8 ns - 200 μs, for 25 - 295 K. Several comp &lt;150 ns at 295 K.</td>
<td>337, 4 ns, 7.</td>
<td>e-h rec and C dot and wires.</td>
</tr>
<tr>
<td>Muller et al. (1993)</td>
<td>1 - 100 μs, depend $E_{PL}$</td>
<td>365 and 458, 7, 7.</td>
<td>Vis PL-carriers in crystallites.</td>
</tr>
<tr>
<td>Takazawa et al. (1993)</td>
<td>RT 60 to 200 μs (1.9 to 1.55 eV).</td>
<td>337, 10 ns, 7.</td>
<td>Lumin centres.</td>
</tr>
<tr>
<td>Teesler et al. (1993)</td>
<td>RT 3 μs and 50 μs (2.77 eV and 1.96 eV).</td>
<td>337, 2 ns, 7.</td>
<td>rec between localised bands, d SiO:H.</td>
</tr>
<tr>
<td>Amato et al. (1994)</td>
<td>300 - 10 K: 25 - 300 μs and 100 - 200 μs (2 eV and 1.5 eV).</td>
<td>480 nm, 7, 7.</td>
<td>e-wires.</td>
</tr>
<tr>
<td>Goh et al. (1994)</td>
<td>RT 20 - 40 μs</td>
<td>400, 5 ns, 7.</td>
<td>Two grain size types.</td>
</tr>
<tr>
<td>Harris et al. (1994)</td>
<td>0.86 ns, at 2.58 eV independent of T (77 - 295 K).</td>
<td>370, &lt;10 ps, 7.</td>
<td>band to band rec and photothermal.</td>
</tr>
<tr>
<td>Mauskner et al. (1994)</td>
<td>At 254 K, 69 and 13 μs (1.58 and 2.123 eV).</td>
<td>457.9, 7, 7.</td>
<td>Vis PL s-band c exciton and s rec.</td>
</tr>
<tr>
<td>Saemoto et al. (1994)</td>
<td>RT, 10-50 μs</td>
<td>dye, 7, 7.</td>
<td>Phonon assisted transitions of QC carriers.</td>
</tr>
<tr>
<td>Wang et al. (1994).</td>
<td>S-b at high RR, 3 - 4 ns (70 - 350 K), f-b 0.5 - &lt;3 ns (150 - 410 K). 10 μs s-b at 10 Hz.</td>
<td>&lt;530, 55 ps, 82 MHz.</td>
<td>c and s mechanism.</td>
</tr>
<tr>
<td>Grivickas and Limnros (1995)</td>
<td>RT: 18, 27, 38, 50 μs (2.0, 1.91, 1.77 and 1.65 eV).</td>
<td>532, 140 ns, 100 Hz.</td>
<td>Free carrier and fast rec channels.</td>
</tr>
<tr>
<td>Li and Fang (1995).</td>
<td>RT: $\tau_1$ (2.7 - 8.1 μs), and $\tau_2$ (5.2 - 23 μs). $E_{PL}$ 2.14 - 1.63 eV.</td>
<td>253.7 and 514.5, 7, 7.</td>
<td>c-model.</td>
</tr>
<tr>
<td>Ookubo and Sawada (1995).</td>
<td>2 ms to 0.1 - 20 μs at 20 - 293 K (2.4 - 1.6 eV).</td>
<td>337, 30 ns, 1-4 Hz.</td>
<td>Cluster model, low PL by carriers rec.</td>
</tr>
</tbody>
</table>
Fig. 8.2 PL lifetime ($\tau_1$) for the decay at various PL emission energies for orange porous Si sample: as prepared (a), 2 hr after preparation (b), 13.5 hr after preparation (c), 3.5 days after preparation (d), 6.5 days after preparation (e) and 40 days after preparation (f); taken at temperatures, 77 K (□), 150 K (○), 220 K (△) and 295 K (▽).
Fig. 8.3 PL lifetime ($\tau_2$) for the decay at various PL emission energies for orange porous Si sample: as prepared (a), 2 hr after preparation (b), 13.5 hr after preparation (c), 3.5 days after preparation (d), 6.5 days after preparation (e) and 40 days after preparation (f); taken at temperatures, 77 K (□), 150 K (○), 220 K (△) and 295 K (▽).
8.4 Evolution of lifetime

Evolution of the visible (red-green) PL lifetime has been determined for two samples of porous Si from the data presented in Fig. 8.2 - 3. A separate group of measurements were performed at room temperature only (i.e. the sample was not subjected to any cooling), for evolution from 0 hr to 7 days.

Fig. 8.4 shows the lifetime ($\tau_1$) as a function of PL emission energy. Each graph shows a sample ageing over six different times at the same temperatures. In Fig. 8.4(a) the lifetimes measured at 77 K are shown, the lifetime values at this temperature are higher than at the others (i.e. the values of $\tau_1$ decrease with temperature increase). It is seen from Fig. 8.4(a), that the lifetime after 2 hr, 13.5 hr, 3.5 days and 6.5 days has nearly the same band of values, while $\tau_1$ after 40 days evolution is higher than all the others. For the as-prepared sample, values of $\tau_1$ at low energies are between that found after 40 days and the other evolutions. It decreases with increasing energy until it becomes lower than all other lifetime values in the energy range 1.95 - 2.15 eV. Fig. 8.4(b) corresponds to a sample temperature of 150 K. In the 2 hr and 13.5 hr evolutions, values of $\tau_1$ are higher than the others (except the as-prepared sample) in the energy range 1.77 - 2.0 eV. For the as-prepared sample however $\tau_1$ values at low energies are higher than the others, then decrease dramatically reaching the minimum value at 2.1 eV. It increases again at ~ 1.95 eV, and finally peaks at 1.77 eV. In Fig. 8.4(c), which corresponds to the sample of 220 K, $\tau_1$ for all evolutions decreases steadily with values less than 5 µs except for the as-prepared sample which begins at about 10 µs and then decreases to a minimum value at 2.1 eV, then increases and peaks at 2.3 eV. For room temperature measurements shown in Fig 8.4(d), the behaviour of $\tau_1$ for all graphs is similar. It decreases nearly linearly with increasing emission energies within lifetime values of 3.1 - 0.3 µs in the energy range 1.77 - 2.48 eV, except the curve that corresponds to the sample after 40 days, which has with higher values in the energy range 1.7 - 2.2 eV, giving a peak value of 5.664 µs at 1.77 eV. For all these samples, the increase in $\tau_1$ with decrease in temperature could be due to the lack of phonons which allow nonradiative recombination paths. The observation of structure in the lifetime as a function of energy suggests the existence of more than one luminescence centre.

Fig 8.5 show curves of the lifetime ($\tau_2$) at different temperatures. The behaviour of most curves here differs from that shown in Fig. 8.4. In Fig. 8.5(a) again the radiative lifetime changes with temperature (i.e. longer lifetimes at lower temperatures) particularly for 40 days ageing, for which the lifetime is higher than the other curves
and is independent of the emission energy in the range 1.85 - 2.48 eV. All other curves undulate slightly with PL energy, with lifetime between 50 µs to 150 µs. The graphs of Fig. 8.5(b, c and d) decrease nearly linearly with emission energy, except in Fig. 8.5(b) which corresponds to the sample at 150 K, where the curve of the as-prepared sample has a shoulder in the energy range 1.9 - 2.2 eV. In general, both $\tau_1$ and $\tau_2$ do not always change in the same sequence with changing temperature.

Other room temperature measurements have been performed on another orange porous Si sample for 9 evolutions, and these are shown in Fig. 8.6. For the lifetime ($\tau_1$) in Fig. 8.6(a), the graphs of all the evolutions between 0 hr (as-prepared) and 7 days are shown. They show nearly similar behaviour except the one for 7 days, which shifts to higher values of $\tau_1$. In the graphs of the lifetime ($\tau_2$) shown in Fig. 8.6(b) more difference has been found. The values of $\tau_2$ for the 4 day evolution are less than all the other lifetimes and those for 7 days are higher than all others. The differences in the lifetime values on evolution can be ascribed to the compositional changes due to environmental exposure. Porous Si layers have an open structure made of very fine pores and very thin walls (except the porous Si prepared in highly doped n-silicon in the dark) it has a continuous highly interconnected pore network. Complete oxidation of the structure can be obtained at relative low temperatures (as expected from the very thin wall thickness) and the low temperature oxide remain porous [Bomchil et al. (1989)]. The PL spectra has also been found by other researchers to change if the porous Si samples are placed in air for a couple of days [Lin et al. (1994)]. As mentioned before, it seems that all the lifetime graphs for this sample decrease nearly linearly with increasing emission energies. At room temperature, nonradiative de-excitation dominates for all energies, and nonradiative recombination is more dependent on photon energy [Vial et al. (1992)].
Fig. 8.4 Evolution of the PL lifetime ($\tau_1$) for various PL emission energies for orange porous Si at temperatures: 77 K (a), 150 K (b), 220 K (c) and 295 K (d): as-prepared sample (□), and 2 h (○), 13.5 h (△), 3.5 days (▽), 6.5 days (x) and 40 days (+) after preparation.
Fig. 8.5 Evolution of the PL lifetime ($\tau_2$) for various PL emission energies for orange porous Si at temperatures: 77 K (a), 150 K (b), 220 K (c) and 295 K (d): as-prepared sample (□), and 2 h (○), 13.5 h (△), 3.5 days (▽), 6.5 days (x) and 40 days (+) after preparation.
Fig. 8.6 Evolution of PL lifetime $\tau_1$: (a) and $\tau_2$: (b); for various PL emission energies for orange porous Si at room temperature. The time of 0 min corresponds to the as prepared porous Si sample.
8.5 Photoluminescence lifetime for red-green light emitting porous Si

It was decided to compare the PL lifetimes as a function of temperature for three porous Si samples prepared under different conditions. The PL properties of porous Si are strongly controlled by preparation conditions as well as by the substrate utilised [Di Francia (1993)]. Three stable porous Si samples (green/yellow, yellow/orange and red) have been chosen for these measurements. They were prepared about 8 months prior to the measurements and kept in the laboratory environment. In the meantime, some other PL energy and lifetime measurement were performed on these samples. These earlier PL lifetime measurements gave nearly the same results as the more recent measurements. Fig. 8.7(a, b, and c) show the PL lifetimes ($\tau_1$) as a function of emission energies for the above porous Si samples respectively. Looking at Figs. 8.7-8, one can see that $\tau_1$ and $\tau_2$ do not greatly depend on the porous Si sample, but strongly change with temperature. There is a small but significant change in $\tau_1$ with the emission energy (especially for porous Si of red emission), but largely the curves are energy independent. Also you can see from Figs. 8.7-8 that each sample emits PL in an energy range that shifts from higher to lower energy, as the nominal sample colour move towards the red.

