

Mechanically and Thermally Induced Defects in Silicon Nanostructures

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Declaration

This thesis is an account of research undertaken between January 2004 and October 2004 at The Department of Electronic Materials Engineering, Research School of Physical Sciences and Engineering, The Australian National University, Canberra, Australia.

Except where acknowledged in the customary manner, the material presented in this thesis is, to the best of my knowledge, original and has not been submitted in whole or part for a degree in any university.

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Abstract

Mechanical and thermally-induced deformation of silicon nanostructures causes changes in their optical and structural properties which are studied in this project.

Nanoindentation is used to investigate the effects of mechanical introduction of defects to silicon nanocrystals (Si-nc). The process is found to introduce non-radiative defects to the crystals which quench their luminescence in the localised region of the indent. The transformation to high-pressure metastable phases in the underlying silicon is characterised by Raman spectroscopy and transmission electron microscopy, with the critical load found to be between 50 and 100 mN for a spherical indenter and between 25 and 50 mN for a Berkovich indenter. The results are consistent with computer simulations of the indentation process on identical systems.

Annealing conditions are used to investigate the effects of thermally inducing of defects to Si-nc as they form. The effect of slow cooling rate used in annealing is found to increase PL intensity, even after passivation. This is explained by the difference in thermal expansion coefficients between the Si nanocrystals and the amorphous SiO₂ matrix. In annealing Si-nc, a slow cooling rate has the effect of allowing good adhesion between the Si nanocrystals and the SiO₂ matrix, which has sufficiently low viscosity to flow at temperatures above the viscoelastic temperature (~ 850 °C). Faster cooling rates are shown to result in higher concentrations of non-radiative defects, reducing overall PL intensity. This is caused by the nanocrystals contracting faster than the SiO₂ matrix can follow, resulting in poor contact between the two media at their interface. The thermally-induced strain creates non-radiative defects which decrease the overall PL intensity.

Studies of thin film Si are conducted, using transmission electron microscopy and nanoindentation. They reveal no sign of phase transformation to the high-pressure metastable phases. Computer simulations of the thin film system indicate that the level of hydrostatic stress required to nucleate phase transformation is present. Nanoindentation testing of Si thin films ranging from ~ 200 nm to ~ 5 nm reveal amorphisation of the material, but no pop-outs on unloading which are indicative of a phase change to Si-III/XII.

Nanoindentation is used to create nanometre-sized crystalline grains in bulk silicon which are analysed for photoluminescence (PL) emission resulting from quantum confinement. No such emission is measured.

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List of Acronyms

AFM atomic force microscope

a-Si amorphous silicon

bc8 body-centred cubic structure with 8 atoms per primitive cell

CL cathodoluminescence

c-Si crystalline silicon

FIB focussed ion beam

PL photoluminescence

PSi porous silicon

QC quantum confinement

r8 rhombohedral structure with 8 atoms per primitive cell

SEM scanning electron microscopy

Si-nc silicon nanocrystals

TEM transmission electron microscopy

UMIS ultra micro-indentation system

XTEM cross-sectional transmission electron microscopy

INTRODUCTION

1.1 Background

Silicon is by far the most common material used for making integrated circuits. However, the ineffective light emission from bulk silicon limits its practical use in microphotronics. [1] A breakthrough occurred in 1990, when visible light emission was observed from porous silicon (PSi) at room temperature. [2] This stimulated a strong interest in silicon-light emitters throughout the 1990s. [3] The fabrication of a solid-state electroluminescent device was a prominent goal as well as a fundamental understanding of the physics of nanoscale materials. [4] Significantly, photoluminescence was also observed from samples of silicon with dimensions of the order of 1 to 20 nm, so-called silicon nanocrystals (Si-nc). [1], [3] Quantum confinement (QC) in crystalline silicon was the first model proposed to explain the strong, visible, room temperature photoluminescence (PL) from PSi, and structures or crystallites in the nanometre size range present in PSi and other forms of light-emitting silicon are responsible for the PL. [5]

The PL from Si-nc is important because it opens up the possibility for microphotonic applications while exploiting the already well-established infrastructure of the silicon-based semiconductor industry. Both silicon light-emitting diodes [3] and optical waveguides made from luminescent Si-nc have been recently demonstrated. [6] In addition, Intel has produced an optical modulator that operates at 1 GHz, a fifty-fold increase in the speed of data encoding, [7] and Motorola has produced a 4-Mbit silicon nanocrystal memory device. [8]

In this current study, we aim to investigate the effects of defects on the structural and optical properties of silicon nanostructures. These defects will be introduced via mechanical deformation and thermally-induced stress. The results from this study may have technological relevance in the area of novel memory devices. The use of indentation technology to mechanically introduce defects at specified positions in samples of Si-nc is the first time such a spatially selective quenching of emission has been attempted. Thermally introduced defects in Si-nc will also be studied, although the introduction of such site-specific defects is obviously not possible using temperature control.

Silicon nanocrystals offer several advantages over PSi. Porous silicon is structurally fragile, and the chemical etching techniques used to fabricate it are difficult to integrate into current circuit technology. In addition, the large internal surface area in PSi makes it very reactive, which is undesirable in photonic devices. Porous silicon oxidises spontaneously in air, and there is a reduction in light output after prolonged exposure to the atmosphere, as well as light-induced degradation. [9] In contrast, Si-nc implanted in a SiO_2 matrix are stabilised by

the matrix, and there is less degradation of their luminescent properties. [10] Researchers have also managed to effectively control the size and composition of the nanocrystals, with the use of variety of Si-nc fabrication techniques.

Research in materials with novel electronic properties such as Si-nc has also developed increasingly advanced methods for studying semiconductors and other materials. Differences between the macroscale and nanoscale properties of materials have resulted in the need for methods that can accurately study nanoscale material properties. One such method is nanoindentation. [11] Nanoindentation refers to depth-sensing indentation testing which records the load and displacement with very high accuracy and precision. This test is most commonly used to measure a material's hardness, modulus and other mechanical properties, however, it is also possible to use the data to study the mechanical deformation processes in the sample during indentation. Nanoindentation enables a high degree of control on the deformation process, which will be exploited in this project.

This project combines materials science with silicon-based photonics. Few groups study the deformation processes that occur in the material during indentation, and no such studies have been done on Si-nc. There are also only a few reports [12] on the mechanical properties of Si-nc as opposed to its optical properties. This project will fill the gap between these two distinct branches of electronic materials science by achieving the objectives listed below.

1.2 Project Objectives

This project will study the effects of mechanical and thermal deformation on Si-nc luminescence and thin film silicon. The optical and mechanical properties of the structures resulting from such deformation will be characterised using various techniques, including nanoindentation, photoluminescence spectroscopy, cathodoluminescence imaging, atomic force microscopy, Raman microspectroscopy, and transmission electron microscopy.

1.2.1 Mechanical Deformation of Bulk Silicon

Nanoindentation will be used to mechanically deform bulk and thin-film silicon to create small regions of phase transformed material with novel electronic properties and optical properties. These properties will be studied for the first time. The process of nanoindentation creates high-pressure metastable phases directly beneath the indent. The sizes of these grains is of the order of nanometres. [13], [14] This study will ascertain whether the PL caused by quantum-confinement observed in PSi [2] and Si-nc [15] can also be observed in the crystalline grains created beneath the indent.

1.2.2 Mechanical Deformation of Silicon Nanocrystal Systems

Samples of SiO_2 containing Si-nc will be made and subjected to nanoindentation. The effect of nanoindentation on the optical and mechanical properties will be studied in the regions of the indents.

1.2.3 Thermal Deformation of Silicon Nanocrystal Systems

Thermal strain can introduce defects to Si-nc. Heating and cooling rates used in annealing Si-nc will be studied to determine whether these are a significant contributor to interface quality and the concentration of non-radiative defect centres.

1.2.4 Mechanical Deformation of Thin Film Silicon

Thin-film silicon is widely used in magnetic storage systems, micro-electromechanical systems and other industrial applications. The mechanical characterisation of silicon is an important area of research in ensuring optimum product performance and reliability. Surprisingly, the literature contains very little on the deformation mechanisms of thin film silicon. This experiment will characterise the deformation mechanisms involved in thin film silicon during indentation, through the use of electron microscopy, nanoindentation and simulation. This will ascertain whether the mechanical deformation will induce behaviour similar to that observed in the bulk and Si-nc samples.

1.3 Thesis Outline

Chapter 1 - Introduction: A general overview of the fields of nanoindentation and PL from Si-nc is covered, as well as what has already been done by other research groups, and the aims and significance of the current project.

Chapter 2 - Theory and Previous Research: This chapter will describe some background theory relating to indentation theory and the origins of luminescence in Si-nc.

Chapter 3 - Experimental Method: This chapter outlines the use of scanning electron microscopy, cathodoluminescence imaging, focussed ion beam milling, transmission electron microscopy, atomic force microscopy, photoluminescence spectroscopy, Raman microspectroscopy, ion-implantation and nanoindentation.

Chapter 4 - Results and Discussion: This chapter discusses results from studies on mechanical deformation of bulk crystalline silicon, mechanical deformation of silicon nanocrystals, thermal deformation of silicon nanocrystals, and the mechanical deformation of silicon ultra-thin films.

Chapter 5 - Conclusions and Further Work: This chapter summarises what this project has discovered, how it ties in with other work, and outlines directions for future research.

CHAPTER 2

THEORY AND PREVIOUS RESEARCH

2.1 Mechanical Deformation of Silicon

2.1.1 Indentation and Nanoindentation

The hardness of a material can be measured using the technique of indentation. In traditional indentation testing, a diamond tip is pressed into the sample with a known load and then removed. The residual plastic impression is then measured. From this, the hardness, which is defined as the ratio of the maximum load to the residual indentation area, can be calculated. *Nanoindentation* refers to indentation testing at submicrometre depths with continuous depth-sensing, allowing testing of very small volumes of material. [11]

Different tip shapes are used in nanoindentation testing for different purposes. Spherical tips are often used as they can be described analytically, whereas deformation under pyramidal Berkovich tips (three-sided pyramid) can only be modelled by finite element analysis. However, Berkovich tips are commonly used as they induce plasticity at lower loads, and as such are ideal for thin-film testing.

2.1.2 Models used in Nanoindentation

A material is said to behave elastically if it retains its original shape after unloading, and plastically if it remains deformed after unloading. This behaviour is shown in Figs. 2.1.2 (a) and 2.1.2 (b), respectively. Models to describe the both behaviours are briefly described below. [11]

Elastic models

Elastic models, as the name suggests, assume purely elastic unloading. The compliance of the sample and indenter tip are modelled as springs in series with a combined modulus, E_r given by

$$\frac{1}{E_r} = \frac{1 - \nu_i^2}{E_i} + \frac{1 - \nu_s^2}{E_s} \quad (2.1)$$

where ν_i and ν_s are the Poisson's ratio of the indenter and sample respectively, and E_i and E_s are the Young's moduli of the indenter and sample respectively.

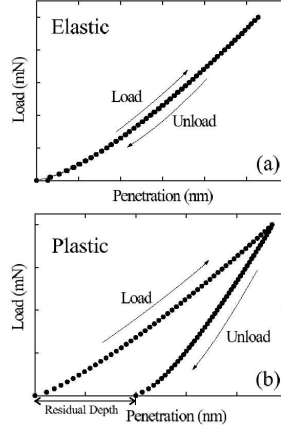


Figure 2.1: Nanoindentation load-displacement curves showing (a) elastic and (b) plastic behaviour. [14]

According to Hertzian theory, the relationship between load and displacement then becomes

$$\delta = \left(\frac{9}{8}\right)^{1/3} \left(\frac{1}{E_r}\right)^{2/3} \left(\frac{1}{D}\right)^{1/3} P^{2/3} \quad (2.2)$$

where δ is the depth of penetration, D is the diameter of the spherical indenter, and P is the applied load.

Elastic/plastic models

Models that account for plastic deformation of the material include the approach of Field and Swain. [11] Here, indentation is treated as a reloading of an impression already formed in the material. By loading and partially unloading, the hardness and reduced modulus can be calculated.

$$H = \frac{P_{max}}{\pi a^2} \quad (2.3)$$

$$E_r = \frac{3}{4} \frac{P_{max}}{a(h_{end} - h_f)} \quad (2.4)$$

where H is hardness, P_{max} is the maximum load, a is the contact radius of the indenter and h_f is the plastic depth of the indent.

Thin film systems

Conventionally, indentation tests on thin-film systems are conducted to no greater than 10% of the thickness of the film, in order to prevent adverse influence from the substrate. While some models exist to explain thin film/substrate

systems, [11] the complication with these models eventuates when attempting to separate properties of the film from properties of the substrate.

2.1.3 High Pressure Phases of Silicon

Silicon exhibits a variety of structures, depending on the applied pressure and temperature. At atmospheric pressure, Si forms a cubic-diamond structure. The pressure induced by indentation can cause Si to transform from cubic-diamond (Si-I) to other structures. [16] Upon loading, Si-I undergoes a phase transformation to the Si-II (β -Sn structure) phase. This process requires high pressure (~ 11.3 GPa, for a spherical tip radius of ~ 4.2 μm , this is equivalent to a load of 15.5 mN). When the pressure is released, Si-II transforms to a metastable crystalline phase of either Si-III (bc8 structure) and/or Si-XII (r8 structure) or amorphous silicon (a-Si), with proportions of each phase depending on the unloading conditions. This is in contrast to pressure-induced transitions obtained by diamond-anvil cell experiments, where only the crystalline structures are formed on pressure release. [17] It is important to note that in a diamond-anvil hydrostatic stress experiment, shear stress and residual stress play minor roles, but they are an important consideration in nanoindentation.

One technique for identifying these pressure-induced phase transformations relies on the depth-sensing information provided by nanoindentation. [18] It has been shown that slow unloading rates (~ 1 mN/s) tend to give rise to crystalline material and a “pop-out” (a discontinuous change in displacement at constant load) in the unloading curve, as shown in Fig. 2.2 (a). The discontinuity in the unloading curve has been shown to result from an abrupt phase transformation from metallic Si-II to either Si-III or Si-XII, as shown by Raman spectroscopy. [14] The sudden volume increase causes the material surrounding the indenter tip to lift up abruptly. In contrast, a fast unloading rate (~ 3 mN/s) results in the predominance of amorphous phases and an “elbow” (gradual change in slope) as shown in Fig. 2.2 (c). [14] The gradual slope change of the unloading curve is caused by the formation of amorphous silicon. The silicon expands as it transforms slowly from metallic to amorphous semiconducting phase, and this lifts up the indenter tip gradually. [19] Thus there is a strong correlation between the shape of the unloading section of the indentation load-displacement curve and the structural changes that occur in silicon during indentation.

2.1.4 Nanoindentation of Thin Films

Silicon thin films are a scientific research interest because the length scale at which plasticity size effects (i.e. dependency of plastic deformation on tip radius) become significant is of the order of tens of nanometres. [20] The mechanical properties of thin films are difficult to measure by indentation, however, scaling functions can be used to determine the mechanical properties of thin coatings from indentation testing, [21] and methods of determining the elastic properties of thin films has been described. [22] While Chudoba claims that it is difficult to obtain correct Young’s modulus measurements by conventional indentation measurements with the Berkovich indenter, [23] a blunt Berkovich tip approximates a spherical tip over small penetration depths.

Of particular interest is the possibility of causing phase transformation in

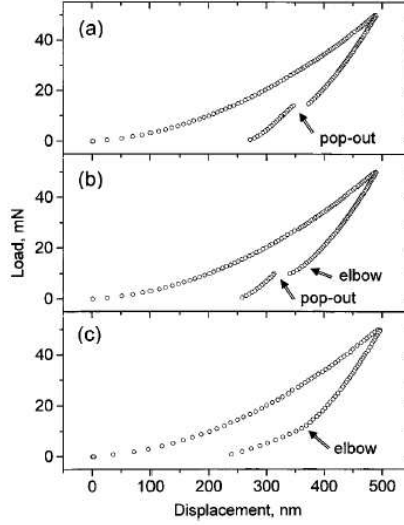


FIG. 1. Three types of load-displacement curves in the nanoindentation of Si, obtained at the loading rate of 3 mN/s and maximum load of 50 mN.

Figure 2.2: Indentation load-displacement curves for Si showing (a) pop-out, (b) pop-out and elbow, and (c) elbow features on unloading. [19]

thin-film Si. The smaller volume of thin film samples results in a smaller number of possible nucleation sites for the phase transformation. Since the phase transformation process is nucleation-limited, thin-film samples are thus less likely to undergo a phase transformation than a bulk sample given identical indentation conditions.

2.1.5 Simulations of Nanoindentation-Induced Deformations in Silicon

Experimental observations of Si deformation by indentation have been confirmed by simulations of the same system. *Ab initio* total energy calculations considering Gibbs free energies, predict a pressure induced high-density amorphisation of crystalline diamond-cubic silicon around 15 GPa. [24] Molecular dynamics simulations of the structural transformations and plastic deformation which occurs in silicon surfaces (depths of a few nm) as a result of nanoindentation provide evidence from an atomistic viewpoint that structural transformations occur in silicon surfaces during nanoindentation, also confirming experimental observations. [25], [26] These simulations also suggest that thermal vibrations play a role in the recovery of the indented region during unloading, and that a transformation from β -Sn to amorphous can take place even when the indenter's radius is a few nanometres. [27] The high-speed deformation of pure silicon nanocrystals has been simulated with the use of molecular dynamics, [28] which showed that plastic deformation or compression of the crystals is possible at room temperature with high speed (10 ms^{-1}). The effects of strain on the elec-

tronic spectrum of Si nanocrystals with diameter 10 nm has also been simulated in truncated hemispherical crystals. [29] The geometry dependent strain was found to induce greater quantum confinement with the crystal, indicating that nanocrystal shape affects the resulting PL emission.

2.2 Optical Studies of Silicon

The understanding of the optical properties of Si-nc has progressed phenomenally since the discovery of room temperature PL in PSi in 1990. [2], [4] Some key points are outlined in the following.

2.2.1 Photoluminescence

Photoluminescence refers to light emission from a material induced by its exposure to light. In the band theory of semiconductors, the incident photon is absorbed by an electron in the valence band. This electron is excited into the conduction band, leaving a hole (absence of an electron) in the valence band. The electrostatic attraction of the two particles keeps them close to each other and the system is called an exciton. The electron-hole pair can recombine radiatively, leading to the emission of a photon; or non-radiatively, leading to phonon emission. Various PL emission pathways are shown in Fig. 2.3(a). The photons produced have energies equal to the band gap (i.e. the difference in energy between the conduction and valence bands).

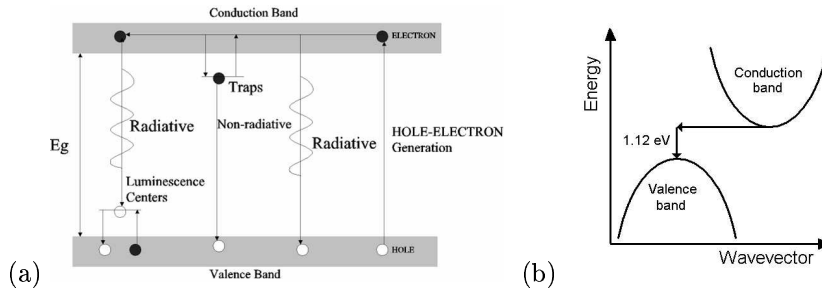


Figure 2.3: (a) Photoluminescence pathways (b) Indirect bandgap of silicon

2.2.2 Bulk Silicon

Bulk silicon is an indirect band gap semiconductor as shown in Fig. 2.3(b), since the point in k -space (where k is the wavevector of the particle) with the lowest energy in the conduction band does not coincide with the point of highest energy in the valence band. Light emission is a phonon-mediated process with a low probability of occurring. The transition thus has a long lifetime, τ (of the order of milliseconds). The long lifetime increases the volume of space over which the exciton travels and as a result, there is a higher probability that it will settle into a nearby defect, causing non-radiative recombination. The quantum efficiency is given by

$$\eta = \frac{\tau_{nr}}{\tau_{nr} + \tau_r} \quad (2.5)$$

where τ_{nr} and τ_r are respectively the non-radiative and radiative lifetimes.

In direct gap semiconductors, η , is of the order of 10%, because the radiative lifetimes are short enough (a few nsec) to compete with non-radiative lifetimes. In bulk silicon, η , drops to 10^{-6} . In Si-nc, quantum efficiencies greater than 10% at room temperature and 50% at cryogenic temperatures have been demonstrated. [3]

2.2.3 Silicon Nanocrystals

Like bulk Si, Si-nc are indirect gap semiconductors (for all but the smallest crystals). [12] Interestingly, despite this, Si-nc exhibits strong, visible PL. [2] The difference in behaviour can be explained via the quantum and spatial confinement model of photoluminescence.

