Optical Properties

Of

Silicon Nanocrystals

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I certify that, except where due acknowledgement is given, the work presented in this thesis is my own. None of this work has been previously submitted for a degree at this or any other institution.

Stephanie Cheylan
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Abstract

(English Version)

This thesis studies the variations in the optical properties of Si nanocrystals embedded in a SiO2 matrix, upon changes in the processing parameters. The main aspect being to find a way of improving Si quantum efficiency, so as to increase its application abilities from the electronic technology into optoelectronics. Observing the influence of processing parameters on the growth, size and optical efficiency of nanocrystals should lead to a better understanding of the emission mechanism, which is still nowadays under debate. A lot of work has been done in trying to correlate clearly the size of the nanocrystal and the emission observed. As long as the study of one single nanocrystal is not possible, it is important to understand the effect of the size distribution of the nanocrystals on the emission. The work in this thesis underlines the fact that the emission mechanism is governed, not only by the intrinsic properties of the nanocrystals, but also by their environment, in terms of size distribution and density.

Si nanocrystals embedded in an amorphous SiO2 matrix were fabricated by ion implantation followed by high temperature annealing. Basically, excess Si is introduced in the SiO2 matrix and annealed at 1100°C to nucleate and grow nanocrystals. A broad size distribution of nanocrystals is obtained and this generally results in broad optical features.

As implanted samples exhibit luminescence around 700 nm due to implantation-related defect. Upon annealing at 1100°C, this emission disappears and is replaced by a strong emission around 800 nm, attributed to the formation of Si nanocrystals in the SiO2 matrix. The growth of the nanocrystals as the implant dose increases is reflected in a continuous red-shift of the PL peak position, which agrees well with the quantum confinement theory. However, studies of the emission intensity and of the decay lifetime as a function of implant dose show that quantum confinement can not solely account for the luminescence observed. Non-radiative surface states and tunnelling of
the carriers through the oxide matrix play an important role in the luminescence mechanism. Low dose samples can be considered as a system of isolated nanocrystals due to the low nanocrystal density. High dose samples behave like a well interconnected network of nanocrystals, where nanocrystals-nanocrystals interaction become important. Non-radiative sites are present at the surface of Si nanocrystals, but the probability for non-radiative emission is stronger for large nanocrystals compared to small ones. Such effect also explains the size dependence of the luminescence intensity observed.

The second part of this thesis deals with the passivation of non-radiatives sites at the Si nanocrystal/SiO$_2$ interface. The kinetics of passivation by hydrogen annealing have been established. The effect of hydrogen on the luminescence shows an important increase in intensity accompanied by a red-shift of the PL emission. Both effects are observed to be size dependent, increasing with increasing nanocrystals size. A model based on the disproportionate passivation of large nanocrystals compared to small ones explains such size dependence. The hydrogenation has for effect to skew the optically active nanocrystals distribution towards larger nanocrystals. The increase in decay lifetime also follows the same size dependence, giving a stronger decrease in non-radiative emission for large nanocrystals. The fact that the decay lifetime increases upon hydrogenation also shows that defect sites are still present in the system even after high temperature anneals.
Abstract

(Version Française)

Cette these presente les changements des proprietes optiques des nanocristaux de Silicium lorsque les parametres de fabrications sont modifies. Il est important de pouvoir ameliorer l’efficacite quantique du Silicium, pour pouvoir agrandir son champ d’applications du domaine electronique jusqu’au domaine optoelectronique. Observer l’influence des parametres de fabrication sur la croissance, la taille et l’activite optique des nanocristaux devrait conduire a une meilleure comprehension du mecanisme d’émission, qui est encore de nos jours tres controverse. De nombreux travaux ont ete realisees dans le but d’obtenir une relation simple entre la taille d’un nanocristal et l’émission observee, provenant de celui ci. Il est aussi important de comprendre le role que joue la proximite d’autres cristaux de tailles variees sur l’émission. Le travail presente dans cette these montre que le mecanisme de l’émission est gouverne, non seulement par les propriete intrinseque des nanocristaux, mais aussi par leur environnement, c’est a dire la densite et la large distribution de taille de nanocristaux.

Les nanocristaux de silicium enfouis dans une matrice de SiO2 amorphe sont fabriques par la technique de l’implantation d’ions, suivi d’un chauffement a haute temperature. Principalement, l’excès de silicium introduit dans la matrice de SiO2 est chauffe a 1100°C pour generer la nucleation, suivit par la croissance des nanocristaux. La distribution de tailles obtenue est tres etendue.