Looking again at $\tau_1$ in Fig. 8.7(a and b) one can see it decreases with energy and increases for temperatures 180, 230 and 295 K, though similar having lifetimes. Undulating spectra are found for the other two temperatures (i.e., 77 and 150 K). This behaviour is found in all spectra of Fig. 8.7(c). In Fig. 8.8, $\tau_2$ spectra measured at 130, 180, 230 and 295 K are shown to be weakly dependent on the emission energies. In general, the spectra for 77 K have different behaviour. In (a) $\tau_2$ increases with energy in the range between 2.0 - 2.2 eV, but for the energy range between 2.2 - 2.6 eV it becomes energy independent. In (b) however it decreases slightly with increasing energy. Finally in (c) $\tau_2$ undulates with energy.

Comparing the spectra of lifetimes ($\tau_1$ and $\tau_2$) in Figs. 8.7 - 8(a, b and c) it can be seen that the decay times for green/yellow and yellow/orange porous Si samples are more stable than the red sample with increase of emission energy.
Fig. 8.7 PL lifetime ($\tau$) for various PL emission energies for porous Si [green/yellow (a), yellow/orange (b) and red (c)] at various temperatures [77 K (□), 130 K (○), 180 K (△), 220 K (▽) and 295 K (x)].
Fig. 8.8 PL lifetime ($\tau$) for various PL emission energies for porous Si [green/yellow (a), yellow/orange (b) and red (c)] at various temperatures [77 K (□), 130 K (○), 180 K (△), 220 K (▼) and 295 K (x)].
8.6 Photoluminescence at different excitation intensities

Measurements of the PL decay time as a function of excitation intensity at 2.0 eV has been performed on an orange porous Si sample. PL decay pulses for five different excitation intensities, at temperatures at 77 and 295 K are shown in Fig 8.9. From the two sets of PL decays in the above figure, one can see that the decay shape of the first three PL decays very similar, and there are only minor difference in the last two pulses compared with the first three. Insets in the above figure clearly show this minor difference, i.e., faster decay for the PL pulses of lower excitation intensities. All PL decay curves represent a nonexponential decay because they show no observable rise time [Xie et al. (1994)] and no significant changes with the change of excitation intensity [Takazawa et al. (1994)]. Muckner et al (1994), reported curves of similar shape at different excitation intensities, stating that high injection effects leading to quadratic recombination can be ruled out as a source of nonexponential behaviour.

Fig. 8.10 shows PL lifetime (τ₁) of orange porous Si as a function of emission energy at different excitation intensities, measured at (a): 295 K and (b): 77 K. From Fig. 8.10 at 295 K, the lifetime τ₁ for the first three spectra (corresponding to 100, 56 and 34% excitation intensities) are the same for emission energies higher than 2 eV. For energies below 2.0 eV these three spectra separate, the higher excitation intensities give longer lifetimes (i.e., slower decay). For the other two lifetime spectra (which correspond to 7 and 12% excitation intensities) the lower the excitation intensities the lower the lifetimes. At 77 K the first two lifetime spectra (i.e., 100 and 56% intensities) are the same and the others decrease with decreasing excitation energy. The values of τ₂ in Fig. 8.11 are nearly the same for all PL energy spectra where different excitation energies at 295 K, which means the slow band decays in the same way for all excitation intensities. But at 77 K the spectra split into two groups, the first three spectra of τ₂ (which correspond to excitation intensities 100, 56 and 34%) are nearly the same, and differ from the other two (12 an 7%) which are of shorter lifetime and decrease with decreasing excitation intensity. In general the shape of all τ₂ curves is the same for excitation intensities of 7% - 100%. Yamada et al (1992), found that the lifetimes do not change with changing excitation intensity by more than three orders of magnitude. Wang et al (1994) reported no intensity dependent changes in the lifetime or the spectrum peak position could be observed when the laser intensity was increased by more than one order of magnitude. Looking at Figs. 8.10-11, and comparing with the results described above by other researchers, indicates agreement with these results at least for excitation energies between 34% and 100%. In this thesis the PL measurements at different excitation energies have been taken
over a wide range of PL emission energies. Such a wide range of energy measurements could not be found in the literature.

Fig. 8.9 PL decays at emission energy 2.0 eV of orange porous Si at 295 K (a) and 77 K (b), taken at various excitation intensities: from the top to bottom 100%, 56%, 34%, 12% and 7% respectively. The ordinate scale is in arbitrary units for each curve, and the zero has been adjusted for clarity.
Fig. 8.10 PL lifetime ($\tau_1$) for various PL emission energies for orange porous Si at various laser intensities [100% (□), 56% (○), 34% (△), 12% (▽), 7% (×)]; measured at 295 K (a) and 77 K (b).
Fig. 8.11 PL lifetime ($\tau_2$) for various PL emission energies for orange porous Si at various laser intensities [100% (□), 56% (○), 34% (△), 12% (▷), 7% (×)]; measured at 295 K (a) and 77 K (b).
8.7 Temperature dependence of PL decay and integrated PL intensity

As explained earlier in this chapter, PL measurement have been recorded at a series of different temperatures between 77 - 295 K. The increasing of the temperature changes the behaviour of the PL decay (see Fig. 8.1). In general, the PL intensity follows a nonexponential decay, which has been described in § 8.3, by two exponential processes, i.e. a fast- and slow-band decay. The temperature dependence of $\tau_1$ and $\tau_2$ is shown in Fig. 8.12. It could be seen that both $\tau_1$ and $\tau_2$ are strongly temperature dependent. For $\tau_1$ we can divide it into three temperature regimes:

(i) At temperatures below 100 K it becomes nearly independent of temperature, and can no longer be regarded as a 'fast' decay.

(ii) In the temperature range 100 K to 240 K, $\tau_1$ decreases dramatically with increasing temperature. The nonradiative transfer of quantum confined excitons into the localised surface states is thermally activated.

(iii) At temperatures above 240 K, $\tau_1$ become less dependent on temperature, and much shorter than the previous two regimes. The carriers are mostly transferred from the quantum confinement excitation states into localised surface states [Wang et al. (1994)].

For $\tau_2$ similar behaviour is found except at regime (i), where $\tau_2$ is more temperature dependent than $\tau_1$. This is in agreement with the PL lifetime of porous Si reported by Tsuboi et al. (1995).

By cooling the sample from 295 to 77 K the integrated PL decay intensity taken at emission energy 2.21 eV is found to increase with decreasing temperature, as shown in Fig. 8.13.
Fig. 8.12 Temperature dependencies of $\tau_1$ (a) and $\tau_2$ (b), for orange porous Si, at PL emission energy 2.21 eV. The excitation energy is 3.68 eV.
Fig. 8.13 Temperature dependence of integrated PL decay for orange porous Si, at PL emission energy 2.21 eV. The excitation energy is 3.68 eV.
Investigation of optical, electrical and structural properties of reactively sputtered InO\textsubscript{x} and ITO\textsubscript{x} thin films

Chapter 9

9.1 Introduction

Indium oxide (IO) and indium tin oxide (ITO) films have been the subject of many investigations since they were found to be electrically conductive and optically transparent in the late 1960s, and were therefore extremely attractive for various optoelectronic applications. Transparent IO and ITO films have therefore been widely used over the last 25 years in a range of applications including special glazing (heat reflecting windows), and transparent electrodes in information displays, solar cells, flat panels, liquid crystal displays, electrochromic window devices, electromagnetic interference shield coatings and storage cathode ray tube technologies [Bosnell and Waghrone (1973), Itoyama (1979), Avaristiotis and Howson (1981), Gordon et al. (1989), Suzuki et al. (1989), Murali and Sambasivam (1990), Kawada (1990), Bellingham et al. (1991), Nomura et al (1991), Parent et al. (1992), Shigesato et al. (1992), Naseem et al (1993), Kim et al. (1994), Lee and Huang (1994), Ozaso et al (1994), Rauf and Brown (1994), Cai et al. (1995) and Kamei et al. (1995)]. In addition, for ohmic contact electrodes of InP devices, ITO provides the most compatible physical and electronic interface properties [Hanak and Ahrenkiel (1988), Bregman et al. (1990), van den Meerakker et al. (1993), Lee and Huang (1994), Fauchet (1995) and Yi et al. (1995)]. Furthermore the transparent conductive material of more expensive and durable electronic and optoelectronic devices are made of indium oxide. A key advantage of these oxides is that they are physically stable and chemically inert.