Quantum Confinement

In the QC model, the excitons created by photon absorption are physically confined to a small region of space, where there are few or no defects that act as non-radiative recombination centres. Physical isolation of the excitons from these defects causes the radiative recombinations of the excitons to dominate over non-radiative recombinations. QC also rearranges the density of electronic states by reducing the dimensionality of the system. The increase in overlap between electron and hole wavefunctions increases the probability of a radiative transition.

Quantum confinement effects are only significant for systems in which the Bohr radius of the exciton is of the order of, or larger than, the size of the confined system. Along with the increased probability of radiative transfer, QC also results in an increase in the bandgap energy. As in the particle-in-a-box model, the system's energy levels spread out as the degree of confinement increases. The extra momentum required for the indirect transition comes from incident photons or electrons scattering the confined exciton at crystal boundaries, negating the need for phonon-mediation. [30]

It has been well-established that Si-nc exhibits strong PL in the red region of the visible spectrum. The peak intensity increases and the edge of the absorption spectra shifts towards the blue as the mean size of the crystals decreases. This has also been confirmed by theoretical calculations on the electronic properties of Si-nc. [31] The PL is tunable throughout the visible range by changing the crystallite size. [1], [32] While some groups claim that the dominant contribution to the visible light emission comes from nanocrystals smaller than 2 nm, [33] others claim that sizes below 4 nm produce the strongest luminescence. [32]

Photoluminescence mechanisms which do not involve QC have also been proposed to explain Si-nc PL, but these have been largely discredited. [4] These include models which cite hydrogenated amorphous silicon, surface hydrides, siloxene molecules and defects as sources of PL. The diversity of models put forward arises from the diversity of often contradictory experimental evidence that developed during the 1990s. This, in turn, was brought about due to

the many methods researchers used to fabricate Si-nc. There are a multitude methods, [3] including ion-implantation, [34] plasma enhanced chemical vapour deposition, [1] ex-situ fabrication, [35] laser microstructuring, [36] sputtering, [37] molecular beam epitaxy, [38] and gas evaporation [39].

Defects and Passivation

The PL intensity of Si-nc is decreased by the presence of dangling bond defects which act as non-radiative recombination centres. Silicon dangling bonds occur when a silicon atom has a lone pair of electrons in the valence shell, and will tend to occur at the interface between Si and silica (SiO_4). One type of defect caused by Si dangling bonds at the Si/ SiO_2 interface is called a P_b centre, which acts as a non-radiative recombination centre. [40] The intensity of the PL emission can be enhanced by using phosphosilicate glass instead of pure SiO_2 as the host matrix. As the P concentration (in the form of P_2O_5) increases, the PL also increases, while the emission caused by the P_b centres decreases. [41]

A more common method of reducing the effect of non-radiative defects is passivation, whereby atoms or molecules are introduced to bond to the Si atoms, removing the dangling bond defect. Common methods of synthesising Si-nc have the crystals embedded in SiO_2 thin films, where the crystals are oxygen terminated, and the corresponding PL spectra are confined to a specific wavelength range. This is in contrast to the hydrogen-terminated nanocrystals, which show a continuous shift of peak energy from the bulk energy bandgap to the visible region, in good agreement with QC theory. [1] Oxygen passivation increases the PL intensity of Si-nc, but also introduces defects that cause the appearance of a blue band alongside the Si-nc emission. [42] Hydrogen passivation increases the luminescence intensity and lifetime of Si-nc by reacting with the dangling bonds to form Si-H bonds. This effectively decreases the number of available defects. Atomic hydrogen appears to passivate more effectively than molecular hydrogen.

Conversely, quenching of the PL in Si-nc can be achieved by simply introducing non-radiative defects to the sample. Thus the material behaves like bulk Si, where non-radiative transitions dominate and radiative transitions are negligible. PL from Si-nc can also be degraded by the application of an electric field. [43]

Cathodoluminescence

Cathodoluminescence refers a similar process as photoluminescence, where the stimulus is electron irradiation, not light irradiation. Past studies on mechanically milled nanocrystals using cathodoluminescence spectra have attributed a band at 1.61 eV (770 nm) to QC effects. [44] Bands centred at 400 nm and 650 nm have also been attributed Si-nc formed by low-pressure chemical vapour deposition. [45]. However, the large variety of sample preparation techniques and detector responses used by various groups has meant that assignments of peaks to various transitions is often wrought with controversy. Cathodoluminescence images of indents have been captured before in materials other than Si (GaN). [46] In these samples, the CL is quenched at the position of the indent, and the crystallographic nature of these samples is revealed in the Star-of-David-like rosettes that appear around the indents.

Nanocrystal Properties

Two characteristics of nanocrystals commonly measured are the absorption cross-section and size distribution.

The absorption cross-section the nanocrystal is a measure of the probability of an incident photon causing a transition to occur. It is important in modeling absorption or luminescence properties of nanocrystal systems. It's value is the product of the density of electronic states and the oscillator strength of the optical transition. The use of photoluminescence selects a particular size by exciting a particular subset of nanocrystals with that particular size.

Ion-implantation followed by annealing creates nanocrystals with a distribution of diameters, and this is more accurately modelled by the logarithmic normal distribution, as it describes many small, multiplicative random effects (many more small crystals). [47] The size distribution of the nanocrystals in this study was found by fitting the Eq. A.6, A.7 and A.8 to the PL spectra using MATLAB.

2.3 Defect Luminescence

Defect luminescence is another PL mechanism. The introduction of defects into a semiconductor creates new electronic states, which can take part in electronic transitions giving rise to PL. This carrier recombination occurring at defects and the QC-related luminescence are distinguished by their behaviour upon annealing. If annealed at high enough temperatures, the larger silicon clusters will tend to amalgamate with the smaller clusters (in a process known as “Ostwald ripening”). This would cause a redshift in QC-related PL emission as the degree of confinement is reduced, and excitonic energy decreases. [9] For defect luminescence, however, annealing would eliminate radiative and/or nonradiative defect sites, which would alter the intensity of the PL, but this will not alter its wavelength.

Defect luminescence occurs in PSi in the form of oxygen-induced defect states with a broad distribution of 2.5 ± 0.3 eV. [48] Other defect luminescence mechanisms have been attributed to defects related to Si-OH groups (2.9 eV) [49]

In silicon-rich silica, an emission band at 2.2 eV has been attributed to defect luminescence from states at the silicon cluster SiO₂ interface. Luminescence at approximately 1.9 and 2 eV in amorphous silica and quartz is generally associated with defect states produced by implantation or irradiation, but has also been attributed to non-bridging oxygen hole centres. These defects are created by the evolution of hydrogen upon annealing, that occurs at a faster rate than the diffusion of interstitial oxygen can compensate the resultant dangling bonds. [9]

2.3.1 Pure Silicon

In pure silicon, defect luminescence has been attributed to three categories of defects: dislocations, vacancies, and interstitials. Polycrystalline Si also exhibit PL.

Dislocation-Related Luminescence

A set of four PL bands is associated with the presence of dislocations in silicon. They are known as D1 (0.807 eV), D2 (0.870 eV), D3 (0.935 eV) and D4 (1.0 eV). [50] The D1 and D2 bands are due to pointlike defects induced by dislocations, whereas D3 and D4 bands are intrinsically related to the dislocations. [51] The intensity of D luminescence bands increases with dislocation density. Point defects such as V_6 and I_4 have enhanced stability at a dislocation core, as the strain surrounding the defect can be relieved at the dislocation. [52] Cathodoluminescence has been used to investigate the room-temperature light emission from dislocations in silicon generated by ion-implantation, and a peak wavelength of 1154 nm was observed and was attributed to electron-hole recombination at the dislocations. [53]

Luminescence from Vacancies and Interstitials

A V_6 vacancy centre contains dangling bonds which have a tendency to reconstruct in pairs, creating acceptor levels. The V_6 defect has six dangling bonds above and six below a hexagon of absent Si atoms and is the only vacancy aggregate known to be optically active in the 1 eV region. [52]

The I_4 tetra-interstitial defect is built out of four split-interstitials. A split-interstitial consists of two orthogonal dangling bonds. These react with other defects, and can be passivated. The geometry of the I_4 defect is such that the dangling bonds are eliminated, resulting in enhanced stability of the defect. [52]

Polycrystalline Silicon Thin Films

Photoluminescence has been observed in polycrystalline silicon films. A peak at 0.98 eV attributed to band-tail luminescence due to disorder at grain boundaries in polycrystalline silicon films at 4 K. The average grain size was in the range 100 - 300 nm. [54] Room temperature PL has also been observed in polycrystalline silicon wafers. A band-to-band emission peaking at 1.09 eV and a defect luminescence band at 0.8 eV were observed. The 0.8 eV PL band was attributed to the accumulation of impurities, such as oxygen, at the grain boundaries. These polycrystalline regions become unstable at 200 °C. [55]

2.4 Effects of Pressure and Deformation on Optical Properties of Silicon

2.4.1 Silicon

PL spectra similar to that observed in PSi has been observed in silicon subjected to severe deformation. [56] At hydrostatic pressures of 6 GPa, Si develops fine-grained polycrystallinity with an average crystallite size of 15 - 40 nm. The PL spectra were obtained for such severely deformed silicon is similar to that obtained from a sample of PSi, with both spectra peaking at 655 nm, and slightly weaker PL intensity from the deformed Si sample. The PL in the deformed sample is attributed to QC effects.

Similar effects are seen for strained Si. When Si single crystals are subjected to torsion straining, the formation of nanostructures occurs, with a mean grain size of 5.5 nm. [57] The PL from these nanostructures has a peak at 650 nm with a FWHM of 80 cm^{-1} and is attributed QC effects.

2.4.2 Porous Silicon and Silicon Nanocrystals

The effects of pressure on the PL of light-emitting Si nanostructures have been studied, with some ambiguous results. The room-temperature PL of PSi films decreases with increasing pressure and there is an initial blueshift of the PL peak from 0 to ~ 20 kbar, followed by a redshift of the PL peak at higher pressures. [58], [59] These results are consistent the QC model where the initial blueshift is caused by an initial nanocrystal size decrease and redshift caused a by a pressure-induced transformation in PSi. A different study [60] indicated that the pressure dependence of the PL from PSi varies with the choice of pressure media used, implying that the origin of the PL cannot be explained in terms of the standard QC model, and that the characteristics of the surface play a dominant role in the PL energy.

Another predicted effect of pressure on Si-nc is a shape change. [12] SiO_2 coated Si nanocrystals show large elevations in the pressure required to induce a semiconductor-to-metal structural transformation, as compared to bulk Si. This is due to the absence of available nucleation sites and to the destruction of the nucleating Si/ SiO_2 interface at the structural transformation. These results indicate that phase transformation in small volumes in silicon, such as thin films or individual nanocrystals is more difficult to induce than in bulk Si. Direct observation of the shape change under TEM requires crystals of relatively large size (~ 20 nm) which is outside the scope of this project.

2.5 Silicon Nanocrystal Nucleation

Si-nc nucleation has been studied as a function of the annealing temperature [61] and a models describing the nucleation and growth of Si-nc formed by ion-beam synthesis in SiO_2 have been developed. [62]

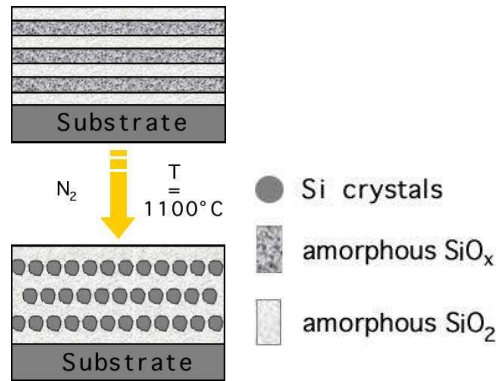


Figure 2.4: Silicon-rich oxides are annealed at 1100°C to produce Si-nc

In order to fabricate the Si-nc, samples of silicon-rich SiO_2 (eg. from ion-implantation) need to be annealed at high temperature (1100 °C). As the temperature is decreased to room-temperature, a phase-separation occurs, as the excess Si in the SiO_2 matrix aggregates and crystallises out into nanometre-sized crystals. This is shown schematically in Fig. 2.4. Ambient gases commonly used to anneal the samples include N_2 and Ar. The presence of oxygen in a high temperature environment is not tolerated, as it would lead to oxidation of the Si to form SiO_2 .

After annealing, samples are passivated with hydrogen to eliminate non-radiative defects that inhibit the PL intensity. This involves heating the sample to 500 °C in the presence of forming gas (N_2 with 5% H_2) for one hour. It has been shown that it is the excess Si atoms that form the Si-nc after thermal annealing. However, a fraction of excess Si remains in the amorphous matrix. At temperatures above 1000 °C, a complete phase separation occurs between the Si-nc and the SiO_2 matrix. [61]

While there is well-established background of knowledge on the length of time and temperature used to anneal the nanocrystals, no research in the literature states the optimum heating and cooling rates for growing highly luminescent nanocrystals. This is significant, because these rates may have an affect on the concentration of luminescence-quenching defects.

P_b defect centres (Si dangling bonds) are responsible for quenching the PL, and can be created by straining the crystals. This strain may be introduced thermally due to the difference in thermal coefficients of expansion between Si and the surrounding SiO_2 .

The linear thermal coefficient of expansion of Si varies with temperature as depicted in Fig. 2.5, and is greater than that of SiO_2 (0.55×10^{-6} at room-temperature). As the sample is cooled, the Si crystals decrease in size. The surrounding SiO_2 matrix does not contract as rapidly as the Si crystals do, and the difference in contraction rate results in thermal strain. Differences of more than 25% between the crystalline Si-Si interatomic distances (0.235 nm) and SiO_2 ($\sim 0.31 \pm 0.05$ nm) also result in intrinsic interfacial strain, which is tensile in the Si and compressive in SiO_2 at ideally bonded Si- SiO_2 interfaces. [63] One way that this strain can be relieved is by allowing SiO_2 to relax around the nanocrystals. SiO_2 has sufficiently low viscosity above it's viscoelastic temperature (850 - 950 °C) such that it can relax around the nanocrystals over laboratory timescales (of the order of hours). Once it sets in below the viscoelastic temperature no more relaxation can take place.

If one considers the effect of thermal expansion in only the Si and ignores the effect of SiO_2 , then in going from 1100 °C to room temperature, the volume change in a spherical crystal of Si is 1.3% which is enough energy to nucleate a dangling bond defect. [29] However, most of this volume change occurs below the viscoelastic temperature (0.93% volume change) and little of it occurs above the viscoelastic temperature (0.40% volume change). Because the cooling rate can only have an effect on the system while the SiO_2 matrix has sufficiently low viscosity, and the defects induced by thermal strain while the SiO_2 matrix is rigid will be present regardless of the cooling rate used, it is unclear whether a slow cooling rate used above the viscoelastic temperature during annealing will have a significant effect on the number of defects produced. This project will experimentally determine whether the effect is significant or not.

The defects produced by thermal strain are expected to occur at the inter-

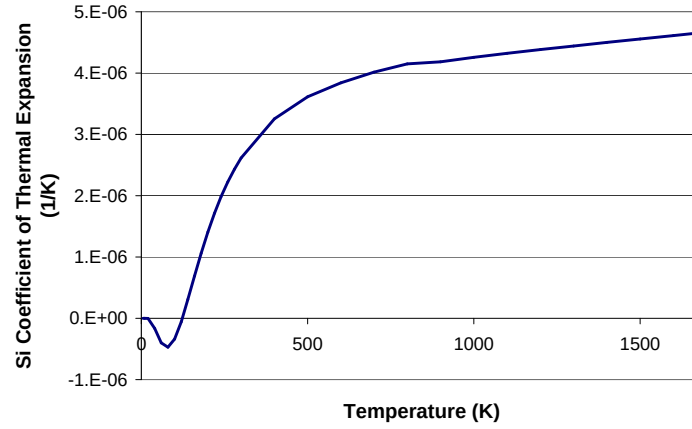


Figure 2.5: Temperature variation of the coefficient of thermal expansion for Si

face. Unless there is extremely good adhesion at the interface between Si and SiO_2 , then the thermally-induced strain causes the defects to occur at the interface, rather than in the interior of the Si nanocrystals. Being amorphous, the SiO_2 matrix does not contain defects.

CHAPTER 3

EXPERIMENTAL METHOD

A variety of experimental techniques were used to prepare and study the samples in this project. These can be broadly classified as microscopic, spectroscopic and sample preparation techniques. They are outlined below.

3.1 Experimental Techniques

3.1.1 Microscopy

Scanning Electron Microscopy and Cathodoluminescence Imaging

Cathodoluminescence (CL) is the light emitted by a sample as a result of electron bombardment. A schematic of the process is shown in Fig. 3.1. Cathodoluminescence microscopy and spectroscopy in a scanning electron microscope (SEM) can detect defect centres in materials with high spatial resolution and sensitivity.

An Oxford instruments Mono CL2 system installed on a JEOL 35C SEM at the University of Technology in Sydney was used for collecting CL images.

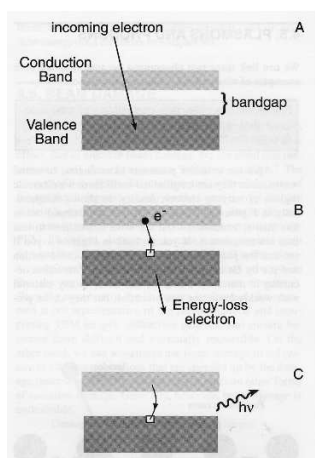


Figure 3.1: Schematic of cathodoluminescence (CL) process

Focussed Ion Beam Milling

In focussed ion beam (FIB) milling, a fine, energetic beam of gallium ions is rastered across the sample as illustrated in Fig. 3.2. At high beam currents the gallium beam rapidly sputters away the specimen surface. The secondary electrons generated by incident ions can be used to image the sample. This technique may be used to mill cross-sections of samples to electron-transparent thickness.

Cross-sectional transmission electron microscope samples in this project were prepared using the FEI xP200 FIB located at the University of New South Wales.

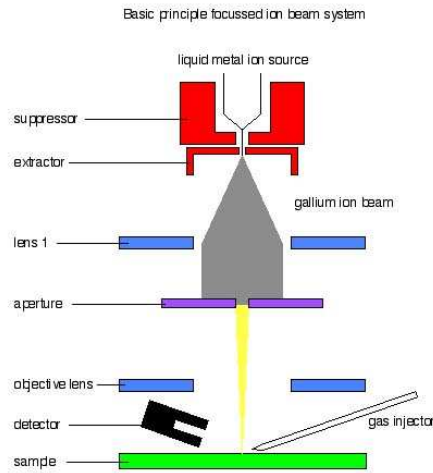


Figure 3.2: Schematic of the principle of focussed-ion beam (FIB) milling

Transmission Electron Microscopy

Transmission electron microscopy (TEM) uses a finely focussed electron beam of uniform current density as shown in Fig. 3.3. The electric field established by the sample's atomic nuclei and surrounding electron clouds scatter the incoming electrons, and thus the beam's phase and amplitude is affected. If the sample is precisely oriented, an electromagnetic lens may focus the exiting altered beam to project an image of the samples column of atoms.

Electrons emitted from the electron gun illuminate the sample through a two or three stage condenser lens system. The unique arrangement of atoms affects the phase of the electrons in a characteristic way. An objective lens is used to form the image or diffraction pattern of the sample. The image can be recorded by direct exposure of a photographic emulsion on an image plate or digitally by a CCD camera.

A CM300 FEI electron microscope was used for the TEM work in this project.

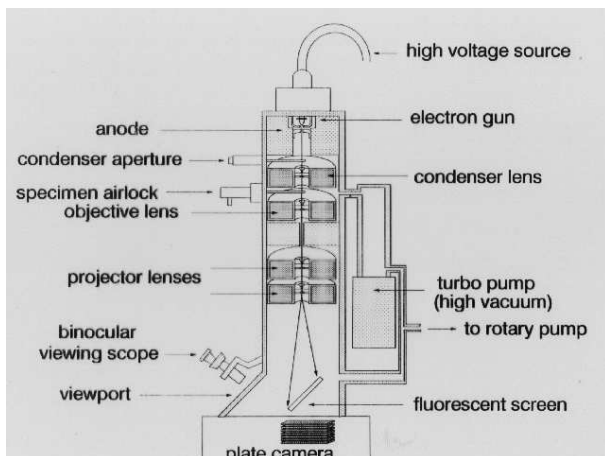


Figure 3.3: Schematic of transmission electron microscopy (TEM)

Atomic Force Microscopy

Atomic force microscopy (AFM) measures the height of a sample by rastering a tip very close to the sample, allowing measurements to be taken over a small area. The variation in height is detected by variation in light intensity received at a photodiode from a laser beam that is deflected off the tip and cantilever.