Les echantillons implantes emettent autour de 700 nm, du a des defauts introduits par le procede d’implantation. Apres chauffage de ces echantillons a 1100°C, l’émission jusque la observee disparaît et est remplacée par une forte emission autour de 800 nm, attribuee a la formation des nanocristaux de silicium dans la matrice SiO2. La croissance des nanocristaux en fonction de la dose d’implantation se traduit par un deplacement de l’émission vers les larges longueur d’ondes, resultat qui s’explique parfaitement par la theorie du confinement quantique. Les etudes de l’intensite de l’émission ainsi que de la
duree de vie en fonction de la dose d’implantation montrent que le confinement quantique seul ne peut expliquer l’émission observée. Les niveaux d’énergie à la surface (non-radiatifs) ainsi que le "tunnelling" des porteurs à travers la matrice d’oxide jouent un rôle important dans le mécanisme de l’émission. Les échantillons à faible dose peuvent être considérés comme un système de nanocristaux isolés (faible densité de nanocristaux). Les échantillons à forte dose se comportent comme un réseau de nanocristaux reliés, où les interactions entre nanocristaux sont importantes. Les niveaux d’énergies présents à la surface des nanocristaux sont non-radiatifs, mais la probabilité pour une émission non-radiative est plus importante pour les gros nanocristaux. Cet effet est aussi une explication de la dépendance de l’intensité de l’émission en fonction de la taille des nanocristaux.

La deuxième partie de cette these traite de la passivation des sites non-radiatifs présents à l’interface entre les nanocristaux de silicium et la matrice de SiO₂. La cinétique du phénomène de passivation par le chauffement dans un milieu contenant de l’hydrogène a été établie. Les effets de l’hydrogenation sur la luminescence montrent une importante augmentation de l’intensité ainsi qu’un déplacement vers les longues longueurs d’onde de l’émission. Ces deux effets sont en fait dépendant de la taille des nanocristaux, augmentant quand la taille augmente. Un modèle de base sur la passivation disproportionnée des larges nanocristaux par rapport à celle des petits nanocristaux explique la dépendance de taille observée. L’hydrogenation a pour effet de distordre la distribution de nanocristaux optiquement actifs vers les grands nanocristaux, sachant que les petits nanocristaux sont les meilleurs émetteurs. L’augmentation de la durée de vie montre aussi une dépendance par rapport à la taille des nanocristaux, due à une plus importante réduction de l’émission non-radiative pour les larges nanocristaux. Le fait que la durée de vie augmente après hydrogenation montre que des défauts sont toujours présents dans le système après le chauffement à très haute température.
# Table of Contents

**Chapter 1 Introduction**  
English version: 3  
French version: 7  
References: 11

**Chapter 2 Literature Review**  
2.1 Preparation Technique: 15  
2.2 Quantum Confinement Theory: 16  
2.3 Optical Properties: 19  
2.3.1 Absorption: 22  
2.3.2 Luminescence: 22  
2.3.2.1 Room Temperature: 22  
2.3.2.2 Temperature Dependence: 24  
2.3.3 Time-Resolved Photoluminescence: 26  
2.3.3.1 Room Temperature: 26  
2.3.3.2 Temperature Dependence: 27  
2.4 Passivation: 28  
References: 32

**Chapter 3 Experimental Techniques**  
3.1 Processing Techniques: 43  
3.1.1 Ion Implantation: 43  
3.1.2 Helicon Activated Reactive Evaporation (HARE): 47  
3.1.3 Furnace Annealing: 49  
3.2 Optical Characterisation Techniques: 50  
3.2.1 Optical Absorption (OA): 50  
3.2.2 Fourier Transform Infra Red Spectroscopy (FTIR): 51  
3.2.3 Photoluminescence (PL): 52  
3.2.4 Time Resolved Photoluminescence (TRPL): 55  
3.3 Transmission Electron Microscopy (TEM): 56  
References: 57

**Chapter 4 Silicon Nanocrystals Synthesis and Luminescence**  
4.1 Luminescence of Irradiation-induced Defects: 61  
4.2 Optical Properties of Nanocrystals: 65  
4.2.1 Absorption: 65  
4.2.2 Luminescence: 70  
4.2.2.1 Theoretical Modelling: 77  
4.2.2.2 Temperature Dependence: 80  
4.2.2.3 Excitation Intensity Dependence: 84  
4.2.3 Luminescence Decay: 86
CHAPTER 1

INTRODUCTION
Silicon has always been the dominant material for microelectronic applications [1] as well as for the solar cell industry [2]. Nowadays, the telecommunication industry requires optoelectronic devices that can generate, detect, transmit and process data fast. The transmission of the data is realised through optical fibres, while generation and detection of optical signals is realised by compound semiconductor devices, and signal processing is performed with silicon devices. Being able to integrate both optical and electronic devices on a single Si wafer would revolutionise the communication world [3].