In order to investigate optoelectronic properties such as electroluminescence from porous Si it is of course necessary to prepare a device. IO and ITO films are the prime materials of interest for contacting nanostructured devices such as those based on porous Si [Kalkhoran et al. (1992), Koshida and Koyama (1992), Namavar et al. (1992), Xu and Steckl (1994), Xu and Steckl (1995) and Steiner et al. (1995)]. Although there have been many studies on IO and ITO, these have mainly concentrated on the composition region over which high conductivity is observed.
Investigation of optical, electrical and structural properties of reactively sputtered InO\textsubscript{x} and ITO\textsubscript{x} thin films

[Pashmakov et al. (1993), Kim and Li (1994) and Lee and Huang (1994)]. Furthermore there have not been detailed structural characterisation of the materials reported. There is even less reported on the suboxide systems, which for IO is reputed to exist in 3 crystalline forms: In\textsubscript{2}O, InO and In\textsubscript{2}O\textsubscript{3}. Here concentration has been on the local structure determination, and the correlation of the structural, optical and electrical properties in order to understand the evolution with oxygen content of the bonding appropriate to these systems. This is relevant for the understanding of the operation of a LED based on a porous Si 'sandwich' structure, as described in the following chapter. Also of interest is an understanding of any difference between the properties of the thin films and those of the corresponding bulk materials.

In this chapter as described the investigation of the influence of oxygen content (x) in the indium sub-oxide (InO\textsubscript{x}) thin films on the film structure for x ranging from 0.16 to 1.5. Composition has been determined from energy dispersive X-ray analysis (EDX) and estimated from X-ray absorption step-heights. Optical absorption and band gaps for InO\textsubscript{x} and ITO\textsubscript{x} have been obtained from reflectance and transmission data, refractive indices from ellipsometry. Film thicknesses have also been obtained from ellipsometry, as well as from scanning electron microscopy (SEM) and optical interference effects. Information on the local structures has been obtained from extended X-ray absorption fine structure (EXAFS).

9.2 Determination of composition of InO\textsubscript{x} and ITO\textsubscript{x} thin films

The In and In/Sn composition of the dc sputtered films (InO\textsubscript{x} and ITO\textsubscript{x}) was determined by EDX. The EDX analysis was carried out at the Institute of Polymer Technology and Materials Engineering, Loughborough University, on a Leica Cambridge S360 SEM equipped with a LINK Analytical AN10000 energy-dispersive analyser. Thin films were analysed and the ratio of X-ray counts/nm was taken to obtain the In/Sn composition from different samples of similar thickness. To determine the oxygen content (x) normalised count-rates/nm were used, and thus it was necessary to assume the films were thin enough to give insignificant amounts of absorption and fluorescence (or little difference from one sample to another). Fig. 9.1 shows the variation of composition (x) vs. oxygen partial pressure (O\textsubscript{pp}) for InO\textsubscript{x} films.
Determination of optical properties of InO$_x$ and ITO$_x$ thin films

The considerable theoretical and experimental investigation on the optical behaviour of thin films deals primarily with optical reflection, transmission and absorption and their relation to optical constants of thin films. In device applications knowledge of the absorbance and surface reflectance of sputtered films is fundamental. The ophthalmic and optoelectronic industries rely on accurate assessment of these optical variables in order to consistently guarantee the performance of devices. Optical transmittance and reflectance were measured in order to determine the band gap and absorption coefficient of the sub-oxide films.

9.3.1 The dual-beam spectrometer

To measure the transmittance, reflectance and absorption spectra of the films, a dual beam spectrophotometer was used. Fig. 9.2 shows a schematic of a Perkin-Elmer 323
UV-VIS-NIR recording spectrophotometer used throughout this study. It has a spectral range of 185 to 2500 nm and a photometric accuracy of better than 0.5% of full scale in transmittance mode. The following description of the optical path through the instrument is for the transmittance mode of measurement. The apparatus is set to switch between two light sources depending on the spectral region being examined. A tungsten source is used for visible and near infrared ranges, and a deuterium source for ultraviolet measurements. Light of the appropriate wavelength is focused on the entrance slit by the source selector mirror and an angled flat mirror. On leaving the slit, it is directed to the quartz prism by the collimating mirror, and the light dispersed by the prism is directed to the exit slit by collimating mirror once more. The light beam emerging from the exit slit enters the photometer and is split into two by the rotating sector mirror, which allows the beam to pass and then reflects it, alternately. One beam passes through the sample and the other beam through an uncoated substrate, to recombine into an alternating pulsed signal at another sector mirror. Depending on the wavelength of incident light, the pulse is converted into a current signal by either a PbS cell or photomultiplier tube, and passes through an amplifier network to convert it to a voltage signal. This voltage signal is split into three components: the reference, sample and zero signals, and each is changed to dc voltage by a corresponding circuit. The output from the reference circuit is applied to the motor controlling the slit width, and the slit width is automatically varied between 5 µm and 2 mm by a servo circuit to control the energy of light incident on the detector so that the reference voltage is a constant 3 volts. A divider circuit accepts amplified reference and sample hold voltage, and generates a signal proportional to the transmittance of the sample.

Transmittance calculations were begun by calibrating the 100% and 0% base lines across the wavelength of interest. The instrument does not initially indicate a flat 100% transmittance over the entire range, due to the 100% base line bending caused by a reduction in reflection efficiency of the mirrors. Calibration involved inserting two identical substrates over the reflectance and sample windows, and coarsely adjusting the position of the recorder pen to the 100% line at 500 nm, the centre of the visible. Finer adjustment could then be achieved by moving through the wavelength range from 300 to 700 nm, adjusting the 100% line compensation knobs, which are tuneable at 310, 340, 355, 400, 500, 600 and 700 nm in the visible, and at 1050, 1700, 2300 and 2600 nm in the infrared. The zero line is calibrated by moving through the spectrum with the slit closed. Evaluation of the transmittance spectrum of a sample film is then achieved by placing the film and substrate combination over the sample
window of the instrument with the uncoated substrate over the reference window, and scanning through the spectral range. Since the reference is an uncoated substrate and not air, the resulting output will be the difference between the transmittance of the coated and uncoated substrates.

Fig. 9.2 also shows the reflectance attachment which replaces the transmittance attachment. The optical path is longer, but the operation is similar. Two aluminium mirrors were sputter deposited simultaneously to give identical reflectance, and their absolute reflectivity was quantified. If the absolute reflectivity was not suitably close to the theoretical reflectance of the pure aluminium at 633 nm, a new pair was deposited with different thickness to the first pair. When the absolute reflectance was close to theoretical, the two mirrors could be used over the spectrophotometer windows to calibrate the 100% line, ensuring that the reduction in reflectance of aluminium towards the blue end was taken into account. Sample measurement is then made, relative to the reference, by scanning through the spectrum as in the transmittance mode.

For many of the single layer films produced in this work, optical absorbance was calculated using the simple relationship between reflectance R, transmittance T and absorbance A:

\[ 100\% = A\% + R\% + T\% \]  \hspace{1cm} (9.1)

9.3.2 Reflectance and transmittance spectra

Normal-incidence transmittance (T) and near-normal-incidence reflectance (R) at room temperature were recorded as a function of photon energy (hv). Figs. 9.3 and 9.4 show the dependence of R and T respectively on hv and composition x for a series of InO\(_x\) films, and Fig. 9.5 shows R and T for ITO\(_x\) films. T was corrected for the presence of the mylar substrate. It can be seen that R increases with decreasing x especially at low energy. The optical properties in the near-infra-red region are controlled by free electrons, which give a high (Drude-like) reflectivity for films of low x at low hv. This also appears as a decrease in T at long wavelength [Fan and Bacher (1975), Gouskov et al. (1983) and Bellingham et al. (1991)].

In the InO\(_x\) films of higher x it is found that T increases with increasing x, and peaks just above 86% in the near-infra-red region (hv \(\approx\) 1.2 eV). In ITO\(_x\) films it is found that T also increases with increasing x and peaks about 76%. High values of T (and
Investigation of optical, electrical and structural properties of reactively sputtered \( \text{InO}_x \) and \( \text{ITO}_x \) thin films

Low values of \( R \) occur because there is no absorption due to valence-to-conduction band transitions [Fand and Bachner (1975)]. That is, the higher optical transparency of these oxide films in the visible and near-infra-red regions is a direct consequence of their being wide band gap \( (E_g) \) semiconductors [Nagatomo et al. (1990)]. \( T \) decreases with decreasing wavelength, this decrease becomes sharp in the UV region for films of higher \( x \).

![Optical Layout of Perkin-Elmer 323 UV-VIS-IR Spectrometer](image)

Fig. 9.2 Optical Layout of Perkin-Elmer 323 UV-VIS-IR Spectrometer.