The AFM images were collected using a Digital Instruments MultiModeTM scanning probe microscope.

3.1.2 Spectroscopy

Photoluminescence Spectroscopy

Photoluminescence (PL) spectra of the samples were obtained by using an Ar⁺ laser (532 nm emission line) and a Triax 320 spectrometer with a CCD detector. The wavelength range of the spectrometer is 550 - 950 nm. Figure 3.4 shows the PL setup used in this project.

The same setup is also used to record time-resolved PL spectra for lifetime measurements. The CCD is also capable of recording PL images of the sample, enabling PL imaging. Alternatively, an InGaAs detector can also be used to record spectra at wavelengths longer than 1000 nm.

Owing to instrument sensitivity to alignment, environmental conditions and rearrangements of the setup for other experiments, the PL intensities are in arbitrary units and the PL intensities recorded on separate occasions cannot be directly compared. However, wavelengths are measured in absolute units and can be compared.

Raman Microspectroscopy

The Raman effect occurs in the interaction between a photon and a molecule, described by a collision satisfying the law of conservation of energy. If the

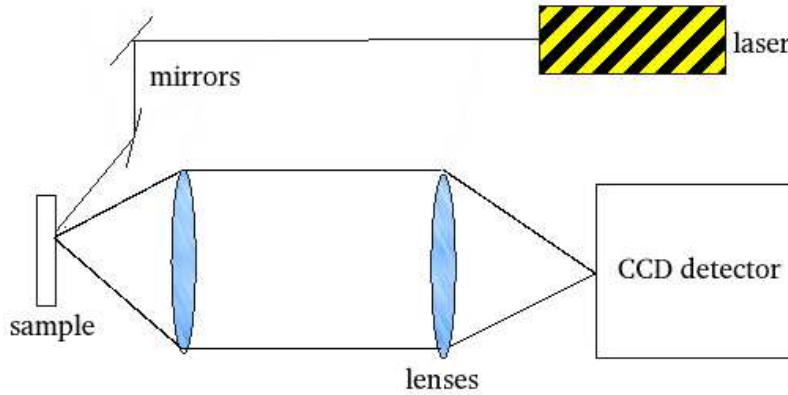


Figure 3.4: Schematic of the PL setup used in this project

photon loses energy during the collision, it appears in the resultant spectrum at a longer wavelength (called a Stokes line), while the molecule that takes up the energy goes into a higher level of rotation or vibration. The photon may also collide with a molecule already in an excited state. In such a collision, the molecule may give up some energy to the photon and relax to a lower energy level, while the emerging photon appears in the spectrum at a shorter wavelength (called an anti-Stokes line). In both cases, the spectral shifts from the parent line give a measure of the rotational or vibrational frequencies of the molecule. The Raman spectra of a material is used to extract information about the material's structure.

Measurements were taken using the Dilor SuperLabram Laser Raman microprobe located at GeoSciences Australia.

3.2 Sample preparation

Ion-implantation

Ion implantation accelerates ions to a target at energies high enough to bury them below the target's surface. Typical acceleration energies range from a few keV to MeV. Due to its speed, accuracy, cleanliness and controllability, ion-implantation has become the standard method for doping semiconductor elements of integrated circuits.

Negative dopant ions are selected from a source using a high electric field. The appropriate ion is selected by mass and charge via a magnetic mass analyser. A high voltage (~ 150 kV) is applied to give accelerate the ions toward the surface to be implanted. The ion beam is scanned across the sample electrostatically to ensure a uniform dose. In this way, excess Si can be introduced into SiO_2 .

A 175 kV Low Energy Ion Implanter equipped with a SNICS II ion source was used to implant samples in this project.

Nanoindentation

One of the nanoindentation instruments used in this project was the load-controlled Ultra-Micro Indentation System (UMIS), a schematic of which is shown in Fig. 3.5. It has a load feedback system that ensures that the applied load equals the set force. A piezoelectric element, connected to the indenter shaft by leaf springs, expands to apply the load. When the indenter contacts the sample, the amount by which the leaf springs are deflected is measured by a force Linear Variable Differential Transformer. It is a highly robust and stable system.

The other instrument used was the Ubi1 Hysitron indenter, located at the Sydney Dental Hospital. This instrument offers superior resolution at lower loads and offers in-situ scanning probe microscopy imaging.

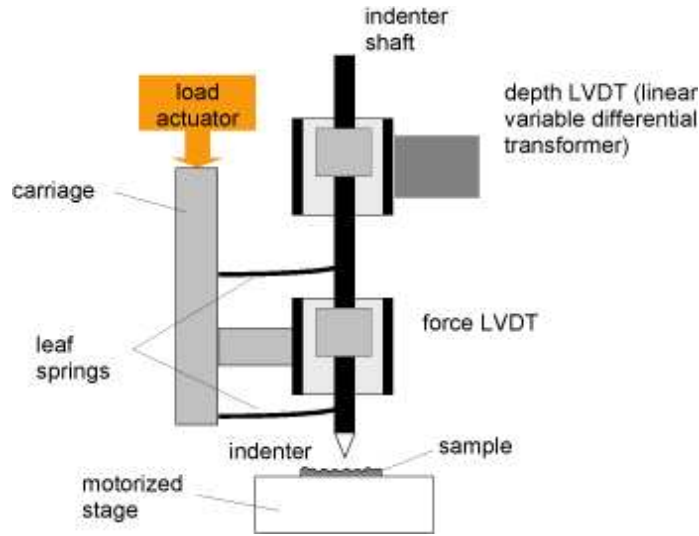


Figure 3.5: Schematic of the UMIS

3.3 Experimental Details

3.3.1 Bulk Silicon

Photoluminescence spectra were taken of indents in bulk Si in order to determine whether the metastable phases created beneath the indents produced detectable PL emission.

The indents were made in samples of c-Si with a $\sim 5 \mu\text{m}$ spherical indenter to a maximum load of 80 mN with 8 load/unload increments with a continuous cycle. This routine has been previously found to induce phase transformations. [14] Each grid measured $90 \times 100 \mu\text{m}$ and contained 190 indents as shown in Fig. 3.6.

An array was formed from four grids in a pattern consisting of 2×2 grids, visible to the naked eye. These arrays were created on four separate samples

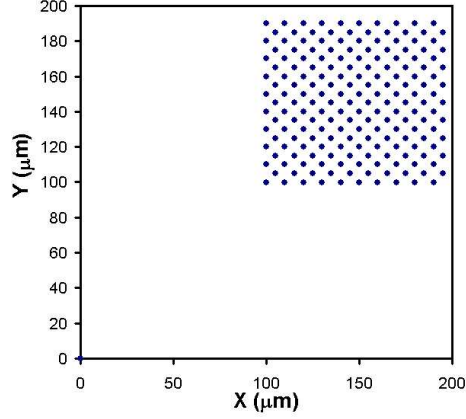


Figure 3.6: Pattern used for the grid of indents. Axis scales are in microns.

and the PL emission from these arrays was collected. The ~ 5 mW laser spot on the sample had an area of 1 mm^2 and the array has an area of 0.036 mm^2 . The sample was positioned using an x-y sample stage, and the incident laser light was strongly scattered upon hitting the array. This ensured correct positioning of the sample. Samples were taken off and repositioned to take multiple spectra in order to obtain representative spectra.

The PL spectra of pristine bulk Si, scratches in bulk Si, and indents with amorphous regions in the underlying Si were also collected and compared with the results for indents with phase transformed material in the underlying Si. The scratches were created with a diamond scribe, and the amorphous regions were created by using only one load increment in the nanoindentation process as opposed to the usual eight for creating samples with polycrystalline regions beneath the indents.

3.3.2 Silicon Nanocrystals in Oxide Layers

Nanocrystal luminescence

Samples of 100 nm SiO_2 thin films on Si substrates implanted with 6×10^{16} Si ions/ cm^2 at 30 keV to give a peak concentration at ~ 44 nm below the surface. These were annealed for 16 hr at 1100°C and passivated in forming gas ($\text{N}_2 + 5\% \text{H}_2$) for 1 hr at 600°C . PL spectra from the samples were measured.

Load-Displacement Curves

The UMIS was used to both create the indents under various loads in the Si-nc-containing oxide, as well as characterise the phase transformations that occurred in the underlying Si substrate during indentation. Due to the small size of the nanocrystals ($\sim 2 - 5$ nm) used in this project's experiments, any direct characterisation of the nanocrystal using nanoindentation was not feasible, as the amorphous oxide matrix flows under indentation.

Cathodoluminescence Quenching

The nanocrystal sample was indented with maximum loads of 25, 50, 100 and 200 mN using a Berkovich tip. The CL spectrum of this sample was recorded and CL images of the resulting indents were collected in order to correlate the quenching with the indents' location. Pan-chromatic images (i.e. taken over all wavelengths) and a monochromatic image at 510 nm were taken with a voltage of 15 kV at $\times 2000$ magnification at room temperature and at 80 K.

Photoluminescence Quenching

The CCD detector of the spectrometer was also be used in imaging mode. The setup was the same as that of collecting PL spectra, but instead of producing a PL spectrum, the software produced an image of the sample with regions of the sample are highly luminescent appearing bright and non-luminescent regions appearing dark. The scale of the image was determined by obtaining an image of a scratch of known dimensions.

A grid of 80 mN Berkovich indents was made in a sample of Si-nc using the same pattern used for the bulk Si studies shown in Fig. 3.6. Photoluminescence images of this grid were collected.

Cross-section Transmission Electron Microscopy of Indents

Indents of 50 and 100 mN were made in Si-nc using a spherical tip in the UMIS. These high loads were necessary for the indents in transparent, amorphous SiO_2 to be readily visible under an optical microscope. Cross-sectional TEM samples of these indents were prepared by mechanically polishing indented samples were down to a thickness of approximately $80\text{ }\mu\text{m}$, which were subsequently milled down using FIB milling to reveal electron transparent cross-sections of the indents.

Raman Microspectroscopy

A sample of Si-nc was indented with various maximum loads (25, 50, 100, 200 mN) using Berkovich and spherical tips in the UMIS. Individual indents in this sample were tested with Raman microspectroscopy and compared with Raman spectra of pristine Si.

Atomic Force Microscopy

A sample of Si-nc was indented with various maximum loads (25, 50, 100, 200 mN) using Berkovich and spherical tips in the UMIS. These were analysed by AFM in order to measure the area and depth of the residual impressions.

ELASTICA Simulation of Oxide Layer

The indentation of the Si-nc containing oxide layer is modelled using the commercially available ELASTICA 2.1. [64] For the 50 and 100 mN indents, the tip radii used in the program were 4 and $3.3\text{ }\mu\text{m}$ respectively, in a 100 nm SiO_2 layer on Si. The load-displacement curves from these simulations were correlated with those obtained experimentally from the UMIS to confirm that they

corresponded to experimental observations. It is important to note that this software only simulates elastic, spherical indentation of materials.

3.3.3 Thermally-Induced Defects

A set of Si-nc samples was created for the study into thermally-induced defects. Fused silica plates, 1 mm thick, were implanted with 100 keV Si⁻ ions to a fluence of $8 \times 10^{16} \text{ cm}^{-2}$, corresponding to an excess Si concentration of 10 at. % at the projected range of 150 nm. They were then annealed for four hours at 1100 °C to form Si-nc.

Nanocrystal Properties

The Si-nc were characterised according to their absorption cross-section, size distribution, and size dependence of the transition lifetime. To measure the absorption cross-section of the nanocrystals, the PL intensity was modelled by a two-level system with steady-state pumping, given by the equation [65]

$$I_{PL} = \frac{N\sigma\phi}{1 + \sigma\phi\tau} \quad (3.1)$$

which, at low excitation intensities (i.e. $\sigma\phi\tau \ll 1$), reduces to the following proportionality

$$I_{PL} \propto \sigma\phi\tau \quad (3.2)$$

At high excitation levels, PL saturation occurs, as all the excitable electrons are excited. Thus, given a constant decay lifetime, radiative lifetime and number of emitters, the optical absorption cross-section is given by the gradient of the PL intensity as a function of incident flux.

The decay lifetime, τ , was measured by pulsing the sample with a square wave laser pulse at 140 Hz recording the time evolution of the PL intensity. The data was fitted to a stretched exponential, described by Eq. A.9. This was done for various wavelengths between 650 and 900 nm, with a straight line used to interpolate the data. The detector response time was measured to be approximately 2 μs , negligible compared to the measured Si-nc luminescence decay lifetime which ranges from 20 - 90 μs .

In order to measure the size distribution of the Si-nc created, PL spectra were collected at various photon fluxes by varying the power of the laser. The laser spot size was measured to be 0.25 mm² using a digital camera and the laser output power was measured with a power meter. At various detection wavelengths, the intensity at that wavelength was plotted as a function of photon flux, and fitted to Eq. A.12. Thus, $\sigma\tau$, was extracted at various wavelengths. Since τ was measured over a range of wavelengths, σ could be extracted over the same range of wavelengths, which were correlated with an energy bandgap.

To measure the size dependence of the transition rate of the luminescence, time-resolved PL measurements of the Si-nc were made to extract the decay lifetime of the luminescence. The inverse lifetime, which is the effective transition rate from excited state to ground state, was plotted against crystal diameter

L. This was done by using the data from the wavelength dependence of the lifetime, and translating the PL wavelength to an equivalent energy bandgap. The bandgap was correlated to a crystal diameter using Eq. A.1 and $x = 1.4$ [66]. The corresponding lifetimes were inverted to give the transition rate. The resulting plot was fitted to the power law

$$y = Ax^{-\beta} \quad (3.3)$$

with $A = 1.89 \pm 0.96$, $\beta = 3.3 \pm 0.43$.

Variation of Heating and Cooling rates

The Si-nc samples were annealed under various heating and cooling rates in order to determine the effects that such processes have on the PL intensity and peak wavelength of the resulting nanocrystals. Faster cooling rates are believed to lead to more defects as the amorphous oxide does not have enough time stay in close contact with the surfaces of the contracting Si crystals. Such an effect would be inversely proportional to the relative intensity of PL emission from the sample. The heating rate could also affect the size distribution of the nanocrystals, which would in turn affect the peak position of PL emission. The PL peak wavelength and intensity were thus measured as a function of various heating and cooling rates to see what effects emerge.

In the first round of experiments, all four samples were annealed at 1100 °C for one hour. The heating and cooling rates used were 3 °C/min from and to 850 °C. When the sample was heated quickly, it was put directly into the 1100 °C furnace, and when it was cooled quickly, it was removed directly from the furnace to room temperature. These heating and cooling rates were used to independently identify the effects of heating rates and cooling rates separately, and to ensure that where possible, samples spent the same length of time at the annealing temperature of 1100 °C. The annealing conditions used to anneal these samples is listed in Table 3.1. Figures 3.7(a) to 3.7(d) show the temperature profiles used to anneal these samples.

Sample	Annealing time (hours)	Heating rate (°C/minute)	Cooling rate (°C/minute)
A1	1	3	-
B1	1	-	-
C1	1	-	3
D1	1	3	3

Table 3.1: Annealing conditions for the samples annealed for one hour

In the second round of experiments, all four samples were annealed at 1100 °C for four hours. The annealing conditions used to anneal these samples are shown in Table 3.2. The corresponding temperature profiles are shown in Fig. 3.8(a) to 3.8(d).

The effect of H-passivation was also studied. The samples which had been annealed for four hours with a slow heating rate (3 °C/min) to 1100 °C were

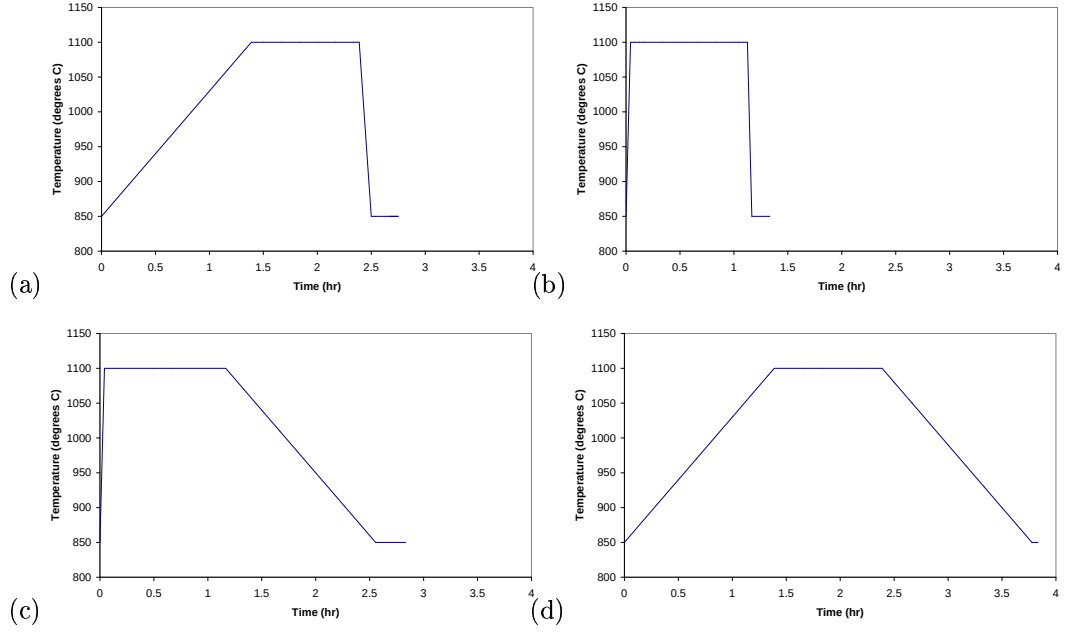


Figure 3.7: Temperature profile used to anneal the samples annealed for four hours (a) A1 (b) B1 (c) C1 (d) D1

passivated with forming gas for 1 hour at 500 °C under identical conditions. One was the slowly cooled sample (D4) while the other was the quickly cooled sample (A4).

Sample	Annealing time (hours)	Heating rate (°C/minute)	Cooling rate (°C/minute)
A4	4	3	-
B4	4	-	3
C4	4	-	3
D4	4	3	-

Table 3.2: Annealing conditions for the samples annealed for four hours

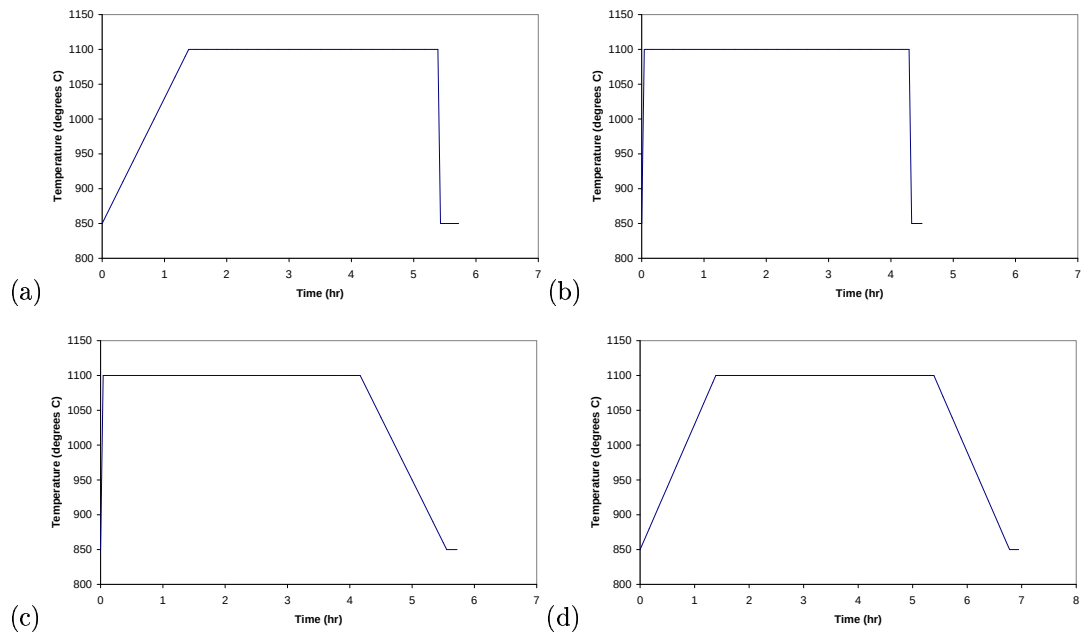


Figure 3.8: Temperature profile used to anneal the samples annealed for four hours (a) A4 (b) B4 (c) C4 (d) D4

3.3.4 Silicon Thin Films

The Si thin film samples consisted of three layers. A 200 nm thin film of Si sat on a 3 μm thin layer of SiO_2 buried oxide. This was supported by a Si handle wafer, which was approximately 500 μm thin. A schematic of this is shown in Fig. 3.9. The PL spectrum of the pristine 195 nm thin film was collected.