Unfortunately, the use of silicon in optoelectronic applications is severely limited by its poor light emission efficiency at room temperature, due to its indirect bandgap and strong non-radiative processes. Improving the light efficiency of silicon has been a major area of research for the last decade. Various methods have been investigated with promising results, ranging from doping with rare earth ions such as erbium [4, 5] to the engineering of superlattices and quantum wells composed of silicon, germanium and carbon [4]. The most promising approach so far has been the fabrication of porous Si by electrochemical etching of single crystal Si, which exhibited strong luminescence at room temperature [6].

Porous Si was discovered in 1956 [7] and was obtained by electrochemical anodization of the surface of a silicon wafer. Its structure consists of a network of nanometer-sized silicon regions surrounded by void space. However, interest in the optical properties of this material has only recently been stimulated following reports in 1990 [6] of efficient tunable room temperature luminescence at energies higher than the Si bandgap. These results were attributed to changes in the band structure of Si due to quantum confinement effects associated with the small dimensions of the crystalline regions. One consequence of quantum confinement is an increase in the bandgap of the crystallite with decreasing size. This mechanism was supported by the fact that the
emission could be tuned throughout the visible spectrum by simply changing the preparation conditions [6], this demonstrating a correlation between the size of the crystalline pores and the luminescence wavelength.

Unfortunately, the luminescence observed from porous silicon is unstable and sensitive to surface termination. For example, freshly etched porous Si films react with ambient air and are slowly oxidised ("ageing" phenomena) [8, 9]. As a consequence both the electrical and optical properties of the film vary with storage time. Many workers have studied ways to reduce such ageing effects, including anodic oxidation [10] and chemical oxidation [11], but much more work is required to obtain stable films. This sensitivity to surface conditions, as well as poor mechanical properties, make porous Si unsuitable for many device applications. The need for a more stable material has naturally led to the use of SiO₂ as a surface passivant, and this in turn has led to studies of new material structures, including small nanometered-sized Si crystallites (nanocrystals) embedded in a SiO₂ matrix. This particular material is stable and robust and is regarded as a promising system for optoelectronics applications.

Improving the light efficiency from porous Si and Si nanocrystals requires a good understanding of the luminescence mechanism. Although a lot of effort have been put into this area over the past several years, the luminescence mechanisms are still controversial. Three different models are still being debated nowadays and consist of: the emission from molecular species such as siloxene or polysilane [12, 13], defect mediated recombination in SiO₂ or near the Si/SiO₂ interface [14, 15] and finally exciton recombination in quantum confined Si crystallites [16, 17]. None of these models have so far been able to explain all features of the light emission from the Si nanocrystals or from porous Si.

This thesis presents the results of a study of the optical properties of Si nanocrystals embedded in a SiO₂ matrix, fabricated by ion implantation. The dependence of the observed luminescence on the processing parameters gives insight into its dependence on the size of the nanocrystals. The importance of the size distribution of the nanocrystals on the luminescence is also underlined. The luminescence obtained is the result of a complex combination between the intrinsic light
efficiency of nanocrystals and their interactions with the surroundings (being either another nanocrystal or the oxide matrix).

This thesis is presented as follows:

Chapter 2: reviews the scientific literature of relevance to this thesis, and introduces concepts of importance, such as quantum confinement and its effect on the optical properties of the Si nanocrystals.

Chapter 3: summarises the experimental conditions and procedures used in this study and provides an overview of the experimental techniques employed.