9.4 Film thickness determination

The average thickness is one of the fundamental parameters of interest throughout this study because calculation of the absorption coefficient relies on an accurate determination of this parameter. In a production environment it is essential to have
instant feedback concerning the thickness of the deposited films so that changes in process parameters can be made to maintain efficiency and consistent film properties. The coater used in this work was an air-to-air machine and did not require the in-situ thickness monitoring characteristic of batch processing, so all thicknesses were assessed on removal of the sample from the coater. Three methods have been used to determine the geometrical thickness of the films: SEM [Nakahara and Hebarad (1983), Choudhury et al. (1984), Oka (1988), Igarashi et al. (1989), Kwon et al. (1991), and Sakaue et al. (1992)], interference fringes in reflection [Cisneros et al. (1983) and Piggins (1988)] and ellipsometry [De Smet (19976), Azzam (1976), wallis and Sébenne (1980), Bishop (1986), Oka (1988), Drude (1989), Hall (1993), Lee and Huang (1994) and Fukarek and Kersten (1994)]. Both interference fringes in reflection (assuming both film and substrate are transparent) and ellipsometry provide information on the refractive index as well thickness of transparent films. Good agreement on thickness was obtained using different methods for all films of higher x. The measurement of thickness for films of lower x is less accurate than for films of higher x because it was not possible to use interference fringes or ellipsometry for highly absorbing films.

Fig. 9.3 Reflectance vs. photon energy for the InO_x system, as a function of composition (x).
9. Investigation of optical, electrical and structural properties of reactively sputtered InO$_x$ and ITO$_x$ thin films

![Graph showing transmittance vs. photon energy for the InO$_x$ system as a function of composition (x).](image)

Fig. 9.4 Transmittance vs. photon energy for the InO$_x$ system, as a function of composition (x).

![Graph showing reflectance (R) and transmittance (T) vs. photon energy for ITO$_x$ films where x increases for plots (a) through (d).](image)

Fig. 9.5 Reflectance (R) and Transmittance (T) vs. photon energy for ITO$_x$ films where x increases for plots (a) through (d).
9.4.1 Thickness determination using SEM

A direct measurement of thickness was obtained from SEM for InO\textsubscript{x} and ITO\textsubscript{x} films, after dipping the films in liquid nitrogen and cleaving. SEM micrographs of typical transparent and opaque films, of thicknesses 124 (± 20) nm and 230 (± 50) nm, are shown in Figs. 9.6 and 9.7 respectively. Only a small fraction of the volume of material is viewed in SEM compared to those volumes penetrated using optical techniques, and thus the SEM measurements are less accurate. However SEM was of course useful to identify the topography of the films, and it can be seen that for $x < 0.3$ the films were of a granular nature, whereas for higher $x$ uniform thin films had been deposited.

![SEM micrograph of typical transparent film of InO\textsubscript{x} with $x = 1.0$.](image)

Fig. 9.6 SEM micrograph of typical transparent film of InO\textsubscript{x} with $x = 1.0$. 
9.4.2 Thickness determination using interference fringes in reflection

Thicknesses were determined from interference fringes by the method proposed by Cisneros et al. (1983) using photometric measurements at normal incidence over an extended wavelength interval. If there is little or no absorption of light in a uniform film (e.g. sufficiently parallel for the thickness to vary by only a small fraction of wavelength over the area involved) any edge effects can be neglected, then multiple reflections at the surface of the film can which give rise to a constructive or destructive interference at certain wavelengths [Ellis (1973) and Piggins (1988)]. The set-up is shown schematically in Fig. 9.8.

R₁ and R₂ will combine constructively if the path difference between them is equal to mλ, as described by the Bragg condition:

\[ 2dsin\theta = m\lambda/n \]
Fig. 9.8 Shows the measured reflectance (R) at the front and back of transparent film of thickness (d), and the measured transmittance (T) through the film and substrate.

where d is the film thickness and \( \lambda/n \) is the wavelength of the light in the material of refractive index \( n \). Thus a series of fringes will be obtained in reflectance and transmittance measurements (see Fig. 9.5). Such measurement is potentially the most accurate way of determining the refractive index of the film [Ellis (1973)]. Finding \( n \), the refractive index, by this method is not straightforward because \( m \), the order of fringe, is not known. This is sometimes overcome by measuring the wavelengths at the successive maxima and applying the conditions:

\[
2nd = m\lambda_1 \\
2nd = (m+1)\lambda_2
\]

on eliminating \( m \), one obtains

\[
2nd = \left( \frac{1}{\lambda_2} - \frac{1}{\lambda_1} \right)^{-1}
\]

(9.2)

however this procedure is only correct if \( n \) is known to have no linear wavelength dependence. Fig. 9.9 shows a graph of \( m \) vs. \( \left( \frac{1}{\lambda_2} - \frac{1}{\lambda_1} \right) \) for a typical transparent film of ITOx.
9 - Investigation of optical, electrical and structural properties of reactively sputtered InO\textsubscript{x} and ITO\textsubscript{x} thin films

Fig. 9.9 \(\frac{1}{\lambda_2} - \frac{1}{\lambda_1}\) nm\(^{-1}\), as a function of the order (m) of fringes for a typical transparent ITO\textsubscript{x} film where x = 0.86.

9.4.3 Thickness determination using ellipsometry

It has long been established that thin films could be detected on surfaces by the change in ellipticity of a beam of light following its reflection from the surface [Wallis and Sébenne (1980), Bishop (1986) and Oka (1988)]. Since this early observation the technique has been developed and has become a standard technique for thin film analysis with equipment and computer software being readily available [McCrakin and Colson (1964)]. Ellipsometry is a powerful, non-contact, non-destructive diagnostic tool, and does not even require a film edge. Its sensitivity is such that changes in film thickness of 0.07 Å have been observed using this technique [Archer and Gobeli (1965)]. The basic information required to obtain the film characteristics of thickness and refractive index are the values of \(\Delta\) and \(\psi\), where \(\Delta\) is the relative phase difference for the two polarisations and \(\psi\) is the ratio of the reflected amplitudes for light polarised in the plane of the incidence to that polarised normal to the plane of incidence (\(\tan \psi\)), [Wallis and Sébenne (1980) and Bishop (1986)]. These cannot be
measured directly and have to be derived from other measurements. The ellipsometer used in this work was a Gaertner L117, and a schematic diagram of it is shown in Fig. 9.10. The light source was a HeNe laser which initially passed through a depolariser which converted the beam to one of circularly polarised light. The beam then passed through a polarising drum containing a prism which converted the beam into linearly polarised light. The beam then passed through a compensator containing a \( \lambda/4 \) plate which produced the elliptically polarised beam that was required. With the surface in one particular orientation this elliptically polarised beam when reflected would once again be linearly polarised such that in passing through an analysing prism the beam could be extinguished. The final beam intensity was measured by a photo detector which enabled the conditions to be set that produced the minimum response by the detector. To reduce the systematic and random errors two pairs of readings from the polariser and analyser were taken, \( P_1 \) and \( A_1 \), to give the first minimum and then at a complementary position \( P_2 \) and \( A_2 \) where \( P_2 \approx P_1 + 90 \) and \( A_2 \approx 180^\circ - A_1 \). The technique for finding the initial values \( P_1 \) and \( A_1 \) is to set the polariser and analyser drum to \( 45^\circ \) and to rotate the polariser positively and negatively from this starting point to see in which direction the photo detector minimum lay. Once the signal had been minimised the same procedure was carried out using the analyser drum. The two drums were then moved alternately and the signal would progress towards a minimum. Once obtained and the values noted the same procedure was repeated to obtain the complementary values but starting near to the expected values to reduce the time taken to reach the minimum. The four values obtained were then inserted into the computer along with the angle of incidence and a programme would then calculate either the real and imaginary parts of the refractive index or the refractive index and thickness. To find the refractive index and thickness for the transparent films it was first necessary to determine the refractive index of the substrate. The glass slides were thin and needed to be mounted on a thicker block of glass with a matching fluid to stop the reflection from the back surface of the slide from interfering with the front surface reflection. The polyester substrates were more of a problem, the polyester by its method of production is biaxially oriented and this produces variations in the refractive index depending upon orientation. If the above procedure was adopted and samples were measured along the same film orientation a reliable substrate refractive index of \( n = 1.74 \) and \( k = -0.01 \) (or less) could be obtained. If the value of the \( k \) was much higher than -0.01 then it was an indication that there was still some contribution from the back reflection reaching the photo detector or that the film was absorbing at that wavelength. Further to this the back surface reflection also needed to be eliminated. This was done by abrading the back surface with wire wool.
to roughen the surface and then coating the area with dense black ink. This effectively removed the back surface reflection from contributing to the signal reaching the photo detector.

![Diagram of the ellipsometer](image)

**Fig. 9.10** A schematic diagram of the ellipsometer.

Good agreement between the thicknesses from different methods was obtained for films of higher $x$. Table 3 summarises the thickness determinations, measured by the three methods described above, for five transparent $\text{InO}_x$ films of different oxygen content ($x$).