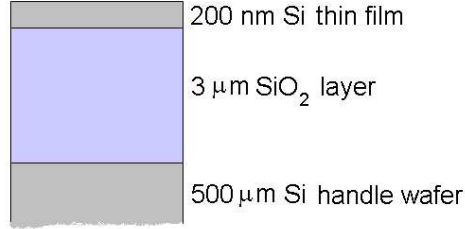


Figure 3.9: The Si thin-film sample

Load-Displacement Curves

Silicon thin-films of thicknesses 195 nm, 82 nm, 56 nm and 4 nm on SiO_2 substrates were prepared. These thicknesses were achieved by oxidising 195 nm thin film Si wafers for various times and then etching away the resulting oxides in a 10% HF solution to reveal the thin film. The films were then subjected to nanoindentation testing. In these tests, Berkovich indents were made in the thin films using a tip with an effective radius of approximately 70 nm. A maximum load of 300 μN was applied at a loading rate of 150 $\mu\text{N/s}$. The 195 nm thin film was also analysed for PL.

This sample was also indented using the Ubi1 Hysitron indenter with various unloading rates (300, 100, 150 and 75 $\mu\text{N/s}$) to determine the effect of unloading rate on the occurrence of a phase transition. The same unloading rates were used to indent bulk Si in order to compare with the thin film results.

Cross-section Transmission Electron Microscopy

A ~ 200 nm thin film of Si on SiO_2 was indented with a maximum load of 80 mN using the UMIS. This was mechanically polished down to an 80 μm thin cross-section of the indent, which was subsequently milled down to electron transparency using a FIB. This sample was analysed by TEM.

ELASTICA Simulation of Silicon Thin Film

In order to learn more about the hydrostatic stress that exists inside the thin film during indentation, ELASTICA was used to simulate the experimentally performed indent under identical conditions. This program simulates elastic deformation processes. In the limit of low loads and small penetration depths, the Berkovich tip may be modelled as a spherical tip (as used in the simulation). The maximum load used in the simulations was 300 μN to simulate a Ubi1 Hysitron indent. The X and Y axes are equivalent, owing to spherical symmetry of the simulated tip.

RESULTS AND DISCUSSION

4.1 Bulk Silicon

4.1.1 Photoluminescence

The first set of PL spectra taken from indent arrays in bulk Si, is shown in Fig. 4.1. The PL spectrum from the indent array is compared to that from a scratch in Si created with a diamond scribe. The peak at 1024 nm is the second order laser line of the 532 nm laser. The broad peak over 760 nm in the the array spectrum is absent in pristine Si, suggesting that the origin of this peak is related to the array. The actual scratch analysed for PL shows similarities to the array and suggest that the PL exhibited by the indents is the same as that of the scratch at a weaker intensity.

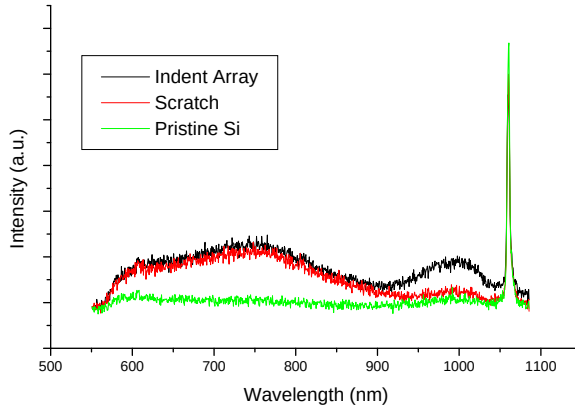


Figure 4.1: PL spectrum of an indent array, scratch and pristine region in bulk Si.

Similar results were observed in the spectrum of an additional array of indents. Again, it shows peaks absent in the spectrum obtained from pristine silicon, and has the same shape as the spectrum of the scratch, at a lower intensity. This is shown in Fig. 4.2(a). The sharp peaks in the spectrum of the scratch are caused by external light sources. Peaks at 760 nm and 600 nm dominate the spectrum of the scratch, and appear in the spectrum of the indent array.

The peak at 600 nm is attributed to the presence of acetone. The original CCD detector was replaced with the InGaAs detector in order to measure at

longer detection wavelengths (900 - 1600 nm). Besides the strong second order laser line at 1024 nm, there are no peaks in this region, indicating that the only band in the wavelength range from 550 - 1600 nm that could be attributed to QC-effects is the one at 760 nm.

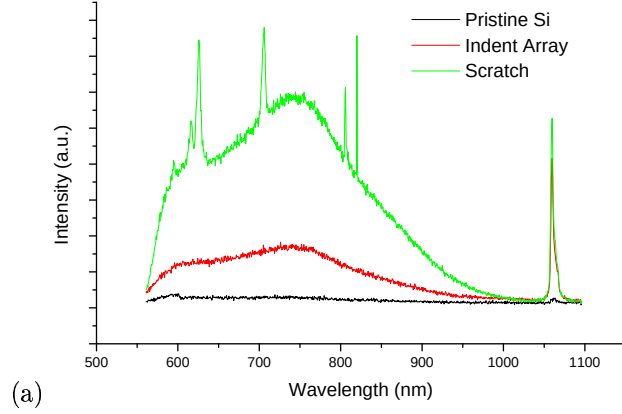


Figure 4.2: PL spectrum of additional indent array, scratch and pristine region in bulk Si.

The spectrum for a third indent array is shown in Fig. 4.3. These samples were cleaned with acetone to ensure that no debris from the scratch or indent were causing the PL. The PL spectrum from pristine Si was taken as a comparison. The spectra for a scratch cleaned with acetone, and a sample with amorphous regions beneath the indents are also shown in Fig. 4.3. These amorphous regions were created by using one load increment during indentation, as described in Section 3.3.

The spectra of the indents and scratch show one peak at 600 nm, and one peak at 750 nm. The 600 nm peak is associated with acetone residue, and thus is particularly strong in the acetone-cleaned scratch. This also results in a spurious 600 nm peak in the spectrum of the pristine Si. The sample with amorphous regions underneath indents does not show much difference to the one with polycrystalline regions underneath the indents, which suggests that the polycrystalline regions do not play a role in the luminescence.

The fourth indent array had no contact with acetone during its preparation. The spectra obtained by from the array and from regions of pristine Si appear similar, as shown in Fig. 4.4. The 750 nm peak of interest in other spectra is very weak. The spectrum from a scratch blown clean with nitrogen, is also shown in Fig. 4.4, showing the peak at 750 nm. The 600 nm peak is reduced as expected, due to the absence of acetone.

The spectra for the first three sets of arrays appear to indicate some sort of luminescence caused by the indents at 750 - 760 nm. Significantly, this is in the same wavelength region as that observed by other research groups for severely deformed silicon. [56] The scratch induces defects in the silicon, and it is possible that a similar mechanism is at work in the indents at a smaller scale. There is also an increase in surface area associated with the scratch, as with the indents, which could be associated with the PL. [56]

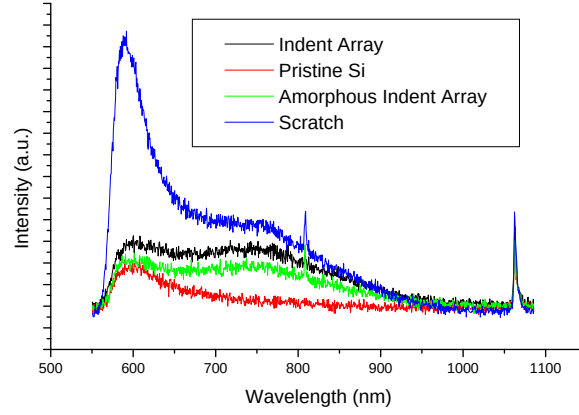


Figure 4.3: PL spectra of indent array, scratch, array of amorphous indents and pristine region in bulk Si. These samples were cleaned with acetone.

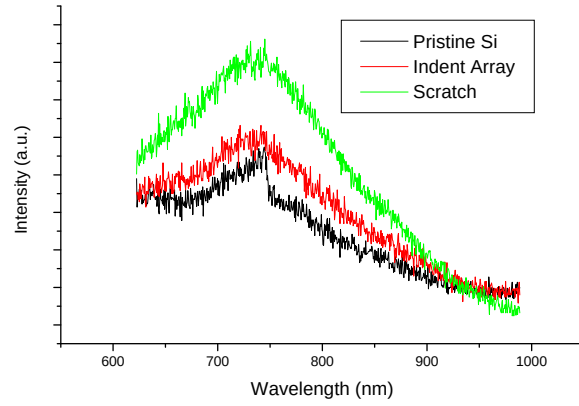


Figure 4.4: PL spectra of array, scratch and pristine region in bulk Si. These samples were not cleaned in acetone.

Interestingly, the positions of the peaks are not consistent with known dislocation-related luminescence bands, which are known to be in the region of 1200 - 1500 nm. [50] The 750 - 760 nm luminescence band is in wavelength region that corresponds to QC-related luminescence, but the appears too broad for this effect, unless this reflects a large size distribution of crystals. The similarity between the spectra of amorphous indents and crystalline indents [Fig. 4.3] indicates that QC is not the cause of the peak. The peak is not found in the fourth set of spectra, and there is the possibility that the indent spectra are weaker intensity manifestations of the scratch spectra because small scratches contaminate the regions of the indents. These spectra do suggest, however, that the peak at 750 nm is associated with deformation caused by the scratch, and not the indents.

As bulk silicon does not luminesce efficiently at room temperature, [67] it was assumed that the silicon that was not indented would not contribute any PL.

This meant that the majority of the incident laser flux ($\sim 96\%$) was incident on an area of bulk Si that did not include the indents, and thus did not contribute to the PL spectrum, causing detection of weak signals to be difficult.

4.1.2 Summary

Thus this study has shown that, no measureable room-temperature PL could be measured from the indents containing polycrystalline Si-III/XII in bulk Si. In the wavelength range from 550 - 1600 nm, no QC-related PL was observed. A very strong peak at 600 nm attributed to acetone residue in the indents was recorded. The broad 750 - 760 nm peak is associated with the luminescence seen from scratched samples. The similarities of the spectra obtained for crystalline and amorphous silicon also suggest that the PL is not QC-related. The reason for this PL may be due to other deformation processes that occur in both indentation and scratching Si aside from phase transformation.

4.2 Silicon Nanocrystal in Oxide Layers

4.2.1 Nanocrystal luminescence

Silicon nanocrystals formed by ion-implantation and annealing typically show luminescence at around 750 nm. [1] The broad distribution of wavelengths is caused by the broad size distribution of luminescent nanocrystals within the sample. Figure 4.5 shows a typical PL Si-nc spectrum. The following section of the thesis will ascertain the effect on this luminescence of introducing defects to the nanocrystals via indentation.

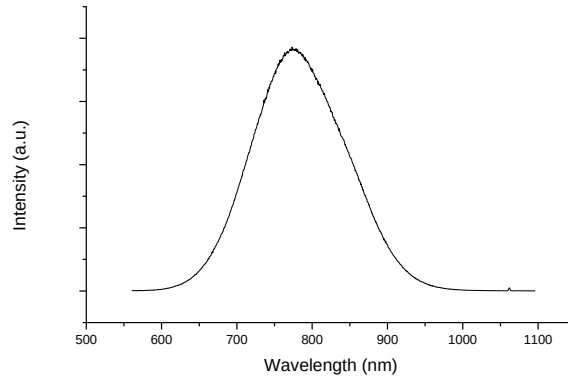


Figure 4.5: Typical PL spectrum of Si-nc

4.2.2 Load-Displacement Curves

Load-displacement curves were obtained during indentation of the oxides containing Si-nc. These are shown in Figs. 4.6 and 4.7. They all show that at their maximum loads, the tip has penetrated to a depth well in excess of the thickness

of the oxide layer (100 nm). Even at loads as low as 25 mN, the maximum load reaches a depth of 270 nm.

The load-displacement curve for the 100 mN Berkovich indent in Si-nc displays a pop-out event (discontinuous change in depth at a particular load on the unloading curve) characteristic of a phase transformation. [19] This is shown in Fig. 4.6(a). The load-displacement curves for the 25 mN Berkovich indents are less definitive. Some curves concur with the results of the Raman microspectroscopy and the presence of a-Si as indicated by the elbow, as shown in Fig. 4.6(b). Other curves do show a pop-out indicating phase transformation to the metastable phases Si-III/XII at different positions along the unloading curve (see Section 2.1.3). These are shown in Fig. 4.6(c) and 4.6(d). Given that the thickness of the oxide layer is 100 nm, the load-displacement curves indicate that the phase transformations to Si-III/XII are occurring in the underlying Si substrate, not in the oxide layer.

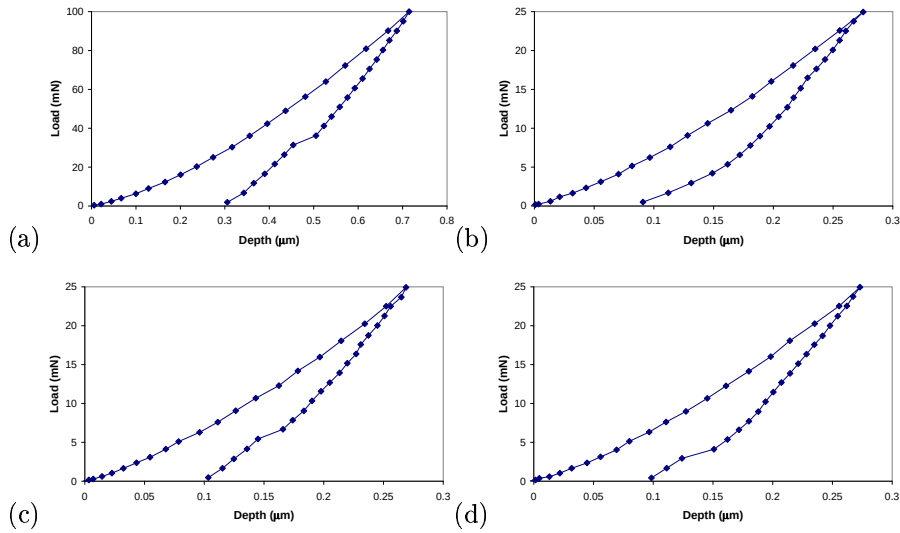


Figure 4.6: Load-displacement curve for Berkovich indent showing (a) pop-out on unloading from 100 mN and at 30 mN (b) an elbow on unloading from 25 mN (c) a pop-out at 6 mN on unloading from 25 mN (d) a pop-out at 4 mN on unloading from 25 mN. The pop-outs are indicative of phase transformation to Si-III/XII in the underlying Si substrate, not in the Si-nc-containing oxide layer.

The load-displacement curve for the spherical tip with a maximum load of 100 mN as shown in Fig. 4.7(a), shows a pop-out on the unloading curve at 30 mN, indicating a phase transformation to Si-III/XII. Again, it indicates that the phase transformations to Si-III/XII are occurring in the underlying Si substrate, not in the Si-nc-containing oxide layer. The corresponding curve for a maximum load of 50 mN shown in Fig. 4.7(b) shows no such pop-out, indicating no phase transformation to Si-III/XII. These results are consistent with what has been observed in the XTEM images (Section 4.2.4).

These results can be understood in the context of unloading rates, since both

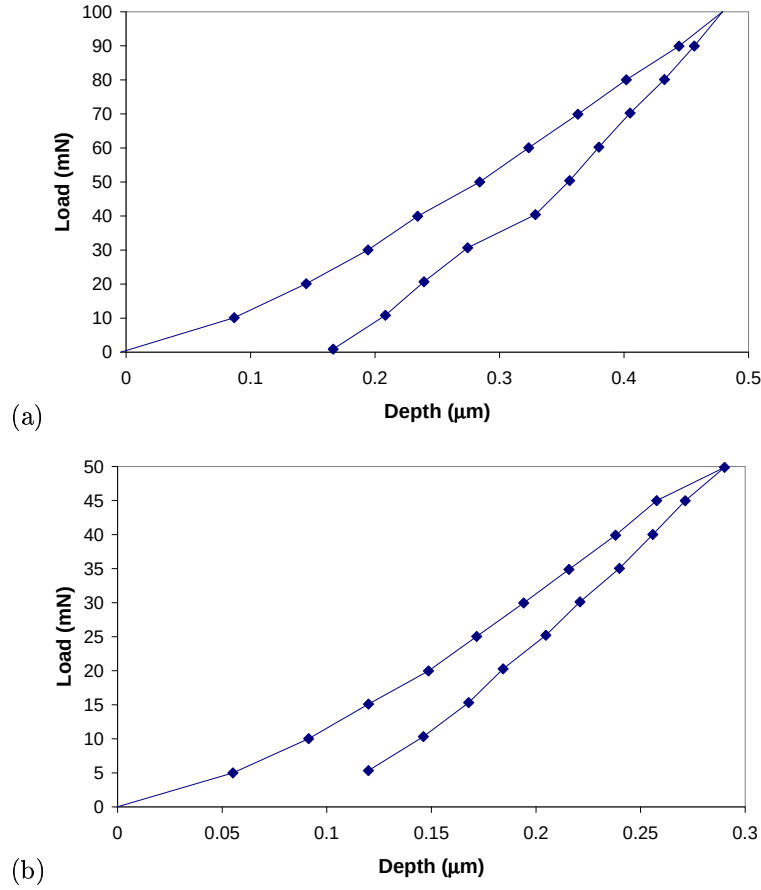


Figure 4.7: Load-displacement curve for spherical indent showing (a) pop-out at 30 mN on unloading from 100 mN and (b) no signs of pop-out on unloading from 50 mN. The pop-out is indicative of phase transformation to Si-III/XII in the underlying Si substrate, not in the Si-nc-containing oxide layer.

loads were indented with the same number of unload increments on the UMIS. Using a lower load over the same number of unload increments as a higher load is effectively equivalent to using a slower unloading rate.

4.2.3 Luminescence Quenching

Nanocrystal samples were indented and imaged using CL in order to determine whether the indentation would cause localised quenching of the emission.

The load-displacement curve of the indent which created this sample is shown in Fig. 4.8(a) and indicates that the tip has penetrated to a total depth (1155 nm) and plastic depth (400 nm) which are both much greater than the thickness of the layer (100 nm). The PL spectrum for this Si-nc sample before the indentation is shown in Fig. 4.8(b), and it shows the characteristic QC-related PL emission.

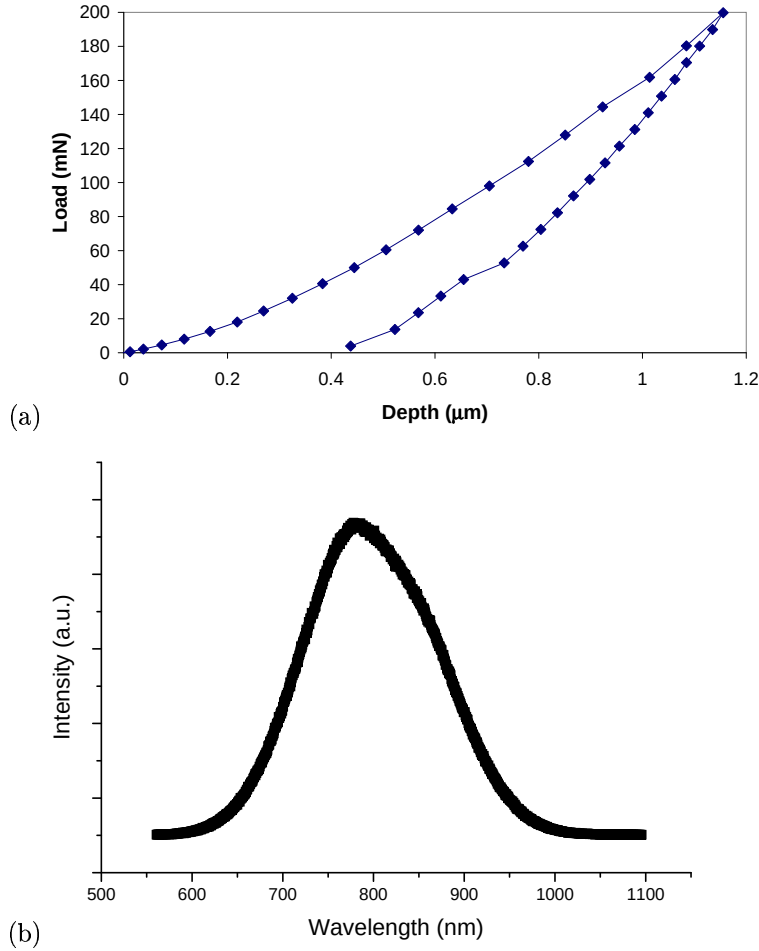


Figure 4.8: (a) Load-displacement curve for 200 mN Berkovich indent in Si-nc. Note the pop-out on unloading at 50 mN (b) PL spectra of the Si-nc used in CL images.