Chapter 4: examines the optical properties of Si nanocrystals fabricated by ion implantation and by a new plasma deposition technique, called HARE (Helicon Activated Reactive Evaporation), and their dependence on processing conditions. The dose dependence of the photoluminescence (PL) is studied and shows good agreement with the quantum confinement theory: an increase in size results in a red-shift of the peak position. The intensity is seen to increase up to a certain dose, and then to decrease as the dose increases. The presence of a maxima for the intensity relates to the presence of competing factors to the radiative emission from Si nanocrystals. Such factors can be either nanocrystal-nanocrystal interactions, which are believed to increase as the density of nanocrystals increases, or simply to the fact that the nanocrystals are becoming too big to be efficient light emitters (oscillator strength varies as $1/d^{2.25}$, with $d$ being the diameter of the nanocrystal). Temperature-dependent measurements of the PL intensity and lifetime are carried out. The decay lifetime is found to be of the order of $\mu$s indicating that the nanocrystal bandgap is indirect. The role played by the environment on the nanocrystals luminescence is important and relates to the dose dependence of the decay characteristics. Low dose samples can be treated as a system of isolated nanocrystals with their decay characteristics only dependent on the intrinsic properties of the nanocrystals. As for the high dose regime, it consists of a system of interconnected nanocrystals where the notion of carrier migration followed by either radiative or non-radiative recombinations is introduced. Finally, TEM imaging gives evidence of the nanocrystals formation, but unfortunately their size distribution could not be extracted.

Chapter 5: focuses on the effects of ion irradiation on the luminescence of Si nanocrystals. The quenching of the nanocrystal emission and its sensitivity to dose is shown to be consistent with the amorphisation of Si nanocrystals upon irradiation. This
is attributed to a preferential accumulation of non-radiative defects at the nanocrystal/SiO₂ interface. This process is also seen to be independent on the irradiation energy, implying that the defect production rate from electronic processes is lower than that from nuclear processes.

Chapter 6: demonstrates the kinetics of the thermal hydrogen passivation. An anneal at 500°C for 1h in forming gas is sufficient to totally passivate the Si nanocrystals. The diffusion of H₂ in SiO₂ being a fast process, the passivation of the dangling bonds by H₂ is found to be the limiting step in the passivation process. Although the passivation does not modify the optical absorption, the luminescence is seen to increase strongly and also red-shift. No further growth of the nanocrystals upon hydrogenation is observed and therefore can not account for the red-shift. The increase in emission results from a decrease of the non-radiative recombination rate, due to the passivation of dangling bonds at the surface of the nanocrystals by hydrogen. This also leads to an increase in decay lifetime at room temperature.

Chapter 7: looks in more detail into the effect of hydrogenation on the optical properties of Si nanocrystals. A study on the size dependence shows that both the increase in intensity and the red-shift exhibit a linear dependence, increasing with size. A disproportionate increase of the long wavelength emission, hence of the large nanocrystals, explains such a dependence. The passivation is more effective for large nanocrystals, shifting the emission towards higher wavelength, as shown in time-dependent PL where a second peak at long wavelength appears stronger after hydrogenation. The decay lifetime increases upon hydrogenation and also follows such a variation with size, being larger for longer wavelengths. All the experimental data shown in this chapter agree with the new model proposed.

Last, in Chapter 8, a short summary of the results is presented.
Le silicium a de tout temps été le matériau de base pour la microélectronique [1] et l'industrie des cellules solaires [2]. Pour cette raison, le développement de la technologie électronique s'est principalement centré autour du silicium. De nos jours, la technologie de communication a besoin de composants optoelectroniques qui permettent d'émettre, de transmettre et de transformer des données rapidement. La transmission des données est réalisée à travers les fibres optiques, leur transformation est réalisée par des composants fabriqués à partir de mélange de matériaux semiconducteurs. Pouvoir intégrer les composants électroniques ainsi que les composants optiques sur une seule et même plaquette de silicium révolutionnerait le monde de la communication [3].

Malheureusement, l'utilisation du silicium dans le domaine de l'optoélectronique est severelement limitée par sa pauvre efficacité à émettre à température ambiante, à cause du caractère indirect de sa bande d'énergie. Améliorer l'efficacité optique du silicium a représenté une part importante de la recherche durant les dix dernières années. Différentes méthodes ont été étudiées avec des résultats prometteurs, allant du "doping" avec des ions terres rares comme l'érbium [4, 5], jusqu'à la réalisation de super-réseaux et de puits quantiques composés de silicium, germanium et carbone [4]. Jusqu'à présent, l'approche la plus prometteuse a été la fabrication de silicium poreux par gravure électrochimique d'une particule de silicium cristallin, qui donne une forte emission à température ambiante [6].