**Table 3. Thickness evaluation of transparent $\text{InO}_x$ films using three techniques.**

<table>
<thead>
<tr>
<th>$x$</th>
<th>Ellipsometry (nm)</th>
<th>Interference (nm)</th>
<th>SEM (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.92 \pm 0.05$</td>
<td>$95 \pm 10$</td>
<td>$94 \pm 30$</td>
<td>$98 \pm 20$</td>
</tr>
<tr>
<td>1.00</td>
<td>108</td>
<td>120</td>
<td>124</td>
</tr>
<tr>
<td>1.32</td>
<td>98</td>
<td>130</td>
<td>98</td>
</tr>
<tr>
<td>1.38</td>
<td>103</td>
<td>145</td>
<td>119</td>
</tr>
<tr>
<td>1.50</td>
<td>107</td>
<td>135</td>
<td>179</td>
</tr>
</tbody>
</table>
9.5 Absorption coefficients and refractive indices of InO\textsubscript{x} and ITO\textsubscript{x} films

Measurements of optical absorption coefficients ($\alpha$) from InO\textsubscript{x} and ITO\textsubscript{x} films are shown in Figs. 9.11 and 9.12, respectively. Here $\alpha$ has been calculated from:

$$\alpha = \frac{\ln \frac{T}{1-R}}{d}$$  \hspace{1cm} (9.3)

where $T$ and $R$ are the measured optical transmittance and reflectance respectively, and $d$ is the film thickness. In the above equation the multiple reflections have been neglected. It can be seen from Figs. 9.11 and 9.12 that the absorption coefficients of the transparent thin films start to increase towards the IR where the free carrier absorption is expected to become dominant, the materials showing metallic-like behaviour [Gouskov et al. (1983)].

Figs. 9.13 and 9.14 show the plot of ($\alpha\nu$)$^{1/2}$ vs. ($\nu$) for the IO and ITO films respectively. Extrapolation of the straight line region at high energies onto the x axis gives an estimate of $E_g$ [Tauc (1970)]. Lack of data at high energies has made it difficult to estimate $E_g$ for high $x$. It can be seen that the absorption edges for InO\textsubscript{x} and ITO\textsubscript{x} films move toward the UV region when $x$ is increased. In the NIR region the free carrier absorption becomes important and this has implications in the use of IO and ITO in antireflection coatings. This is also has implications for the determination of the refractive indices using ellipsometry since the ellipsometer available operated at 633 nm. The relatively high absorption for most of the films only allowed refractive indices to be obtained for films with $x$$>$1.0. The values obtained for the stoichiometric films (data for other values of $x$ are not available) are 1.95 for InO and 1.95 for ITO, both $\pm$ 0.02, and agree within error with the values of 1.8 - 2.1 published previously for highly conducting transparent films [Fukarek and Kersten (1994), Lee and Huang (1994) and Gouskov et al. (1983)]. Indices in this work for InO films with $x$ = 1.3 - 1.4 are around 1.99.
Investigation of optical, electrical and structural properties of reactively sputtered InO\textsubscript{x} and ITO\textsubscript{x} thin films

Fig. 9.11 Absorption coefficients vs. energy (eV) for InO\textsubscript{x} as a function of composition (x).

Fig. 9.12 Absorption coefficients vs. photon energy for ITO\textsubscript{x} system, as a function of composition (x).
Investigation of optical, electrical and structural properties of reactively sputtered InO_x and ITO_x thin films

Fig. 9.13 Tauc plot of $(\alpha hv)^{1/2}$ vs. photon energy for InO_x system, as a function of composition (x).

Fig. 9.14 Tauc plot of $(\alpha hv)^{1/2}$ vs. photon energy for ITO_x system, as a function of composition (x).
9.6 Local structure

A structural investigation has been carried out of the indium suboxide system \( \text{In}O_x \) with \( x \) ranging between 0, where the face-centred tetragonal metal is expected, and 1.5, where the trigonal stoichiometric oxide is expected. Indium L edge EXAFS data were obtained in transmission at room temperature at the CCLRC Daresbury Laboratory SRS, UK. Even though the films were between 150 and 300 nm in thickness it was not possible to stack more than 8 layers to increase the edge steps since the mylar substrates were relatively thick. Fourier transforms (FTs) of the phase-shift-corrected \( k^2\chi(k) \) signals are shown in Figs. 9.15 and 9.16 for 2 suboxide samples with \( x \approx 0.5 \) and 1.2 respectively. As expected the samples with \( x = 0 \) are crystalline and 12-fold coordinated (±1) by In atoms at a distance of 3.21 ± 0.005 Å. For low values of \( x \) the samples show structure characteristic of the pure metal i.e. distorted fcc. By \( x = 0.3 \) there is little evidence for higher shells, but In is still just less than 12-fold coordinated by In and by only 1 O atom, initially suggesting the presence of a high density of 'wrong' bonds. It is more likely that the strongly scattering In atoms mask the presence of O, especially since there is also a good deal of configurational disorder. As \( x \) increases to 0.5 the coordination of In by In drops quickly to 6, still at \( \approx 3.2 \) Å, and the coordination by O is \( \approx 2 \). By \( x = 0.9 \) there are 6 O atoms in the first shell and 6 In in the second, with less configurational disorder in both shells. The stoichiometric oxide is also 6-fold coordinated by O, at 2.16 ± 0.02 Å. Two higher shells of In atoms, each containing 6 atoms occur at 3.2 Å and 4.3 Å [Parent et al. (1992)]. This is in contrast to (i) the expected structure for c-In\(_2\)O\(_3\) of 1 In at 3.1 Å, 3 at both 3.24 and 3.67 Å, a further 7 occurring at 3.99 Å; and (ii) to the data of Parent et al. (1992) who find 6 In at 3.35 Å (and expect 6 more at 3.84 Å) from their stoichiometric thin film samples. The latter samples however were produced by powder pyrolysis and were heat-treated, resulting in microcrystalline films. Comparing the FTs from Parent et al. (1992) and the data shown in Figs. 9.15 and 9.16 there is much less medium range order in our samples and the above suggests a distorted structure at stoichiometry, highly distorted from the cubic bixbyite of c-In\(_2\)O\(_3\). Some second shell structure is also observed in the EXAFS from thick stoichiometric samples of ITO\(_x\) and is the subject of a future investigation.

The structure from x-ray diffraction and transmission electron microscopy of reactively-evaporated IO films has been reported by Muranka et al. (1993). They findings show some similar trends to ours from EXAFS in that below a certain O\(_2\) pressure (in their case 2 x 10\(^{-2}\) Pa), films deposited at room temperature have an In
phase, whereas those deposited above this pressure have amorphous or quasi-amorphous structure. Muranka et al. (1993) find that there is a reluctance for oxidation to occur since films deposited just below the transition pressure but at temperatures above 100°C form a phase-separated composite of In and stoichiometric oxide. In this study, a reluctance to create In-O bonds is also found, although this appears to be at a much higher oxygen content, however a comparison between their results and ours is difficult since they have not specified the composition of their samples. From the study by Kwon et al. (1991) however, it is likely that thermally-evaporated material such as that of Muranka et al. (1993) probably consists of coarser-grained In than in reactively-sputtered films of substoichiometric IO, as described in Hebard and Nakahara (1982). The results of this work are in line with those of Hebard and Nakahara in that there is much configurational disorder even at low x, and suggest that any phase separation is on a very fine scale in our films.

From the x-ray absorption near-edge structure (XANES) there appears to be a small shift in the position of the In levels with respect to the pure metal In sample. This shift is monotonic with increase in x and is \( \approx +2 \) eV for \( \text{In}_2\text{O}_x \) and not within experimental error of the 3d5/2 binding energy shift of \( \approx +1 \) eV found in XPS [Wagner et al. (1987) and Fan and Goodenough (1977)]. However since the In levels appear at the bottom of the conduction band [Bregman et al. (1990)], the weakening of the In DOS as x increases leaves the absolute position of the conduction band minimum virtually unchanged in energy throughout the composition range, Assuming a 2p core level shift comparable to the 3d5/2 shift this gives \( \approx +1 \) eV shift for \( \text{CB}_{\text{min}} \) by \( x = 1.5 \). Based on this, a schematic energy band model is proposed (Fig. 9.17) for the evolution of the indium suboxide system.
9 - Investigation of optical, electrical and structural properties of reactively sputtered InO$_x$ and ITO$_x$ thin films

Fig. 9.15 Fourier Transform (FT) of EXAFS for InO$_x$, where x = 0.5, showing a broad peak due to contributions from an In-In first shell at $\approx$ 3.2 Å, and from an In-O second shell at $\approx$ 3.8 Å.

Fig. 9.16 Fourier Transform (FT) of EXAFS data for InO$_x$, where x = 1.2, showing a large peak at the In-O nearest neighbour distance of 2 Å. There is also clear structure due to outer shells at $\approx$ 3.5 Å and 5 Å.
Fig. 9.17: Schematic energy-band model for InOₓ. Note that at present there is no experimental information on the relative positions of the In 4s, p, d levels.
9.7 Electrical properties of InO\textsubscript{x} and ITO\textsubscript{x} films

The dc sheet resistances of InO\textsubscript{x} films were measured at room temperature using the four-probe technique. Fig. 9.18 shows the variation in log(resistivity (\(\rho\))) with \(x\) for InO\textsubscript{x} films. Higher resistivity was obtained as \(x\) increased from 0.16 reaching a maximum value at \(x = 1.1\), but as \(x \to 1.5\) the resistivity dropped as expected. The conductivity of the InO\textsubscript{x} films shows a strong dependence on the partial pressure of O\textsubscript{2} present during the film preparation [Pashmakov et al. (1993)]. The value of conductivity for InO\textsubscript{x} films varies between \(1670 \pm 50\) to \(1.6 \times 10^{5} \pm 5 \times 10^{3}\) (\(\Omega\text{-m}\))

\(-1\), for \(x = 1.5\) to \(x = 0.16\) respectively. Once again it has not been possible to compare these results with others as there has not previously been a report quoting electrical data as a function of oxygen composition, although the metal-insulator transition has been investigated in amorphous IO and interpreted in terms of variable range hopping between disorder-related states [Graham et al. (1992)]. The samples used here are also highly disordered, certainly at intermediate \(x\), however there is some medium-range order at stoichiometry precluding such explanations which will necessarily involve grain-boundary effects.