Figure 4.9 shows an example of a CL spectrum for the Si-nc layer. It has a strong peak over 470 nm and is associated with defects in the SiO₂ matrix. [68] This was not detected in the PL spectra because it is beyond the wavelength

range of the spectrometer. The expected peak at 750 nm is present, although somewhat hard to discern due to the low resolution of the monochromator used.

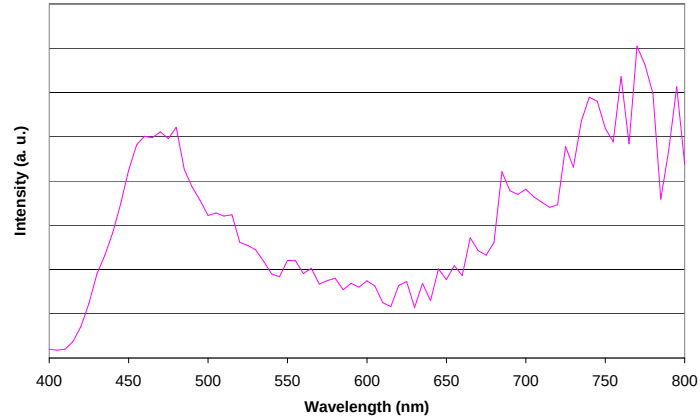


Figure 4.9: CL spectrum of Si-nc.

The room-temperature CL images of the 200 mN Berkovich indent are shown in Figs. 4.10(a) and 4.10(b). The luminescent background of Si-nc is seen, along with a darker, triangular region at the position of the indent. Thus it appears that the defects mechanically introduced by indentation have quenched the luminescence. The area of the quenching is $14 \mu\text{m}^2$. This is consistent with AFM measurements which also report the area of the 200 mN Berkovich indents to be $14 \mu\text{m}^2$ as shown in Fig. 4.11. The depth of this indent was also measured by AFM to be 285 nm. These results indicate that the area of the indent matches the area of the quenched CL. Significantly, the quenched region does not extend beyond the dimensions of the indent, nor is it contained within an area smaller than the indent size.

The AFM measurements showed that the 100 mN Berkovich indent has a depth of 154 nm which exceeds the thickness of the 100 nm oxide layer. Despite this, no quenching was observed for these indents in the CL images, although this is possibly due to the limitations imposed by the SEM's resolution.

For indents at lower loads (5 - 100 mN) CL quenching could not be detected. This is possibly because these loads were not high enough to quench the CL, but also because of the resolution limit of the SEM. It is more likely to be the latter, as 80 mN indents do induce quenching, as the results from the PL imaging will show.

The 200 mN Berkovich indent was also imaged at 80 K and the images are shown in Fig. 4.10(c) and 4.10(d). The first image shows a luminescent region at the centre of the indent. The luminescent region is no longer present in images taken later. The exact origin of this luminescent region in the indent is unknown, but it may be caused by phase transformation beneath the indent or defect luminescence caused by defects that have been introduced by indentation. Regions of phase transformed Si do exist beneath the Si-nc containing oxide layer in these high load indents, as has been identified by XTEM for the case of a 100 mN indent, shown in Fig. 4.15(b) (see Section 4.2.4). It has been shown that luminescence exists in PSi samples that have undergone the

diamond $\rightarrow \beta$ -Sn phase transition, and persist in these samples upon recovery at atmospheric pressure in the bc8 phase. [69] Note, however, that these results were obtained using a diamond anvil cell and not via indentation.

The CL intensity becomes progressively weaker as it is exposed to the electron beam, suggesting that the formation of non-radiative defects is occurring as a result of the incident electron beam. The quality of the images was limited by the intensity of the CL emitted from the samples. The images reveal an intensity fluctuation in the CL across the sample surface, indicating the size distribution of nanocrystals. The grating in the monochromator used to collect these images is more sensitive to the blue end of the spectrum, and smaller nanocrystals which blueshift the emission appear brighter in the image, also contributing to spatial fluctuations in CL intensity.

The CL emission is strongest at 510 nm. This is attributed to emission from the SiO₂. [68] CL emission at 750 nm (QC-related nanocrystal emission) is low in comparison, but still significant. The peak CL emission at 510 nm suggests that the contrast in CL intensity between the indent and the surrounding area is caused by the presence or absence of SiO₂. However, the CL image of the same indent taken at 510 nm and shown in Fig. 4.10(e) does not reveal quenching at the indent, rather there is emission at 510 nm at the indent location. This implies that SiO₂ is present in the indent and throughout the entire sample. Furthermore, it suggests that the quenching of CL observed in the pan-chromatic CL images is caused by quenching of the 750 nm Si-nc luminescence, and not quenching of the 510 nm SiO₂ luminescence. The quenching is not caused by the absence of nanocrystals (because the oxide layer is present throughout), but the absence of luminescent nanocrystals (since it is the quantum-confinement related emission at 750 nm that is being quenched). The nanocrystals are still present, since the 510 nm CL image shows that the SiO₂ layer is intact.

While the corresponding load-displacement curve for this indent, shown in Fig. 4.8(a), shows tip penetration of the oxide layer, the CL image at 510 nm Fig. 4.10(e) still suggests that the oxide layer is still present at the position of the indent. This is also supported by evidence in XTEM images taken of the indent, shown in Fig. 4.12.

The defects introduced by indentation have quenched the luminescence, by offering many more non-radiative transitions to be possible in these crystals within the localised region of the indent. These may correspond to dangling bond defects created during indentation. Assuming that the crystallites are bonded to fixed positions in the matrix, the crystals are present at the indent, but no longer emit light.

These findings are significant because they indicate that while indentation can be used to quench Si-nc PL at 750 nm by introducing non-radiative defects, the process is limited by the phase transformation of the underlying Si substrate. High loads, if indeed they are necessary to quench the CL, will also tend to cause the underlying Si to undergo a phase transformation. However, it is likely that the two sources of luminescence (quantum confined excitons in Si-nc and phase transformed Si) can be distinguished on the basis of their wavelengths. Future research to determine the exact nature of the indentation-caused luminescence is necessary, particularly, its wavelength needs to be measured. Research should also examine whether the quenching defects that are introduced by indentation can be removed by annealing and/or passivation, as this would identify the nature of the defect.

A PL image of an array of indents in a sample of Si-nc are shown in Fig. 4.13. This was taken using the CCD of the spectrometer in imaging mode. The 80 mN indents were placed in the pattern shown in Fig. 3.6.

As shown in Fig. 4.13, there is a luminescent background caused by Si-nc emission, and a region of lower intensity PL. This area has a well-defined rectangular shape, corresponding to the rectangular shape of the indent grid. The width of the rectangular area of low intensity was found to be $\sim 80 \mu\text{m}$, approximating the grid's nominal length of $90 \mu\text{m}$. A survey of the entire sample reveals no other regions of decreased PL intensity.

The PL spectrum of the grid matches that of Si-nc, as shown in Fig. 4.5, indicating QC as the physical origin. Intensity profiles across the area of the grid are shown in Figs. 4.14(a) and 4.14(b) and show that the intensity decrease occurs across a length of $\sim 80 \mu\text{m}$ as expected for the grid's size.

The quenching is incomplete (i.e. the PL intensity in the quenched region is non-zero) because there are residual regions between indents where there is no quenching, and the luminescence remains. There are also bright patches evident which are possibly due to defect luminescence. The non-uniformity of the PL emission from the sample is also apparent.

The grid is nominally $90 \times 95 \mu\text{m}$. Ignoring edge effects, for 190 indents, each indent occupies an area of $45 \mu\text{m}^2$. The Berkovich tip used to make the indents has a contact diameter of $2.12 \pm 0.04 \mu\text{m}$. This was measured by fitting the Hertzian equations of Eq. 2.1 and 2.2 from the elastic model of indentation to the elastic loading region of the load-displacement curve of an 80 mN indent. (Note that different maximum loads result in different contact areas, so the contact area for this load differs from that of other loads.) The area of the indent is thus $\sim 3.5 \mu\text{m}^2$. Assuming that the area occupied by the indent is completely quenched in luminescence (as shown in the CL images), this implies that the PL intensity should be reduced by a factor of $\sim 7\%$. The intensity profiles show a 13% reduction in intensity, which roughly agrees with the 7% fractional coverage of the indents. The profile also shows that the width of the quenched region is approximately $80 \mu\text{m}$, again confirming the previous findings.

These results show that PL quenching occurs in the indented areas of Si-nc. The wavelength of the quenched region corresponds to that associated with quantum-confined excitons in the nanocrystals. This supports the theory that the quenching is caused by the introduction of non-radiative defects into the nanocrystals that have been subjected to indentation.

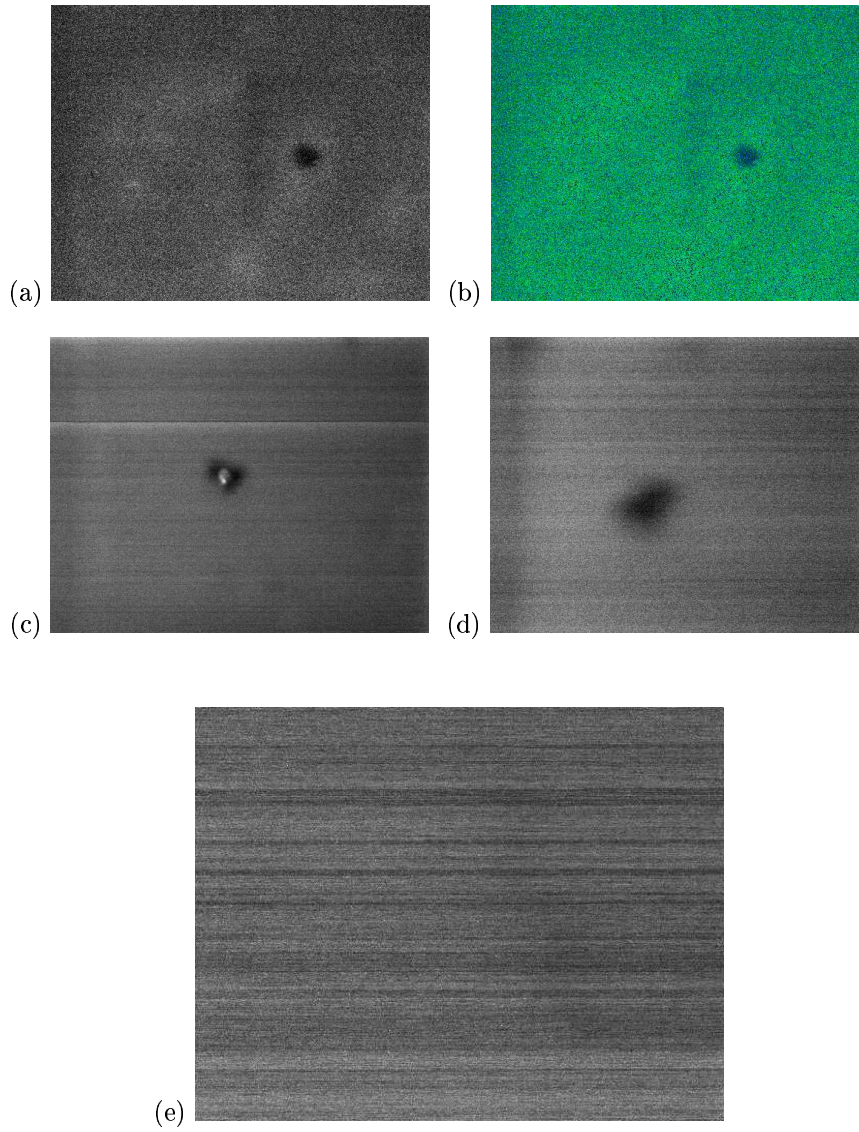


Figure 4.10: Cathodoluminescence images of 200 mN Berkovich indent in 6×10^{16} ions/cm² implant dose Si-nc. The image size is $88 \times 71 \mu\text{m}$. (a) Room-temperature (pan-chromatic) and (b) the corresponding Red-Green-Blue image. (c) Indent area at 80 K (pan-chromatic image) (d) Region of (c) 10 minutes later (e) 510 nm CL image of (c).

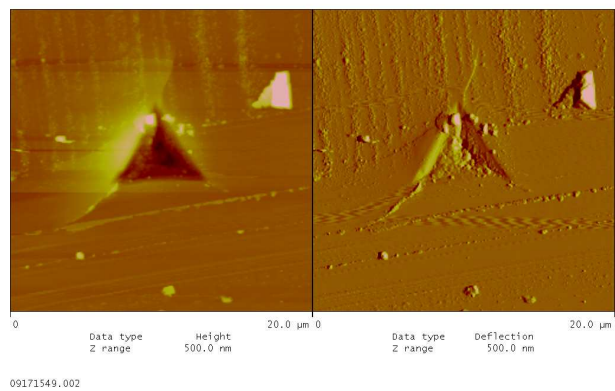


Figure 4.11: AFM image of 200 mN with Berkovich indent in Si-nc.



Figure 4.12: Bright-field TEM images of indent in 100 nm layer of SiO_2 containing Si-nc with maximum load of 100 mN. The oxide layer remains intact.

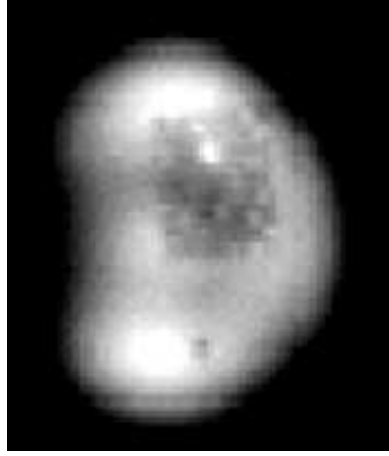


Figure 4.13: CCD image of the PL from an Si-nc sample containing a grid of indents. The image is $240\text{ }\mu\text{m}$ wide. The PL is quenched in the rectangular region of the indents and undisturbed elsewhere.

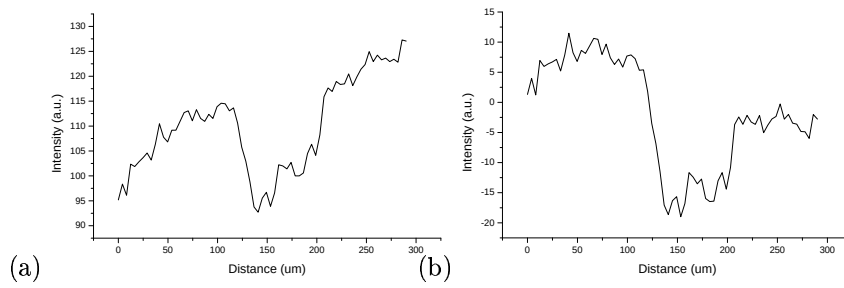


Figure 4.14: (a) PL intensity profile across the grid and (b) with background subtraction

4.2.4 High Pressure Phases in Underlying Silicon Substrate

Figures 4.15(a) and 4.15(b) show cross-sectional bright-field TEM images of indents in a Si-nc-containing oxide layer with maximum loads of 50 and 100 mN respectively. The underlying substrate is c-Si.

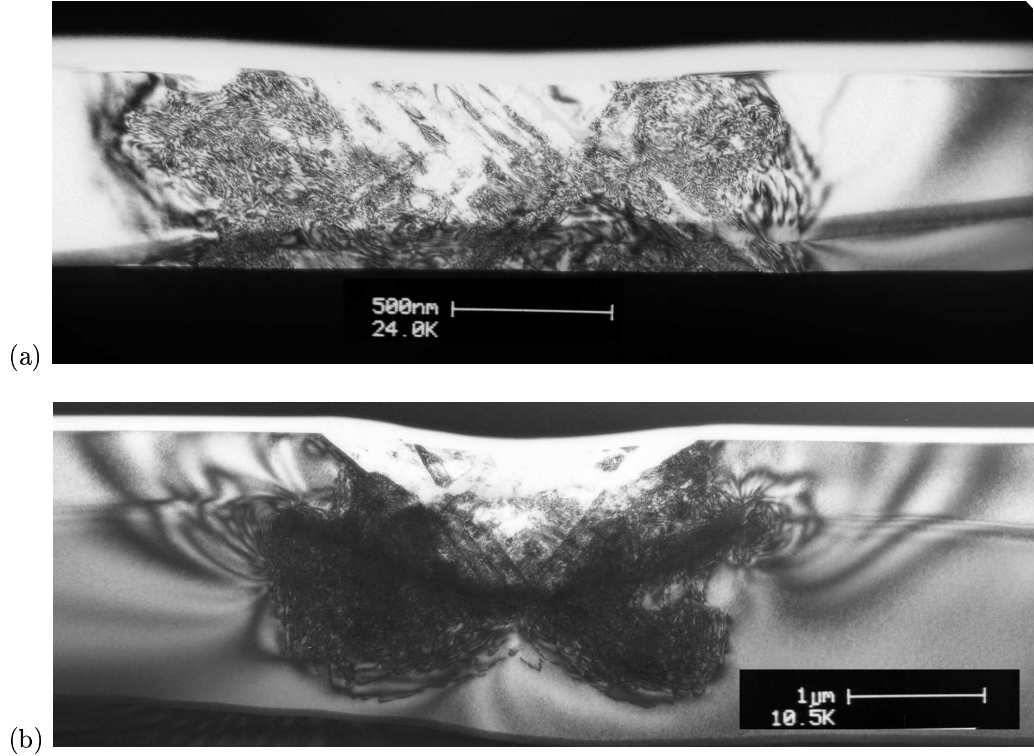


Figure 4.15: Bright-field TEM images of indents in 100 nm layer of SiO_2 containing Si-nc with maximum load of (a) 50 mN and (b) 100 mN. The substrate is c-Si.

In the 50 mN indent [Fig. 4.15(a)], selected area diffraction patterns found no phase transformation in the underlying Si. In contrast, at 100 mN [Fig. 4.15(b)], extensive regions of phase transformation in underlying Si were observed.

Higher magnification studies of these samples failed to clearly image individual nanocrystals due to either FIB-related ion-beam damage during sample preparation or the thickness of the sample along the viewing direction. A higher magnification image of the SiO_2 layer adjacent to the indent is shown in Fig. 4.16.

The diameters of the 50 mN and 100 mN spherical indents measured by AFM were $1.82 \mu\text{m}$ and $2.56 \mu\text{m}$ respectively. This roughly agrees with the corresponding diameters as measured in the XTEM images which were $1.38 \mu\text{m}$

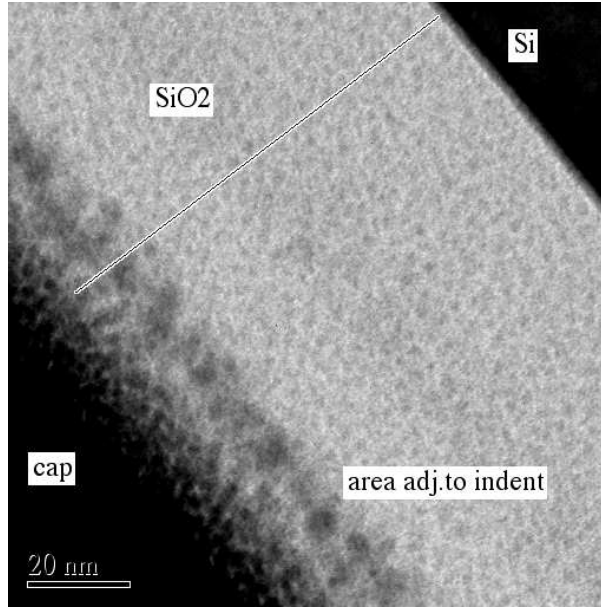


Figure 4.16: An image of the Si-nc oxide layer beneath the indent. Some nanometre-sized patches, possibly nanocrystals, are visible.

and $2.80 \mu\text{m}$ respectively. AFM measurements showed these indents to be 73 nm and 133 nm respectively.