![Graph showing Resistivity vs. composition (x) for InO\textsubscript{x} system. The solid line is a guide to the eye.](image-url)
Chapter 10

Electroluminescence in porous Si

10.1 Introduction

Electroluminescence (EL) in porous Si can be made to occur on application of an electric field [Fauchet (1995), Kozlowski et al. (1995), Qin et al. (1995) and Ünal and Bayliss (1996)], and this requires electrodes of high transparency and conductivity and good contact. As reported in chapter 9 sputtered ITO films are highly conducting, transparent and hence show very low absorbance of visible radiation and provide the most compatible physical and electronic interface properties for application in electroluminescence display devices (in organic and inorganic light emitting diodes) [Burroughes et al. (1990), Kanazawa et al. (1990), Hu et al. (1994) and Saito et al. (1994)]. There have been a large number of reports recently of solid-state EL devices fabricated from a simple sandwich structure of porous Si coated with transparent ITO films [Namavar et al. (1992), Xu and Steckl (1994), Fauchet (1995) and Xu and Seckl (1995)]. EL spectra from porous Si that is sputtered with a transparent ITO thin film have been recorded under forward external bias voltage [Bassous et al. (1992), Steiner et al. (1993), Xu and Steckl (1994), Fathauer (1995), Koch and Petrova-Koch (1995), Qin (1995) and Tsybeskov et al. (1995)]. One of the advantages of making diodes by sputtering ITO on porous Si is the higher efficiency observed than if the contacts were by evaporation, because the evaporated contact does not penetrate into the nanoporous Si structure, and can allow high applied bias voltages [Bsiesy et al. (1995)]. On the other hand, sputtering is more energetic than evaporation and the incident atoms can penetrate in the nanoporous Si structure. The reported characteristics give clear evidence that porous Si can be an excellent material for optoelectronic applications. In this study current-voltage (I-V) characteristics have been measured for both forward and reverse bias conditions.

10.2 Investigation of electroluminescence in porous Si

The EL experiments were performed on a porous Si sample (4.5 x 1.0 cm) coated with a transparent conducting ITO thin film of about 250 nm thickness, typically passing
about 82% at 550 nm and displaying electrical resistivity of 40 Ω\(\square\) (for more information about sample preparation conditions see § 6.2.2). The ITO formed the cathode, and the anode was a Au film produced by vacuum deposition on the back of the p-type substrate. To make a proper contact to the nanostructured porous Si, a thermally-evaporated secondary metal contact with a smaller surface area was prepared on the ITO film. This avoids possible damage to the thin transparent film and indirectly to the silicon nanostructure [see Ünal and Bayliss (1996)]. An external voltage was applied across the porous Si and the p-type Si substrate using the circuit diagram illustrated in Fig. 10.1. This structure is thought to give rise to a Schottky diode between the ITO and porous Si film, while the porous Si/Si substrate interface acts as a heterojunction of two different semiconductors. The forward bias condition corresponds to the case in which the negative voltage is applied to the ITO electrode with respect to the Au electrode. EL takes place under forward bias voltage of the structure and could be seen by the naked eye in a dark background at a voltage of about 4 V (at which the current was higher than 600 mA for a sample of about 4.5 cm\(^2\)). These \(I-V\) values are quite low compared with others: for example Lee and Peng (1993) observed the EL from porous Si by the naked eye at a voltage of 50 V. This could be attributed to the resistivity of the Si-wafer used (25 - 45 Ω/cm) which was higher than that of the wafer used for porous Si preparation in this work, and agrees with the EL obtained at a few volts forward bias by Namavar et al. (1992). EL could result from the potential drop on the low resistivity side of the porous Si layer [Lee and Peng (1993)]. EL was not observed under reverse bias voltage [Steiner et al. (1993), Xu and Steckl (1994), Astrova et al. (1995), Bsiesy et al. (1995) and Tsybeskov et al. (1995)], and the electron-hole pairs recombine to emit visible light via luminescence centres [Qin et al. (1995)]. The spectral response of visible (yellow) EL emitted from beneath the transparent ITO film was measured at room temperature at station 12.1 at CCLRC Daresbury Laboratory. In order to perform EL measurements, the beam of synchrotron radiation was prevented from irradiating the sample. As mentioned earlier (§ 7.2) for steady-state PL measurements using the same beamline, the EL from porous Si sample was analysed using a Spex (Minimate) monochromator and a photomultiplier operating in photon-counting mode. A porous Si sample was mounted at the same position as for the PL measurement, with the porous side facing the collection lens which collimates and directs the EL emission to the entrance slit of the monochromator. As shown in Fig. 10.2, EL emission spectra were wide [as found by Herino et al. (1992)], stable and reproducible [as found by Xu and Steckl (1994)]. This stability could be attributed to partially oxidised porous Si, because the oxide has a good combination of transparent properties and EL stability [Kozlowski et al. (1995) and Tsybeskov et al. (1995)]. As mentioned in § 6.1.2 the
porous Si sample used here for EL experiment was exposed to ambient conditions for a few days before ITO sputtering. In Fig. 10.3 the EL intensity is shown as a function of the forward current measured at room temperature. It is evident that the overall EL intensity increases proportionally to the current [as found by Kozlaowski et al. (1992) and Steiner et al. (1993)]. This implies that the EL emission from porous Si is based on the carrier injection mechanism [Koshida and Koyama (1992)]. As shown in Fig 10.2, the intensity of EL spectra increases with increasing applied voltage across the sample [Lee and Peng (1993)] while the spectrum width remains nearly the same. This could be because the number of emitting crystallites can vary with the passivation of the material, with the excitation energy for PL [Muller et al. (1993) and Motohiro et al. (1995)], or with the applied voltage for EL [Muller et al. (1993)]. The intensity and efficiency of EL from anodised porous Si still needs to be improved in order for solid display device applications to become practical, however here is reported a very encouraging result. The analysis of the potential variations in the structure is quite complicated and is far beyond the scope of this work.

**Fig. 10.1** Circuit diagram of forward applied bias used for EL and I-V characteristics measurement of porous Si.
EL spectra from a porous Si sample recorded at six different bias voltages: from top to bottom 5.00, 4.63, 4.51, 4.39, 4.26, 4.14 V.
Fig. 10.3 EL intensity of porous Si vs. forward current.
10.3 Comparison between photoluminescence and electroluminescence

In order to compare between EL and PL spectra an in-situ PL experiment was performed using synchrotron radiation. After finishing the measurements of EL, the applied voltage across the sample was switched off and an excitation beam of 370 nm wavelength was allowed to excite PL in the same sample. Fig. 10.4 gives examples of typical EL and PL spectra taken at room temperature from the same sample. One can see from this figure that the intensity of the PL spectrum is higher than that of the EL, but the spectrum of EL is wider and the peak is blue-shifted compared to PL [as found by Koshida and Koyama (1992) and Astrova et al. (1995)]. It has been found [Koshida and Koyama (1992), Kozlowski and Lang (1992), Steiner et al. (1993), Propst et al. (1994), Fathauer (1995) and Fauchet (1995)] that EL spectra often resemble the PL spectra, but sometimes they differ [Bassous et al. (1992), Kozlowski and Lang (1992) Kozlowski et al. (1995)]. The PL peaked in the orange and the EL in the yellow in all cases, with a FWHM of about 1.42 and 1.83 eV respectively. The FWHM is greater in the case of EL [Tsybeskov et al. (1995)]. The difference between the intensities of the PL and EL spectra may be attributed to the difference in populations of emitting crystallites in porous Si layer, which it seems is higher in the case of PL emission. This can be seen from the comparison between PL spectra taken for the same sample of porous Si before and after EL measurements. The PL spectrum recorded after EL measurements shifted toward lower energy and its intensity became less than that of the PL spectrum recorded before EL measurements, as seen in Fig. 10.5. It can be considered that the red shift and the lower PL intensity in the spectrum measured after EL measurements arises from the heating of the porous Si sample due to voltage applied to obtain EL. This is in agreement with the previous steady-state PL measurements (§ 7.2) which were taken at different temperatures. Another possibility for the higher intensity of PL recorded before EL could be due to the change in the position of the sample for the two PL measurements (i.e. before and after EL): as mentioned in § 8.1 different regions on the sample might exhibit different PL efficiency. In general the shape of the two PL spectra is almost the same before and after EL measurements, which supports the SEM examination by Propst et al. (1994) on porous Si after EL which showed that the pore structure was the same as before EL.
Fig. 10.4 Comparison between PL and EL spectra taken from the same sample of porous Si. The excitation energy for PL is 3.35 eV and the applied bias of EL is 5.0 V.
Fig. 10.5 Comparison between PL spectra from the same sample of porous Si: (a) before and (b) after EL measurements.
10.4 I-V characteristics of porous Si

The $I-V$ characteristics of ITO/porous Si/p-type crystalline Si substrate/Au electrode structures were measured at room temperature under forward and reverse bias conditions, and are shown in Fig. 10.6 (for the circuit diagram see Fig. 10.1). Both of the samples used for EL and $I-V$ measurements were similar, because they were taken from a wafer prepared under the same conditions. The only difference between the two samples is the sizes: the surface area of the sample used for $I-V$ measurement was about $0.77 \text{ cm}^2$. As seen from Fig. 10.1 for the forward bias circuit the positive voltage is applied to the Si-substrate and in the reverse bias condition the positive voltage was applied to the ITO film. In Fig. 10.6(a) the initial part of the forward $I-V$ curve up to 2 V shows a very slight change in the current density (i.e., the cut-in voltage is about 2 V). However, at voltage higher than 2 V the current values increase exponentially with the applied voltage. The measurements on different samples are found to have similar responses. Fig. 10.6(b) shows the $I-V$ curve measured under reverse bias voltage from the same sample used for forward bias voltage.