These results suggest that the critical load required to induce phase transformation in Si through a 100 nm oxide layer is between 50 and 100 mN. The phase that the Si-I transforms to is a combination of Si-III and Si-XII (r8/bc8) as has been previously observed [27]. This is also consistent with results from Raman spectroscopy of these samples.

The Berkovich and spherical indents placed in the samples of Si-nc at loads of 25, 50, 100 and 200 mN were analysed with Raman spectroscopy. The results are shown in Figs. 4.17(a) and 4.17(b).

The spectra shown in Figs. 4.17(a) and 4.17(b) display multiple narrow bands at 165, 350, 382, 395 and 430 cm^{-1} that suggest the presence of the Si-III and Si-XII phases within the residual imprint of the higher load indents. [70]

The Raman spectra for the spherical indent show that phase transformation to Si-III/XII phases at loads greater 100 mN and no such transformation for loads less than 50 mN, confirming observations in the XTEM images. For the Berkovich tip, a phase transformation is induced at lower loads (between 25 and 50 mN) than for the spherical tip (between 50 and 100 mN). This is consistent with the Berkovich tip being sharper and able to induce plasticity at lower loads.

The shoulder on the 520 cm^{-1} peak is caused by Si-I. In the 100 mN spherical indent, the intensity ratio of the 430 cm^{-1} peak to the 520 cm^{-1} peak, I_{430}/I_{520} , is higher than in other spectra, showing that it contains mostly the Si-III phase. [70] The intensity of the Si-I peak (520 cm^{-1}) decreases as the load is increased for both spherical and Berkovich tips. This indicates that as higher loads are

applied, less of the untransformed Si-I remains and more of it transforms into the metastable phases.

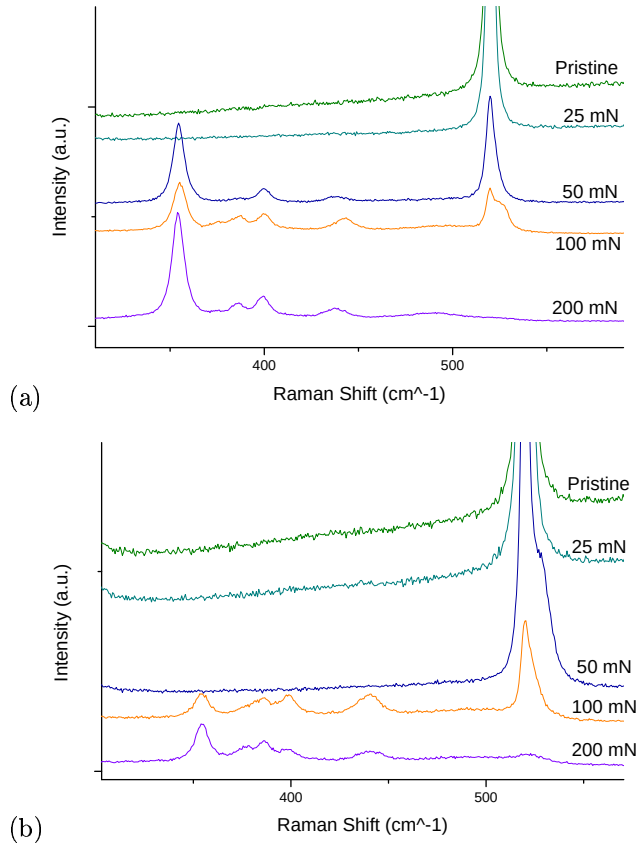


Figure 4.17: Raman spectra of indents under various maximum loads (a) Berkovich indents. The high-pressure phases are seen in the loads at and above 50 mN (b) Spherical indents. The high-pressure phases are seen in the loads at and above 100 mN.

4.2.5 ELASTICA Simulation of Oxide Layer

The load-displacement curves simulated to correlate with experimental data are shown in Fig. 4.18(a) and 4.18(b). In the simulations, X and Y directions are in the plane of the surface and the Z direction is normal to it.

Hydrostatic stress patterns for the 50 mN and 100 mN indent are shown in Fig. 4.19(a) to 4.19(f) and Fig. 4.20(a) to 4.20(f) respectively. The perspective from the YZ plane is identical to that of the XZ plane with Y axis interchanged with the X axis, owing to the spherical symmetry of the tip.

The simulations predict that there is enough stress (over 11.3 GPa) in both the 50 and the 100 mN indents to cause a phase transformation. However, phase transformation was not observed in the corresponding XTEM images of the 50 mN indent, nor in the load-displacement curves. The discrepancy between experiment and simulation is most likely due to plastic deformation occurring in the experimental data, not included in the simulation. The excess stress predicted by the simulation may be relieved by plastic deformation of the oxide layer in the experimental data.

There is a discontinuous jump in the stress curve as the tip penetrates the oxide layer into the silicon. The discontinuous increase in stress is 5.5 and 6.7 GPa in the 50 and 100 mN indents respectively. The sudden increase in stress is caused by the change in material properties of the tip's environment.

These results illustrate the effect that a layer of Si-nc containing oxide has on the indentation-caused phase transformation that occurs in the underlying Si substrate. They reveal that the critical load required to induce a phase transformation in this system is between 50 and 100 mN. Loads greater than 100 mN induce phase transformation and this is evident in the CL study. Further research could aim at accurately determining what the critical load is, and what different effect varying the thickness of the oxide has on the final phase transformation.

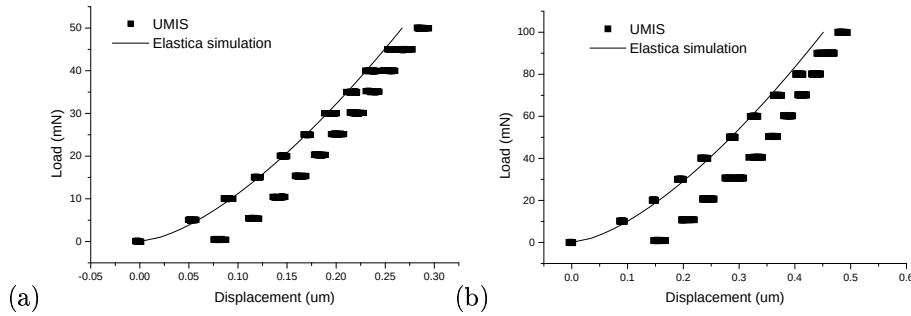


Figure 4.18: Comparison of UMIS and ELASTICA load-displacement curves for maximum load of (a) 50 mN and (b) 100 mN.

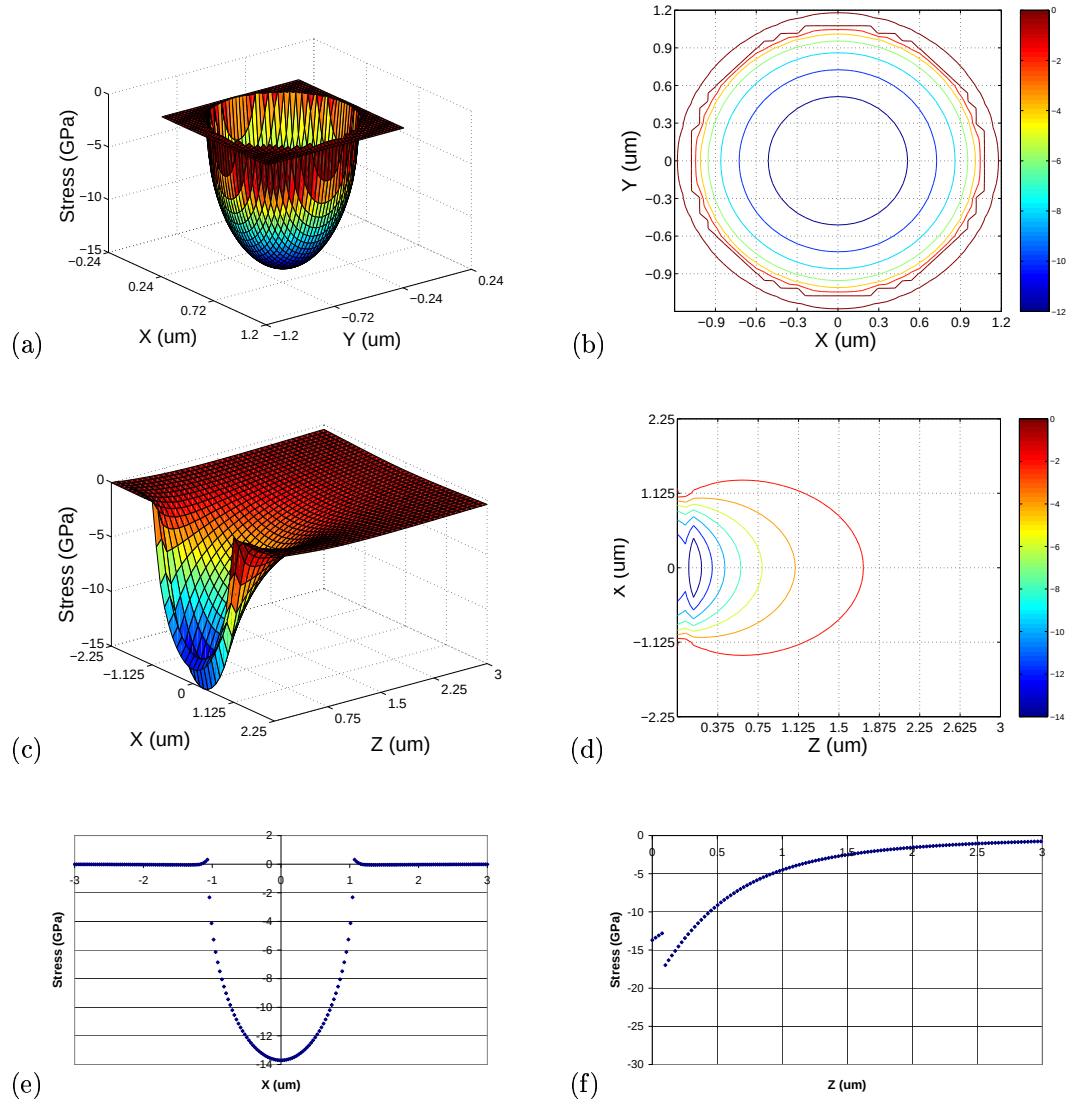


Figure 4.19: ELASTICA simulation of hydrostatic stress for 50 mN indent in 100 nm SiO_2 on Si (a) Hydrostatic stress in XY plane and (b) corresponding contour map (c) Hydrostatic stress in XZ plane and (d) corresponding contour map (results for YZ plane are the same but with the Y-axis interchanged with X-axis) (e) Hydrostatic stress in X and Y directions and (f) in Z direction.

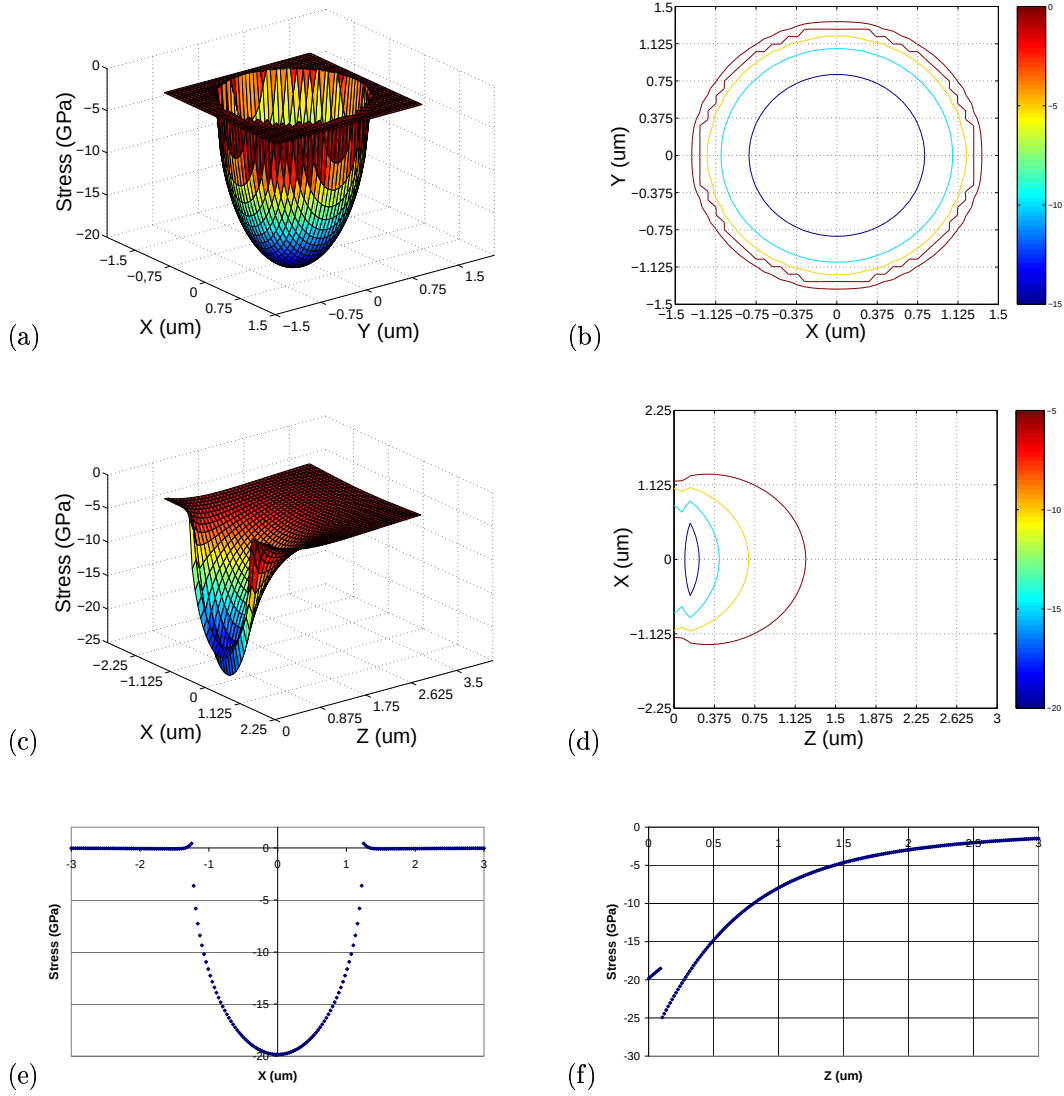


Figure 4.20: ELASTICA simulation of hydrostatic stress for 100 mN indent in 100 nm SiO_2 on Si (a) Hydrostatic stress in XY plane and (b) corresponding contour map (c) Hydrostatic stress in XZ plane and (d) corresponding contour map (results for YZ plane are the same but with the Y-axis interchanged with X-axis) (e) Hydrostatic stress in X and Y directions and (f) in Z direction.

4.2.6 Summary

Both CL and PL images of large-load indents in Si-nc indicate that quenching of the luminescence occurs in the localised area of the indent. The CL image taken at 510 nm that indicates the presence of SiO₂ shows that SiO₂ remains in the area of the indent. This is also supported by the XTEM images, which show the entire layer deforming under the indent. Thus the quenching is not caused by a the indenter punching a hole through the oxide layer to the substrate, rather, it introduces non-radiative defects to the nanocrystals in the layer which quench the luminescence.

The area of the 200 mN indent was measured to be 14 μm^2 which correlates to the 14 μm^2 quenched area observed in the CL images. The amount of quenching observed is consistent with what would be expected based on the assumption that all the material directly beneath the indent is quenched. The PL images show a 13% drop in intensity over the grid, which is roughly consistent with the 7% fractional area of indented material in the grid. The PL spectra show that the quenched luminescence is that of the QC-related nanocrystal PL. The darkened region in the PL image also has the correct dimensions for the indented grid.

For indents with a maximum load of 100 mN or more with spherical tip, a phase transformation occurs in the underlying Si. This is visible in the XTEM images. Cathodoluminescence imaging also shows a luminescent region at the centre of the indent that has quenched the rest of the luminescence, corresponding to the luminescence from the phase transformed material. Raman microspectroscopy shows that this material has transformed to the Si-III/Si-XII phase. For indents with a maximum load of 50 mN or less with a spherical tip, no phase transformation is detected. With the Berkovich tip, the Raman spectra suggest that the critical load for phase transformation is between 25 and 50 mN. Some of the load-displacement curves from the UMIS, however, show a pop-out on unloading from 25 mN, suggesting that there may be a phase transformation to Si-III/XII at this load. The variation between indents of the same load make it difficult to make these judgements with certainty.

The load-displacement curves from spherical tip do show a phase transformation (in the form of a pop-out on the unloading curve) for the 100 mN maximum load and no such event for the 50 mN load, confirming results from both XTEM and Raman microspectroscopy.

The ELASTICA simulations are consistent with the experimental results if one recognises that it is a purely elastic model. While it does predict that the 100 mN maximum load indent precipitates the required level of hydrostatic stress in the Si for phase transformation to the high-pressure metastable phases as observed, it predicts that this level of stress is also reached for the 50 mN maximum load indents. No phase transformation is observed for these indents (in either the XTEM images, Raman spectra or load-displacement curves) and this is because some of the stress that is modelled by ELASTICA is actually relieved by plastic deformation.

4.3 Thermally-Induced Defects

Samples of Si-nc in SiO₂ were fabricated in order to determine the effects of thermally-induced defects on the PL emission. These samples characterised to ensure that the observed PL was caused by quantum-confined excitons in Si-nc. The optical absorption cross-section, nanocrystal size distribution and PL decay lifetimes were measured.

4.3.1 Absorption Cross-section

The results of the absorption cross-section measurement are shown in Fig. 4.21(b). σ varies from approximately $2 - 3.5 \times 10^{-16} \text{ cm}^2$. This in the same range as previous experimental results. [65], [71] However, these measurements show a slight increase of the cross-section with detection energy. This is ascribed to the error in the experimental procedure, particularly with fluctuations in the incident power. The absorption cross-section does not change with passivation or annealing rates.

The small variance of the absorption cross-section over this wavelength range is important, because it suggests that a consistent PL intensities are achievable over this wavelength range without effects caused by varying absorption cross-section to occur. The wavelength range between 650 nm and 900 nm is the one most relevant to Si-nc PL emission.

4.3.2 Nanocrystal Size Distribution

The PL spectra data were fitted to Eq. A.6, A.7 and A.8 to the PL spectra and the results are shown in Fig. 4.22(a).

The bandgap energy dependence of the decay lifetime measured for these samples is shown in Fig. 4.21(a).

For the sample which was heated and cooled at 3 °C/min for a four hour anneal, the model was fit to the experimental data with the following parameters: $N = 133$, $L_0 = 4.75 \text{ nm}$ and $\sigma = 0.135 \text{ nm}$. The mean crystallite size is 4.79 nm. This is consistent with values found in the literature as well as the dimensions required for quantum confinement.

These results confirm that the source of the observed PL is quantum confinement, and not caused by other sources (eg. defect luminescence).

4.3.3 Size Dependence of Transition Rate

Figure 4.22(b) shows the size dependence of the PL transition rate. From this curve it can be seen that transition rate decreases with a power law dependency on crystal size. The values for β differ from the theoretical values for β of 5 or 6 [66], but agree with more recent work that suggests a value of 3.0. [47] This reflects the increased sophistication in the models that explain Si-nc PL that have developed in the past six years. The results indicate that the oscillator strength is more weakly dependent on crystallite size than assumed in the earlier research. This reflects the high level of disorder in the system. This agrees with previous observations that in the region of crystal diameters of 20 - 40 Å, the size dependence of the PL peak is extremely weak. [66] This is also

supported by other work [72] that suggests that for small radii, the PL from Si-nc is governed by silicon-oxygen double bonds, contrary to the traditional quantum confinement model. The error bars arise primarily due to fluctuations in laser power.

The weak dependence of the transition probability on the crystal diameter is important in determining the viability of Si-nc as a successful component in microphotonics, as the ability to tune the emission wavelength by varying the crystal diameter is one of its major advantages.

4.3.4 Variation of Heating and Cooling Rates in Annealing

The PL spectra of the 1-hour annealed samples resulting from varying the heating and cooling rates are shown in Fig. 4.23(a) indicate that the heating rates have little effect on the PL spectra. A slow cooling rate gives rise to intensity that is almost twice as high compared to samples that have been cooled quickly. These results reflect the state of the system in a non-equilibrium state, as after only one hour of annealing, the maximum yield of nanocrystals has not yet been achieved. It is not until after four hours of annealing that the system equilibrates.