Observation of high intensity of both PL and EL (shown in Fig. 10.2), prove the high transparency of the ITO film for visible light, and the sheet resistivity measurement clearly shows in this study the low resistivity of the ITO film ($40 \Omega/\square$). All these characteristics demonstrate that sputtered ITO materials can be used with high efficiency EL applications involving nanostructures.
Fig. 10.6 Room temperature $I$-$V$ characteristics of the porous Si np heterojunction, measured under room light (a) forward and (b) reverse bias voltage.
Chapter 11

Discussion, conclusion and suggestions for further work

11.1 Discussion

11.1.1 Porous Si samples

Porous Si samples produced by electrochemical etching have been investigated by steady-state PL, EXAFS, Electron Microscopy, PL lifetime and EL. Various stable samples of porous Si show red to green PL at temperature ranging between 77 - 295 K.

TEM micrographs and diffraction patterns demonstrate that the porous Si samples used in this work, which were exposed to the air for more than a year, are fundamentally crystalline with a distribution of nanocrystallite sizes, and platelets of diameters ranging between 4 - 10 nm.

11.1.2 Steady-state PL

The high PL efficiency of porous Si is mainly caused by the reduction of the nonradiative recombination processes. The intensity of steady state PL spectra decreases with increasing sample temperature from 77 - 295 K. The broad band spectra of symmetric Gaussian shape, are interpreted by a distribution of confinement energies, which is attributed to the non-uniform size and the shape distribution of silicon nanocrystallites. It was also found that increasing the anodisation time led to a slight decrease in the FWHM of the PL spectra. This behaviour of different FWHM has already been observed and explained by assuming that the PL emission energies come from a different distribution of confined quantum structures. The steady-state PL peak position was found to depend on both sample preparation conditions and measurement temperature. The PL peak position shifts toward higher energies with decreasing temperature and increasing anodisation time of porous Si preparation.
Gardelis et al. (1991) consistently observed that the PL peak was blue shifted with increasing anodisation current density. Zhang et al. (1992) observed the same behaviour of blue shift of PL with increasing resistivity of the initial Si wafer used in anodisation in the range of $5.5 \times 10^{-3}$, 0.74, 11, 75 and $1.2 \times 10^3 \, \Omega \, \text{cm}$, but they found the strength of PL peak for high resistivity samples become weaker with higher resistivity. The anodisation current densities for preparation of porous Si samples in this study were 30 mA/cm² for red and 20 mA/cm² for yellow/orange and green/yellow. No blue shift was observed for this difference in current densities which may have been because the difference in current densities was not enough to give such a blue shift in PL spectra. The resistivities of the Si wafers used were also very similar and therefore it was not possible to see if this gave the different PL emission. However, the parameter which varied most between samples was the anodisation time of the samples and this could be correlated with the PL emission energies (§ 6.1.1).

In spite of the PL blue shift observed with decreasing temperature for all samples in this study, other temperature dependence studies showed that the blue shift of the PL spectra occurred with increasing temperature [Gardelis et al. (1991), Zhang et al. (1992), Xu et al. (1992) and Wang et al. (1993)].

In general, the blue shift in PL emission is thought to be arise from increases in the Si band gap, which supports the quantum confinement model. No permanent damage occurs in the porous Si samples due to cooling, because the PL returns to its original intensity and position when the temperature is ramped back from liquid nitrogen to room temperature. The radiative recombination of carriers in porous Si has been ascribed to an indirect band gap transition, because the observed PL energy in this study is usually below 2.6 eV (in the literature below 2.5 eV) while the direct band gap for bulk Si is 3.4 eV (which would become even larger in a nanoscale unit due to quantum confinement effects [Qin and Jia (1993) and Qin (1995)]), and the transition from the indirect band to direct is not realised for porous Si [Vial et al. (1992) and Hooft et al. (1992)].

11.1.3 EXAFS of porous Si

It has been shown that EXAFS spectroscopy is a valuable tool for a quantitative characterisation of the local structure of porous Si. In particular, the interatomic distances, coordination numbers and Debye-Waller factors have been compared
Discussion, conclusion and suggestions for further work

between different porous Si samples and crystalline Si. The EXAFS absorption spectra and the data analysis show that the porous Si contains a significant amount of oxygen. Because of large specific area in porous Si and since a lot of oxygen atoms exist in air it is probable that the silicon atoms would adsorb oxygen atoms and bond with them when the sample is exposed to ambient conditions. As a result, one would expect the samples exposed to the air to have a lot of Si-O bonds. This result indicates that the surface of porous Si is far greater and perhaps more reactive toward oxygen than c-Si. However, for the same samples exposed to the environment, the degree of oxidation is different due to the different initial number of atoms in silicon wires. There is a similarity in the local structure of the porous Si samples emitting green/yellow and yellow/orange light as revealed by the EXAFS data Fourier transform, and it differs from the porous Si samples of orange/red and red emission. The latter two samples show a more ordered structure as seen from second and third neighbour shells which are absent in a-Si [Schuppler et al. (1994) and Zhang and Bayliss (1996)].

The Si-Si near edge feature is very clear for red emitting porous Si and decreases gradually with PL colour until it disappears for the sample of green/yellow emission. At the same time the Si-O features are clear for all porous Si samples, and these features are also present in c-Si, which can be attributed to native surface oxide. The Si-O-Si Debye-Waller factor values reflect the rigidity of these bonds and provide evidence for the existence of oxygen in the bulk.

The result from EXAFS is that the first shell Si-Si coordination number decreases with increase in PL emission energy, i.e. size decreases with energy increase. The variations in PL energy with Si structure size are consistent with the quantum confinement model, which predicts enlarged band gaps in nanostructures, although this is certainly not the only possible mechanism.

11.1.4 Electron microscopy for porous Si

Electron microscopy observations of the porous Si morphology showed nanostructured platelets of non-uniform diameters. From TEM images of porous Si, platelets diameters were found ranging between 4 - 6.5 nm for red, 4 - 5.5 nm for orange and 4 - 10 nm for green/yellow samples. According to the quantum confinement model the samples of higher PL emission energy should have nanostructure of lower diameters (i.e. the green/yellow porous Si should have smallest
diameter structures). From these observation both red and orange samples agree well with the hypothesis of the quantum confinement model. Perhaps the green/yellow porous sample had isolated clusters in it which would be more confined than platelets connected to produce wires so they could be bigger and still provide the same or even greater confinement, and hence greater emission energy.

The diffuse rings in the TEM diffraction patterns for orange and green/yellow porous Si could be attributed to amorphous SiO₂ on the porous layer, formed by oxidised nanosized c-Si. Nanostructures in porous Si layers are well known, but there are no satisfactory models to explain them and predict their variations with the different preparation methods.

11.1.5 PL lifetime

The lifetimes of PL decay of both as-prepared and aged porous Si samples are in the microsecond region and are also nonexponential. In general, there are large differences between lifetimes measured at 295 and 77 K, ascribed to a change in nonradiative recombination processes. In the case of lifetime evolution measurements, two cases arise and must be considered: (I) lifetime measurements were performed at temperatures ranging between 77 - 295 K, and (II) measurements at room temperature only (i.e., the samples are not subjected to any cooling). In the first group of measurements, higher value lifetimes (τ₁ and τ₂) were found after 40 days at 77 K only. This behaviour was not observed at temperatures higher than 77 K (i.e., 150, 220 or 295 K). It was found that decreases in τ₁ and τ₂ become more steady with increasing PL energies as the temperature rises from 77 K towards 295 K. For the second group, it was found that the values of τ₁ after 7 days of exposure to laboratory environment was longer than all other exposure periods (the longest exposure for this group was 7 days). The values of τ₂ after 4 days of exposure were the lowest and after 7 days the longest lifetimes were recorded. All other values of τ₂ for other exposures (i.e. for the as-prepared up to 18 hr exposure sample), were between those of the 4 and 7 days evolution.

These observations of the differences between the lifetimes (τ₁ and τ₂) for different samples of porous Si can in fact be ascribed to differences in the efficiency of the nonradiative recombination mechanism and the possible compositional changes owing to laboratory environment exposure, which can easily cause more oxidation of porous Si. The differences in the radiative recombinations depend strongly on the variation
Discussion, conclusion and suggestions for further work

of temperature, with the emission efficiency at room temperature being limited by the nonradiative losses.

For PL lifetimes measured at different excitation energies, it was found that the higher excitation intensities give rise to longer lifetimes (i.e. slower decay), while the lower excitation intensities give the shorter lifetimes, except in the case of $\tau_2$ at 295 K where the lifetime values were the same at all excitation intensities.