Figure 4.23(b) shows the PL spectra of the 4-hour annealed samples with various heating and cooling rates. As in the 1-hour annealed samples, the resulting PL spectra show that the heating rate does not significantly alter the PL peak intensity or wavelength, while different cooling rates were found to yield significantly different PL intensities. The PL intensity increased by a factor of approximately 1.7.

These results indicate that the use of fast cooling rates increases the number of non-radiative defects caused by thermal strain, resulting in decreased PL intensity.

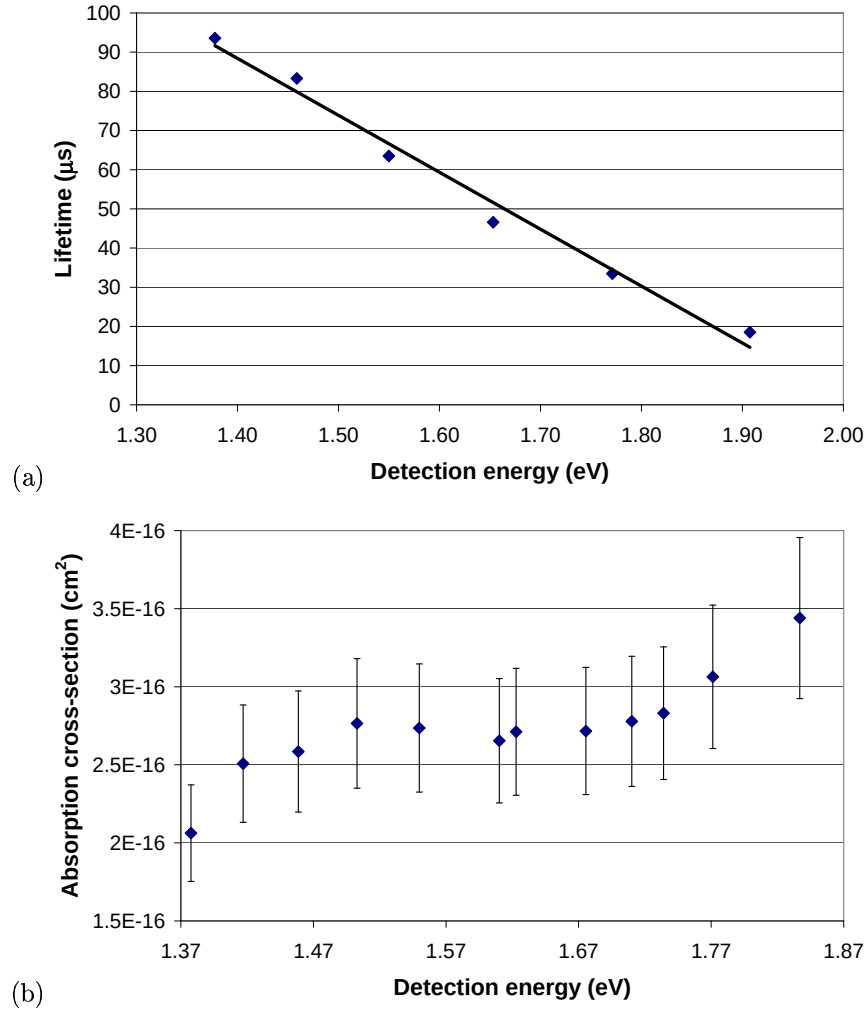


Figure 4.21: (a) Bandgap energy dependence of Si-nc luminescence decay lifetime (b) Detection energy dependence of absorption cross-section.

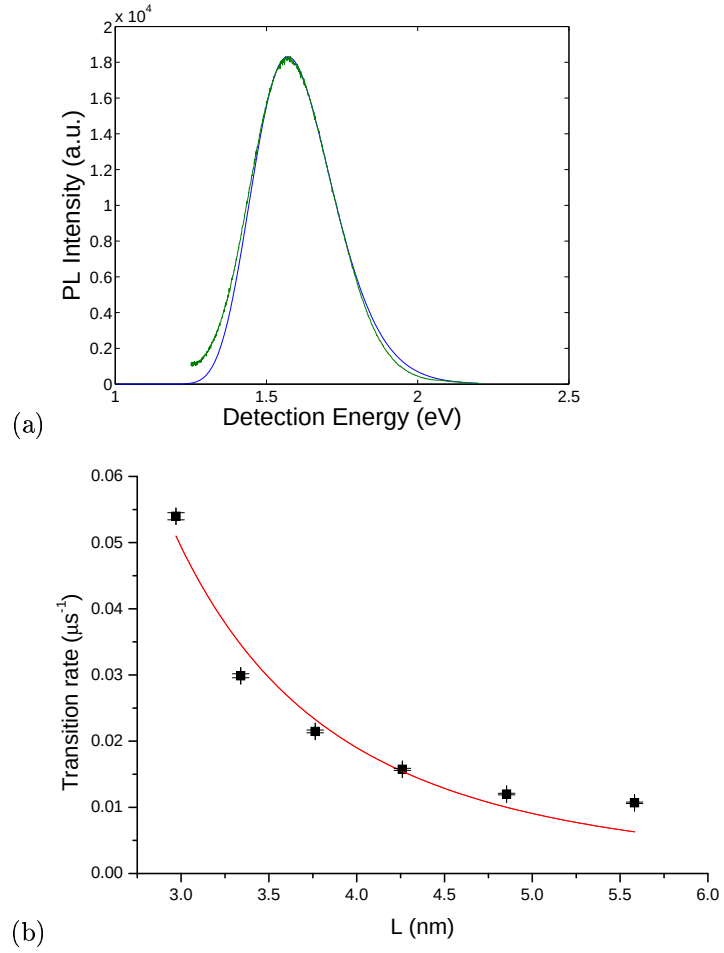


Figure 4.22: (a) The PL spectrum of one of the nanocrystal samples fitted to a theoretical model [47] to obtain the size distribution. The green and blue curves are the experimental data and theoretical fit respectively. (b) The variation of PL transition rate with nanocrystal size.

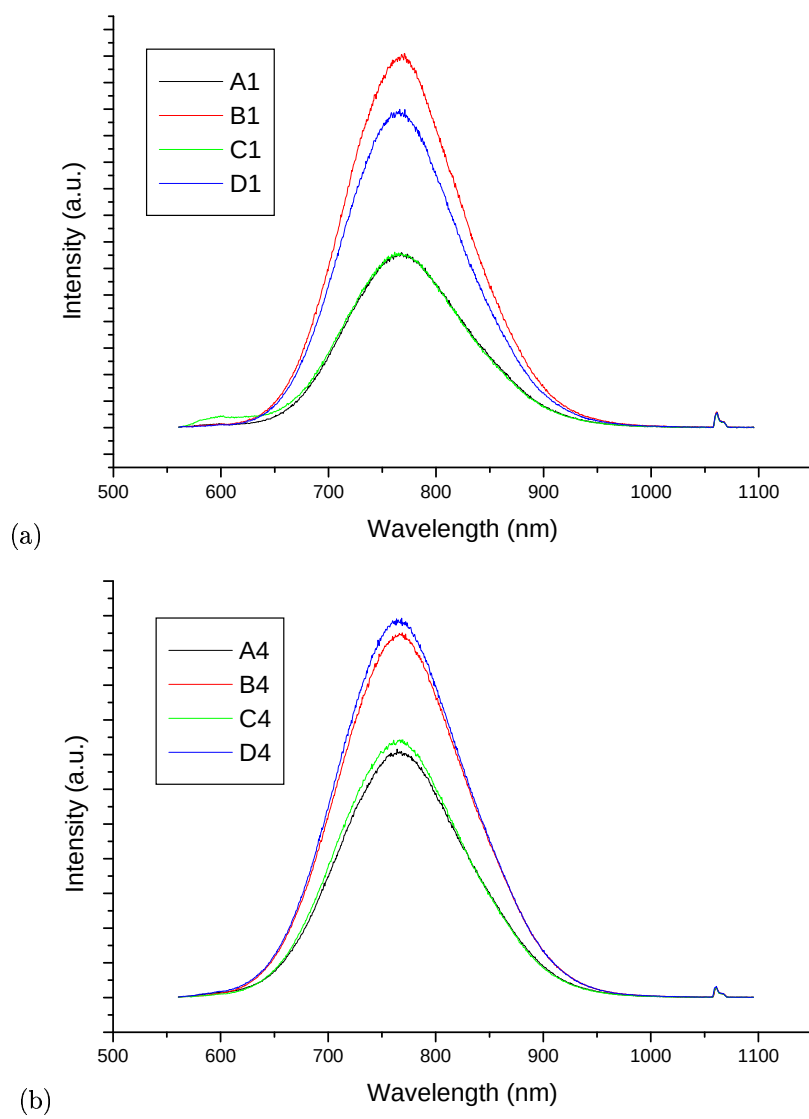


Figure 4.23: PL spectra for nanocrystals annealed at 1100 °C under various heating and cooling rates for (a) one hour and (b) four hours.

4.3.5 Effect of Passivation on Photoluminescence

Figure 4.24(a) shows the PL spectra of the slowly cooled and quickly cooled samples before and after passivation. Upon passivation, both samples exhibit an increase in PL intensity. The factors by which the peak intensity values increase for the quickly cooled and slowly cooled samples are 2.3 and 1.8 respectively, thus passivation has a greater effect on the quickly cooled sample. Significantly, the peak intensity values are different, indicating that even after passivation, the increased number of defects in samples cooled quickly remains.

The ratio the intensity spectra before and after passivation is shown in Fig. 4.24(b). Both show that passivation preferentially increases PL intensity at 850 nm. The greater effect of passivation on the quickly cooled sample is evident (A4). The variations in the curve for the slowly cooled sample (D4) are due to interference effects formed in the air gap between the sample and the sample holder. Due to poor contact between the sample and its holder, an air gap forms between the transparent sample and the backing. This forms a cavity in which incident light can become trapped, as in a Fabry-Perot cavity.

The results of these experiments have shown that in annealing Si-nc, a cooling rate of 3 °C/min is effective in increasing the PL intensity compared to samples that are brought to room temperature immediately. The peak intensity increases by a factor of 2 and 1.7 for samples annealed for one and four hours respectively. The difference in intensities is not completely removed by passivation. Passivation for one hour under forming gas increases the peak PL intensity for the quickly cooled and slowly cooled samples by factors of 2.3 and 1.8 respectively, with preferential increase in intensity at 850 nm. It has been shown that after passivation in hydrogen for one hour, most of the defects prone to passivation have been removed (i.e. further passivation is expected to have negligible effect.) Because these defects do not seem to respond to H-passivation, they may be a type of defect different from the P_b defect, although one can only speculate as to their exact nature at this stage.

These results are significant in terms of Si-nc manufacture, where the PL intensity is maximised while using the least time to anneal the crystals. For 4 hour annealing times, a sample that is cooled from 1100 °C to 850 °C at 3 °C/min spends an additional 83 minutes in the furnace as compared to a sample that is taken out to RT immediately, but the luminescence is increased by a factor of 1.2. The extra 83 minutes also increases the time spent in the furnace by a factor of 1.2. In samples where thermal stress is to be minimised, slow cooling rates are an important consideration.

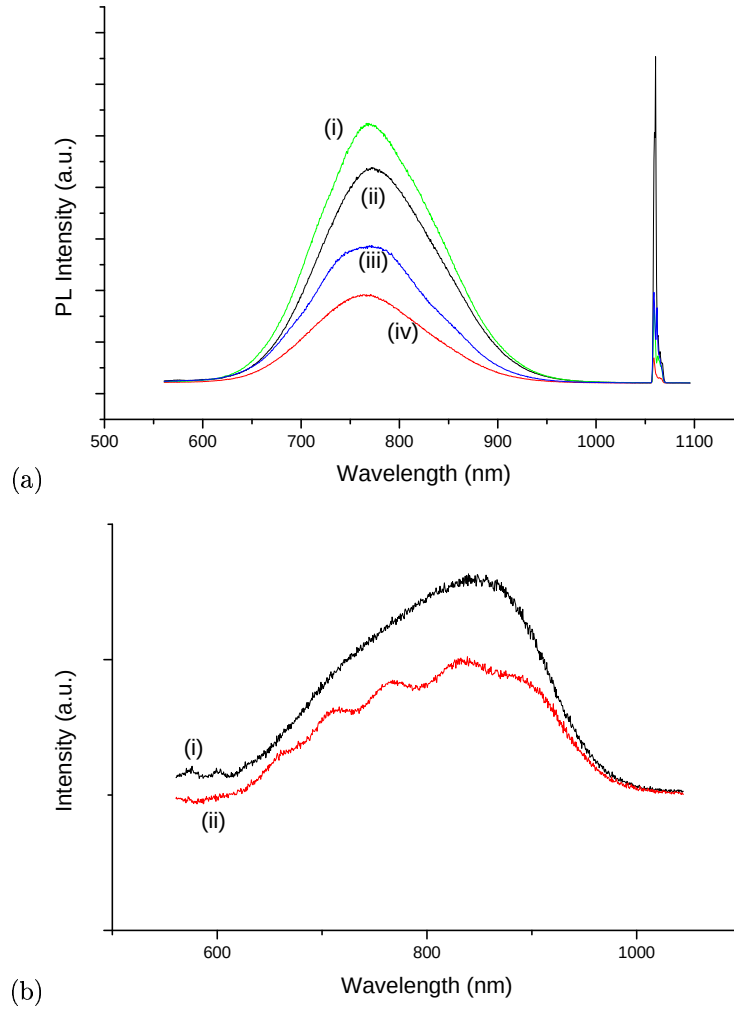


Figure 4.24: (a) PL spectra of quickly cooled and slowly cooled samples after passivation for 1 hour in forming gas for 1 hour at 500 °C, showing the PL spectra of the (i) slowly cooled sample after passivation (ii) quickly cooled sample after passivation (iii) slowly cooled sample before passivation and (iv) the quickly cooled sample before passivation. (b) The ratio of PL spectra after passivation to the corresponding spectra before passivation for (i) the quickly cooled sample and (ii) the slowly cooled sample.

	Decay lifetime (μs)	Error (μs)	Transition rate (μs^{-1})
A1	36.9	0.9	0.0271
B1	37.0	0.8	0.0270
C1	57.8	1.1	0.0173
D1	47.0	1.7	0.0213
A4	60.7	0.6	0.0165
B4	61.1	0.5	0.0164
C4	68.7	0.5	0.0145
D4	68.9	0.5	0.0145

Table 4.1: PL intensity decay lifetimes for the Si-nc samples.

4.3.6 Photoluminescence Lifetime Measurements

An exponent of $\beta = 0.8$ was used to fit Eq. A.9 to the time resolved PL spectra. The measured PL decay lifetimes are listed in Table 4.1. Samples with higher intensities displayed longer lifetimes. This is consistent with the proportionality in Eq. 3.2: if N, ϕ, σ are constant, then higher intensity results in a longer lifetime. The measured PL lifetimes are consistent with previous results that show that the lifetimes vary from about 30 - 100 μs at room temperature. [73]

4.3.7 Summary

This study has synthesised and characterised samples of Si-nc. The absorption cross-section was indirectly measured to be $2 - 3.5 \times 10^{-16} \text{ cm}^2$, and the mean crystallite size was found to be 4.79 nm, both consistent with literature values. The transition rate for the PL was found to be slightly less sensitive to crystal size than expected by some researchers [66] but correlate well with more recent work [47], [72]. The PL decay lifetimes of the samples reflected the trend in their intensities, with higher intensity samples exhibiting longer decay lifetimes.

Furthermore, these experiments have shown that while the heating rate used in the annealing step for nanocrystal fabrication does not strongly influence the PL intensity and wavelength of resulting nanocrystals, the cooling rate does. Using a cooling rate of 3 $^{\circ}\text{C}/\text{min}$ to cool the samples annealed at 1100 $^{\circ}\text{C}$ to 850 $^{\circ}\text{C}$ resulted in higher PL intensity for samples annealed for 1 hour and 4 hours. Furthermore, the discrepancy in PL intensity between samples that are cooled quickly and slowly is not overcome by passivation, which means that this is an effect that has practical implications in Si-nc fabrication.

4.4 Silicon Thin Films

Preliminary studies on samples of Si thin-films on SiO_2 were conducted to compare the thin film system to those of bulk Si and Si-nc. Nanoindentation testing was carried out on thin films of various thicknesses and under various conditions. Cross-sectional TEM images of an indent in thin-film Si were collected,

and a method for producing plan-view TEM samples was developed. These were compared to computer simulations of the thin film system.

4.4.1 Load-Displacement Curves

Prior to indentation, the thin-film Si samples were analysed using PL spectroscopy. No PL peaks observed in pristine 195 or 4 nm thin-film Si samples. This is consistent with previous work on Si thin film PL that indicate that low temperatures (10 K) are required to observe PL from Si thin films. [67]

The 195 nm Si thin film was subjected to nanoindentation hardness testing on the UMIS. The small thickness of film prohibited simple analysis of the plastic deformation mechanism on the UMIS, due to its low load resolution. Using a load as low as 10 mN, indentation using the UMIS failed to induce a plastic response despite penetrating to well over half the thickness of the sample. Thus the Ubi1 Hysitron indenter was required to study these thin-films at lower loads.

The Si thin-films of thickness 195, 82, 56 and 4 nm were subjected to nanoindentation testing at a maximum load of 300 μN . Figures 4.25(b) to 4.25(e) show the resulting load-displacement curves for the four thin films, and the corresponding curve for bulk Si is shown in Fig. 4.25(a). At a load of 300 μN , the tip reaches a depth of 30 - 50 nm. The 82 and 56 nm samples behave similarly, and this is attributed to their small thickness difference. The 4 nm thick sample can be treated as purely SiO_2 , since the Si layer is too thin for its features to become apparent in this test.

Thin film thickness (nm)	Plastic depth (nm)
Bulk Si	8.2
195	6.9
82	6.5
56	6.2
4	12.2

Table 4.2: Indentation depths reached at loads of 300 μN for the Si thin film samples.

In the load-displacement curves for the 195, 82 and 56 nm Si layers, there is a gradual slope change in the unloading curve (or “elbow”) at a load of $\sim 60 \mu\text{N}$ and $\sim 18 \text{ nm}$. In silicon, this has been shown to correspond to amorphous silicon in the final impression. [74] Such behaviour is usually seen on indents with low maximum loads or at fast unloading, causing amorphisation of the silicon upon pressure release. The gradual change in slope of the unloading curve is caused by the material’s expansion during slow transformation from metallic to the amorphous semiconducting phase. This expansion causes the tip to lift up more quickly. [19] High levels of shear stress is also known to cause amorphisation of silicon [26] as well as play an important role in deforming the transformation zone. [27]

The load-displacement curves from the experiment where a maximum load of 300 μN was unloaded at rates of 300, 100, 150 and 75 $\mu\text{N/s}$ in thin film Si are shown in Fig. 4.26(a). They show an elbow on the unloading curve at 20 nm, indicating amorphisation, but no sign of a pop-out that would indicate a phase

transition to the crystalline Si-III/XII phases. Similar results were obtained for bulk Si, as shown in Fig. 4.26(b). There was no phase transformation to the crystalline phase detected at these unloading rates. This is consistent with the nucleation-limited nature of transformation to the crystalline Si-III/XII, which indicate that smaller volumes of material, as seen in thin films, will be less likely to nucleate phase transformation.

These experiments have shown that silicon thin films as thin as 56 nm can be studied with nanoindentation. The behaviour of these films under indentation is as expected, with the thicker samples displaying a greater reduced modulus and more resistance to deformation than the thinner samples. Samples which differ by approximately 30 nm become hard to distinguish, and this offers a limit to the resolution of the experiment. Indentation of the 4 nm sample is effectively indentation of the substrate. The results also show that for the unloading rates of 300, 100, 150 and 75 $\mu\text{N/s}$, and a maximum load of 300 μN , thin-film Si and bulk Si behave similarly by showing no transformation to Si-III/XII, rather amorphisation of the material occurs.