In general, as found in this study and reported by other groups, the lifetimes become shorter with increasing PL emission energies and their range depend on the measuring temperature, attributed to electron and hole relaxation. The low temperature decay times should be representative of the radiative decay times, and those are found to be very slow compared to the room temperature decay times. Looking at table 2 in chapter 8, one can see that the PL lifetimes spread over a wide range from nanoseconds to milliseconds. In this study the PL lifetimes were found to range between less than a microsecond ($\tau_1$) at room temperature for higher PL emission energies to a few tenths of microsecond ($\tau_2$) at liquid nitrogen temperature for lower PL emission energies. This variation in PL lifetime can be ascribed to the variation of electron hole separation. In the PL decay curves there is no observable rise time and no significant change in the shape of PL decay with changing excitation intensity. However, these could play a role in nonexponential decay.

11.1.6 InO and ITO thin films

InO and ITO have been investigated with a view to their use in contacting porous Si in order that EL measurements can be made. As is well known, the optical reflectance of InO$_x$ and ITO$_x$ increases with decreasing x and it has not been possible to measure R for photon energies higher than 4 eV for the films of $x < 0.56$. The films of higher $x$ show high T. At higher values of $x$, both R and T show good interference fringes, and these fringes were used to calculate the refractive indices. A linear wavelength dependence with the fringe orders has been obtained, although the refractive indices were obtained only for films of $x > 1$ due to the relatively high absorption of the films of lower $x$. The absorption edges of InO$_x$ and ITO$_x$ move toward the UV region when $x$ is increased. For thickness measurements of transparent InO films, good agreements were found using ellipsometry, interference fringes and SEM techniques. The thickness of a typical metallic (opaque) film has been determined using only SEM. It
was found for $x < 0.3$ that the films were of granular nature, whereas for higher $x$ the films were less rough on a micron scale.

From EXAFS analysis, more In-O bonds were found for films of higher $x$ and the structure of InO$_x$ and ITO$_x$ showed a dependence on the oxygen partial pressure. There is also a lot of configurational disorder even at low $x$, and these results are therefore in line with those of Hebard and Nakahara (1982).

The weakening of the In DOS as $x$ increases leaves the absolute position of the conduction band minimum virtually unchanged in energy throughout the composition range. For evolution of the indium suboxide system a schematic energy band model has been proposed.

The room temperature electrical resistivity of InO$_x$ films varies with $x$, with higher resistivity found when $x = 1.1$, and dropping again as $x$ increased further. It has not been possible to compare these results with those of others, as there has not previously been a report quoting electrical data as a function of oxygen composition.

11.1.7 EL

EL was obtained from electrochemically etched porous Si using ITO Schottky contacts. It is believed that the use of $n$-type ITO with $p$-type porous Si basically operates as a $np$ heterojunction LED. The junction occurs between the wide band gap, doped $n$-type ITO and the $p$-type porous Si. Yellow EL emission at room temperature from porous Si layers can be seen by naked eye in a dark background. EL is emitted only when the porous Si is subjected to a forward bias voltage due to the injection of minority carrier electrons and holes from ITO contact and $p$-type c-Si into the porous Si layer respectively. The visible light emission could be due to the electron quantum confinement in the thin silicon wires. The broad spectra in EL and PL then can be interpreted as a distribution of confinement energies (i.e. of crystalline sizes). The EL spectrum is blue shifted compared with the PL spectrum. The FWHM of EL is wider than that of PL, while PL intensity is higher than that of EL. Some authors however have found that the PL and EL responses are similar whilst others have found differences. Since the preparation of porous Si is easy and the required equipment is very simple and inexpensive, it is possible to make LEDs of porous Si emit different colours. This can be achieved by changing the preparation conditions. The low EL efficiency of porous Si could be ascribed to an insufficient number of electrons and
holes which recombine in the luminescent active area. Therefore, further studies are still required to improve the EL efficiency. Such results demonstrate a very promising and advantageous technique for fabrication of porous Si based LEDs and electroluminescent flat panel display. In comparison with other work, the EL is quite bright, being observed by naked eye at quite low forward bias voltage (about 4 volts) due to the low resistivity of the Si-wafer (5 Ω cm) used for porous Si preparation in this work. More detailed studies of EL characteristics, including methods for improving quantum efficiency and the control of the EL spectra, are required in order to obtain more understanding of the EL mechanism. This could produce useful information and better understanding the origin of visible light emission in porous Si.

11.2 Conclusions

In the last 5 years research on porous Si has led to amazing new results and to renewed interest in silicon optoelectronic devices, especially LEDs. Although much progress has been demonstrated, more work remains to be done, especially to achieve a better understanding of the light emission mechanism and to demonstrate that LEDs based on porous Si can find commercial applications.

A combined investigation has been performed on various visible light emitting porous Si by steady-state PL, EXAFS, electron microscopy, PL lifetime and EL analysis. The combination of optical and surface analysis offers a better understanding of the physics of porous Si.

The results of this work strongly indicate that the observed PL emission arises due to recombination of quantum confined carriers within crystalline Si. The high PL efficiency of porous Si as compared to bulk Si is thought to be mainly due to the reduction of the nonradiative recombination processes. The values of FWHM, were found (I) to decrease with increasing anodisation time, (II) decrease with increasing PL emission energies and (III) broaden with the decreasing of temperature from 295 to 77 K. This corresponds to a decrease in average size of the Si crystallites in porous Si with increase in PL energy and is considered to be strong evidence that the visible PL is caused by the quantum effect in nanoparticles, although this is certainly not the only possible mechanism.

From EXAFS analysis, red and orange porous Si shows an ordered structure, which differs from that of yellow/orange and green/yellow porous Si samples. This
Discussion, conclusion and suggestions for further work

difference led to a difference in PL emission properties. All porous Si samples contain a significant amount of oxygen. EXAFS shows evidence of crystalline like structure for porous Si very similar to that of c-Si. The results are consistent with the quantum confinement model.

The nanocrystals were investigated by use of electron microscopy. The porous Si electron diffraction rings contain both crystalline (for red porous Si) and some amorphous phases (i.e. diffuse rings in orange and green/yellow porous Si).

As reported by other authors, the PL lifetimes for all porous Si samples, defined as 1/e times the initial intensity of PL decay curve, become shorter with increasing both PL emission energy and temperature. In the case of time evolution, at 77 K, the measured PL lifetime of 40 days ageing is higher than the others, and is independent of PL emission energies. This behaviour was not seen in the other temperatures. For other ageing where the PL lifetime measurements have been performed at room temperature only, it was found that only the sample aged for 7 days showed lifetimes higher than all others. The difference in PL lifetimes for various porous Si samples and time evolutions reported in this thesis can be ascribed to the competition between the radiative and nonradiative recombination mechanism more than the compositional changes. The rationale for this is that only a small variation is observed in the lifetime values of porous Si samples of very different average local structure when taken at same conditions of measurement.

As can be seen from table 2 (chapter 8) and the results of this work, interpretation of the PL lifetime of porous Si is quite complicated, with the lifetimes for different samples distributed over a wide range from ps to ms. It is not then surprising that the kinetics of PL in different porous Si samples prepared in various laboratories may be very different, in addition to any differences in measurement conditions.

To study EL the porous Si samples had to be effectively contacted by a transparent conductor. Previously IO and ITO had been shown to exhibit such very useful electrical and optical properties, even when deposited in large areas onto plastic substrates at room temperature using dc reactive sputtering. In this study the evolution has been followed in thin films of dc reactively-sputtered IO and ITO thin films of the optical and electrical properties with oxygen content, and linked the film properties to the preparation conditions and film composition. As expected the values of absorption coefficient become higher for films of lower x. The change in optical properties ($E_g$ and $n$) has been linked to the evolution of the bonding with oxygen...
content. The formation of a distorted bixbyite structure appears to occur monotonically with increase in electronegativity as oxygen is added. Lastly the electrical properties are related to $x$ as expected, the highest resistivity being obtained for $x \approx 1.1$, the generally high values possibly being due to an increase in defect sites formed during preparation using this deposition method.

Finally, porous Si can emit stable visible EL by applying a forward bias voltage across the porous Si sample using transparent conducting ITO films, as a negative electrode. The EL intensity increases with increasing bias voltage. The low EL efficiency is ascribed to insufficient number of electrons and holes which recombine to produce EL emission, but it is stable, and this is attributed to native oxide on the porous Si nanostructure.

11.3 Suggestions for Further Work

Research on porous Si (both light emitting porous Si and LEDs) should focus on the conditions of (I) improving efficiency and stability/durability, and (II) achieving high quality, long-lived solid state electrical contacts for LEDs. More studies are required of PL lifetimes of a wider range of samples prepared from different Si wafers (i.e., both $n$ and $p$ type and of different resistivities). It has been seen that ITO films are excellent materials in transparency and conductivity for contacting porous Si. Such good characteristics encourage their use in optoelectronic application. Therefore the author recommends its use instead of other materials such as semitransparent Au. Still better efficiencies are required, however, for optical display applications.

Lastly, for device applications, it is essential that the porous Si layers be uniform both in depth and laterally. This is probably achievable by careful design of the electrochemical cell.
References

References


161
References

De Smet, D. J. (1976) Surface science 56, 293.
References


Ellis, B. (1973) in *Semiconductor Opto-Electronics*, (London Butterworths) § 1.5, § 3.1, § 2.4.2, § 7.1 and § 10.3.


References


References


References


Mells Griot (1990), optics guide 5, pp. 4-33 to 4-34, pp. 11-16.


Mott, N. F. (1972b) Phil. Mag. 26, 505.


References

References

References


References


Appendix: List of publications