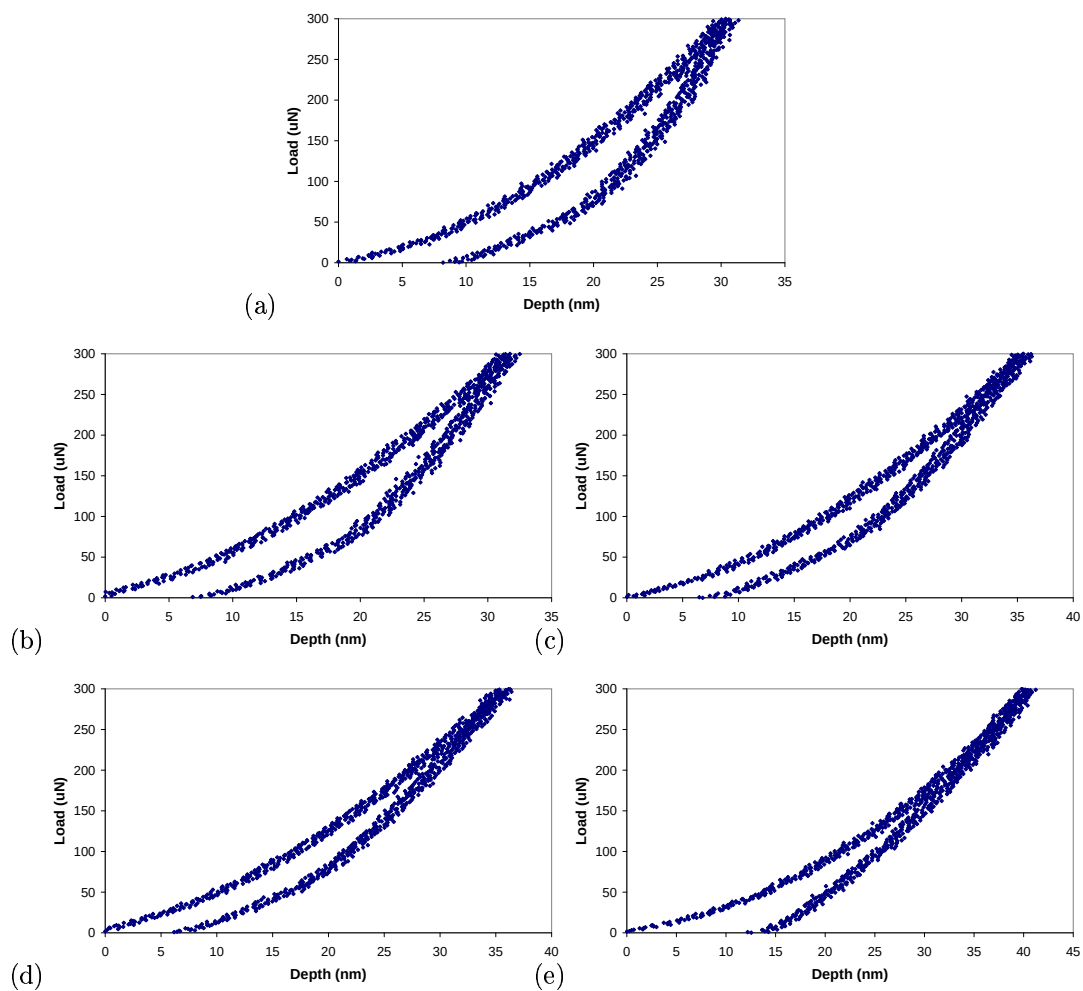


Figure 4.25: Load vs displacement curves for (a) bulk Si (b) 195 nm Si (c) 82 nm Si (d) 56 nm Si and (e) 4 nm Si.

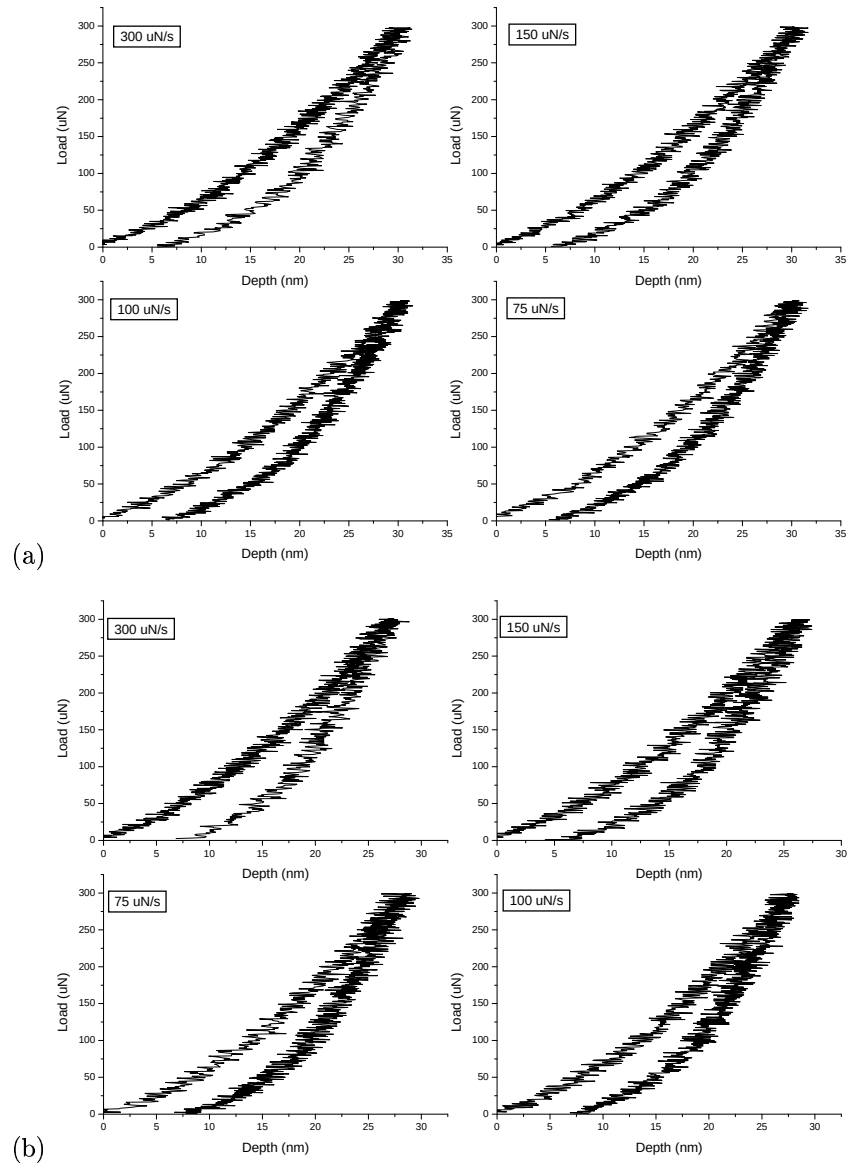


Figure 4.26: Load displacement curves for indents in (a) thin film Si and (b) bulk Si using various unloading rates. No pop-out events are evident, indicating that no Si-II/XII is expected to be found in the residual impression.

4.4.2 Cross-section Transmission Electron Microscopy

The XTEM image of an 80 mN indent in 200 nm Si on SiO_2 substrate is shown in Fig. 4.27. 30 nm of the 200 nm thin layer of Si has been amorphised due to ion beam exposure during FIB milling. Selected area diffraction patterns taken of the pristine-Si film and of the Si layer at the centre of the indent revealed no extra spots indicative of the high-pressure phases. Thus no phase transformation was found to have occurred.

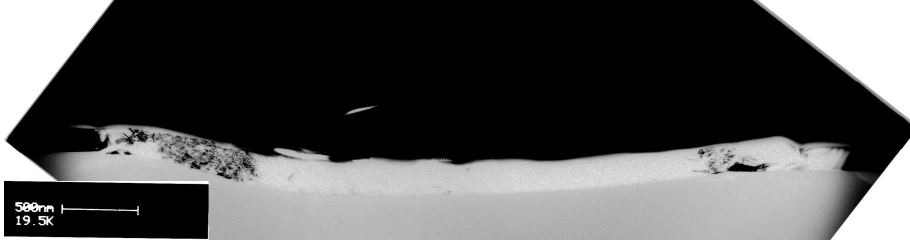


Figure 4.27: XTEM image of indent in thin film Si.

The load-displacement curve corresponding to this indent is shown in Fig. 4.28. It also shows no sign of discontinuities indicative of phase transformation.

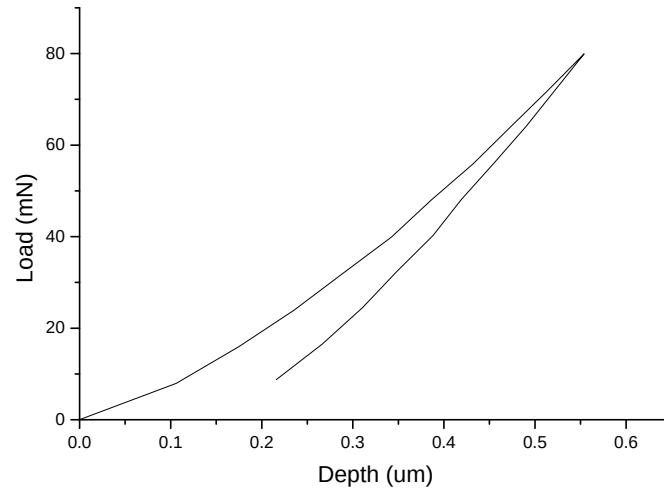


Figure 4.28: Load-displacement curve for spherical indent in 200 nm Si thin film with maximum load of 80 mN showing no sign of phase transformation.

These results are consistent with the nucleation-limited nature of phase transformation induced by indentation, where the reduced volume of the thin film decreases the number of possible nucleation sites and thus restricting the possibility of phase transformation. However, further work is clearly needed to understand this process.

4.4.3 ELASTICA Simulation of Silicon Thin Film

Load displacement curves were obtained by using ELASTICA to simulate indentation of the Si thin film on SiO₂. These were correlated with those experimentally observed by the Ubi1 Hysitron indenter to ensure that an accurate simulation was used, and the correlation is shown in Fig. 4.29. The best fit to the observed load-displacement curve used a 100 nm tip radius.

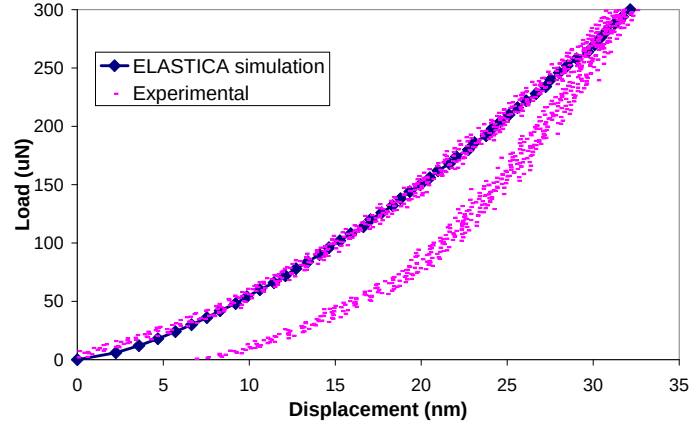


Figure 4.29: Load displacement curves from indentation experiment and from ELASTICA simulation.

The resulting hydrostatic stress fields for indentation by a spherical tip onto a 200 nm layer of Si on a 3 μm layer of SiO₂ over a Si substrate were calculated.

The hydrostatic stress exceeded the threshold value for phase transformation from diamond cubic Si-I to the metallic β -Sn phase, Si-II, of 11.3 - 12.5 GPa [16] (with a volume change of 30%), reaching 44 GPa at the centre of the indent. Hydrostatic stress of approximately 12 GPa occurs at depth of 43 nm. The results are symmetric along the z-axis and results for the x and y axes are equivalent, as is expected for a spherical tip.

These results suggest that during nanoindentation the stress threshold required for a phase transformation has been exceeded in the 200 nm Si thin film. Furthermore, they suggest that the bulk of the stress remains relatively localised, occupying only a 100 nm sized area of the XY-plane directly beneath the indent. It must be noted, however, that the actual stress levels in the experimental indent would be slightly lower, due to stress relief caused by plastic deformation not modelled in this simulation. Nevertheless, it is anticipated that a slow enough unloading rate for the indent would result in phase transformations to the metastable phases.

4.4.4 Summary

The Si thin films show no PL, consistent with previous results. [67] Nanoindentation tests have shown that no phase transformation to Si-III/XII occurs at the unloading rates used in these tests. The XTEM images of indents obtained in thin film Si, also show no evidence of any phase transformation to the high-pressure metastable phases. This may be consistent with the nucleation-limited nature of the process, which indicates that it is more difficult to induce phase transformation in small volumes of material. The thinner films also show no signs of the Si-III/XII phases. The ELASTICA simulation results indicate that the level of hydrostatic stress required to nucleate a phase transformation is reached in experimentally achievable systems, but this stress could be relieved by plastic deformation not accounted for in the simulation.

CHAPTER 5

CONCLUSIONS

This study examined the optical and structural effects of mechanical and thermal deformation on silicon nanostructures. Several key findings were observed.

The regions of high pressure phases Si-III and Si-XII in bulk Si were not seen to display any room-temperature PL. No QC-effects were observed in the phase-transformed material in bulk c-Si.

It has been demonstrated, for the first time, that nanoindentation of Si-nc samples results in localised luminescence quenching. It is thought that by mechanically deforming the Si-nc, non-radiative defects are introduced. This quenching has been observed in PL and CL images with the area of quenching found to correlate with the area of the indent (as measured by AFM). No rupture, cracking or delamination of the oxide layer was found after nanoindentation. Thus it is suggested that the individual nanocrystals are “turned off”. The phase transformations in the underlying Si substrate have been characterised by Raman microspectroscopy and nanoindentation. Both characterisation techniques indicate that the critical load required to nucleate the Si-III/XII phases is between 25 and 50 mN using a Berkovich tip, and between 50 and 100 mN for a spherical tip.

The partial PL quenching of the grid shows that while individual indents at the scale of several microns can completely quench the luminescence in their area (as shown in CL results), larger scale patterns comprised of these indents of the order of 100 μm are harder to distinguish, due to the intervening regions of luminescent material between the indents which reduces the overall quenching effect seen at the greater scale. Thus that any application of the indentation-induced quenching of Si-nc would require micron-level sensing technology.

Samples of Si-nc were characterised according various nanocrystal properties, including their PL decay lifetime, absorption cross-section, and size distribution. Using these samples, an improved method of nanocrystal fabrication has been achieved, which furthers progress in developing more effective microphotronics processing. Specifically, ideal cooling rates for the annealing of Si-nc have been determined. It was found that slower cooling rates (3 $^{\circ}\text{C}/\text{min}$) increased the PL intensity of the the resulting nanocrystals, while slower heating rates had no such effect. The commercial importance of these results are realised when one considers that the non-radiative defects created by fast cooling rates remain in the sample after passivation.

Finally, the silicon thin films studied have shown no evidence of room-temperature PL emission at a thickness of 195 or 4 nm. Interestingly, nanoindentation of these films shows no sign of phase transformation to the high-pressure phases. These results may be consistent with the nucleation-limited nature of phase transformation.

5.1 Further Work

During the course of this project, opportunities for future research optical and structural effects of silicon defects have become apparent.

An obvious extension of this work would be the study of PL from indented bulk Si at low temperatures, as quantum-confined PL is known to be stronger in such a regime. A micro-PL setup employing optical microscopy may also be attempted to ensure more accurate positioning of the sample.

In addition, it would also be valuable to investigate the mechanically-induced quenched region after annealing or passivation. The quenching is caused by the introduction of non-radiative defects introduced by indentation, but it remains unclear what kind of defects and what properties they possess. If it happens that the indentation quenching process is reversible, then a possible application of such a process in memory devices could be explored. More ambitious projects might involve synthesising large nanocrystals (~ 20 nm) to observe the shape change that is predicted to occur upon phase transformation using TEM. [12]

Further work in the studying thermally-induced defects in Si-nc should incorporate finite element analysis in order to model the stress evolution in cooling of Si-nc in SiO_2 . This would shed more light on the annealing process.

Future research in the thin film system may look into indentation tests carried out at low temperature, as this is regime has been shown to favour phase transformation.

APPENDIX A

Modelling the Luminescence from Quantum-confined Excitons in Nanocrystals

The relationship between crystal diameter and PL spectra regarding Si-nc has been modelled [66]. In this model, QC shifts the energy of the bandgap by an amount equal to

$$\Delta E = \frac{c}{d^x} \quad (\text{A.1})$$

where c is a normalisation constant assigned a value of $485.816 \text{ eV}/\text{\AA}^2$. Simple potential wells have $x = 2$. The oscillator strength of a crystallite with diameter d is assumed to vary as

$$f_{osc} \sim d^{-\beta} \quad (\text{A.2})$$

where β has been assigned a value of 5 or 6. This has the effect of giving crystals of smaller diameter a greater contribution to the luminescence spectrum. Assuming a Gaussian crystal size distribution, the general expression for the PL spectrum is

$$P(d) \propto \exp\left(-\frac{(d - d_0)^2}{2\sigma^2}\right) \quad (\text{A.3})$$

where d_0 is the mean crystallite diameter and σ is the mean crystallite size distribution. The number of atoms participating in the radiative process is taken to be proportional to the volume of the crystallite. Thus, the probability of emission from a nanocrystallite of diameter d is

$$P_r(d) = KV(d)f_{osc}(d)P(d) = Kd^m \frac{1}{d^\beta} \exp\left(-\frac{(d - d_0)^2}{2\sigma^2}\right) \quad (\text{A.4})$$

where K is a normalisation constant, $V(d)$ is the volume of the crystal (taken to be d^m), and $m = 3$ for nearly spherical crystals. If transformed to the energy axis, the above equations yield

$$P(\Delta E) = \frac{N}{\Delta E^3} \exp\left\{-\frac{1}{2} \left(\frac{d_0}{\sigma}\right)^2 \left[\left(\frac{\Delta E_0}{\Delta E}\right)^{\frac{1}{2}} - 1\right]^2\right\} \quad (\text{A.5})$$

More recently, the PL has been modelled using a logarithmic normal distribution with the following set of equations [47]

$$\Delta E = E_{PL} - (E_g - E_s - E_b) = C/L^n \quad (\text{A.6})$$

$$I(\Delta E) \propto \frac{(C/\Delta E)^{(6-\alpha+n)/n}}{nC\sigma} \exp \left[-\frac{\{\ln(C/\Delta E)^{1/n} - \ln L_0\}^2}{2\sigma^2} \right] \quad (\text{A.7})$$

$$\mu = L_0 \exp(\sigma^2/2) \quad (\text{A.8})$$

where ΔE is the enhanced energy bandgap, E_{PL} is the energy of the PL, E_g is the bulk crystalline band gap (1.12 eV), E_s is the localised surface state energy (0.05 eV), E_b is the exciton binding energy (0.07 eV), $n = 1.39$ and $C = 4.122$ eV (L in units of nm).

Photoluminescence intensity from Si-nc decays according to the stretched-exponential decay function [73]

$$I(t) = I_0 \exp[-(t/\tau)^\beta] \quad (\text{A.9})$$

where τ is the characteristic PL lifetime and $0 \leq \beta \leq 1$ is the dispersion exponent. This is frequently used to describe dispersive processes in disordered systems with a distribution of relaxation times.

Radiative recombination of confined excitons is governed by exciton generation as governed by the following equation [75]

$$\frac{dN_{exc}}{dt} = \sigma\phi(kN - N_{exc}) - \frac{N_{exc}}{\tau} \quad (\text{A.10})$$

where the number of excitons, N_{exc} , is proportional to the pump photon flux, ϕ , the absorption cross-section, σ , the number of nanocrystals, N , and is limited by a factor k that determines the maximum number of excitons that can exist in a single crystal. The lifetime, τ , is an effective lifetime accounting for radiative and non-radiative recombination

$$\frac{1}{\tau} = \frac{1}{\tau_{rad}} + \frac{1}{\tau_{non-rad}} \quad (\text{A.11})$$

Solving the rate equation gives the time evolution of the exciton luminescence as a function of incident photon flux. Assuming a rapidly rising incident excitation pulse, the solution is

$$N_{exc} = \frac{\sigma\tau\phi kN}{\sigma\tau\phi + 1} \left\{ 1 - \exp \left[\sigma\phi + \frac{1}{\tau} \right] t \right\} \quad (\text{A.12})$$

The exponential term carries the characteristic initial rise time of the exciton population and thus the initial rise time of the emission, which is

$$\frac{1}{\tau_{rise}} = \sigma\phi + \frac{1}{\tau} \quad (\text{A.13})$$

A linear dependence on photon flux is seen, until the exciton population saturates. A plot of reciprocal luminescence rise time as a function of ϕ should give a straight line with gradient σ and intercept τ .

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