Le silicium poreux a été découvert en 1956 [7], obtenu par l'anodisation électrochimique de la surface d'une couche de silicium. Sa structure consiste en un réseau de particules de silicium de dimensions de l'ordre du nanomètre, entourées de vide. L'intérêt porte aux propriétés optiques de ce matériau a été stimulée assez récemment, à la suite de travaux effectués en 1990 [6] concernant une forte emission dont l'énergie peut-être réglable à volonté. Ces résultats ont été attribués aux
changements de structure de la bande d'énergie du silicium, causes par les effets de confinement quantique associés aux petites dimensions de la région cristalline. Une des conséquences majeures du confinement quantique est l'agrandissement de la bande d'énergie du cristal quand la taille de celui-ci est réduite. Ce mécanisme est consolide par le fait que l'émission peut être ajustée à travers le spectre du visible en changeant simplement les conditions de préparations [6], montrant ainsi la relation entre la taille des pores cristallins et la longueur d'onde de l'émission.

Hélas, l'émission obtenue par le silicium poreux est très instable et sensible aux terminaisons de surface. Par exemple, du silicium poreux fraîchement préparé par gravure réagit avec l'air ambiant et est lentement oxide (phénomène de vieillissement) [8,9]. Par conséquent, les propriétés optiques et électriques du film varient enormement avec le temps de stockage. Plusieurs groupes ont essayé de réduire ce phénomène de vieillissement, comme par exemple par oxidation anodique [10] et oxidation chimique [11], mais on est encore loin de la stabilité requise. Cette sensibilité aux conditions de surface, ainsi que ses faibles propriétés mécaniques, font du silicium poreux un matériau non propice aux applications opto-electroniques. Le besoin d'un matériau plus stable a logiquement mené à l'utilisation de l'oxide thermique SiO₂ pour obtenir une bonne passivation de la surface.

Améliorer l'efficacité optique du silicium poreux ainsi que celle des nanocristaux de silicium demande une compréhension très poussée du mécanisme d'émission. Bien que beaucoup d'efforts aient été concentrés dans ce domaine durant ces dernières années, ce mécanisme est encore trop controversé. Trois différents modèles sont encore de nos jours très prises. Le premier considère des espèces moléculaires, comme le siloxène ou le polysilane [12, 13] comme la source de l'émission observée, un autre considère le rôle de la recombinaison à des sites de défauts soit dans le SiO₂, soit à l'interface de Si/SiO₂ [14, 15]. Finalement, la recombinaison d'excitons confinés dans les nanocristaux de silicium [16, 17] constitue la troisième hypothèse. Aucun de ces modèles n'est capable d'expliquer toutes les propriétés expérimentales de l'émission observée pour le silicium poreux et les nanocristaux de silicium.

Cette thèse présente les résultats de l'étude des propriétés optiques des nanocristaux de silicium enfouis dans SiO₂, fabriques par l'implantation d'ions. La
La these se presente de la facon suivante:

*Le chapitre 2:* donne une introduction a l'effet du confinement quantique et de ses consequences sur les proprietes optiques des nanocristaux de Silicium.

*Le chapitre 3:* explique les differents appareils ainsi que les differentes techniques utilises pour ce travail.

*Le chapitre 4:* decrit principalement les proprietes optiques des nanocrystaux de silicium fabriques par l'implantation d'ions, ainsi que par une nouvelle technique de deposition plasma, appelee HARE (Helicon Activated Reactive Evaporation). Une dependence de l'emission par rapport a la dose d'implantation est etudiee, montrant un deplacement de l'emission vers les longueurs d'ondes elevees lorsque la taille des nanocristaux augmente, phenomene qui correspond parfaitement a la theorie du confinement quantique. L'intensite de l'emission augmente jusqu'a une certaine dose pour ensuite diminuer alors que la dose d'implantation augmente continuellement. L'existence d'un maximum obtenu pour l'intensite de l'emission correspond a la presence de facteurs competitifs a l'emission radiative venant des nanocristaux. Ces facteurs peuvent-etre soit des interactions nanocristaux-nanocristaux, qui augmentent a mesure que la densite de nanocristaux augmente, ou tout simplement, le fait que les nanocristaux deviennent trop larges et ne sont plus d'efficaces emetteurs (la force d'oscillation varie avec $1/d^{2.25}$). La variation de l'intensite ainsi que de la duree de vie de l'emission par rapport a la temperature est aussi etudiee. La duree de vie est de quelques $\mu$s, ce qui traduit la nature indirecte de la bande d'energie. La notion de migration de porteurs, suivie par une recombinaison soit radiative, soit non-radiative est introduite pour expliquer les resultats obtenus. Le role que joue l'environnement des nanocristaux sur leur luminescence est mis en evidence lors de l'etude d'échantillons a faible et haute doses d'implantation.
Le chapitre 5: concerne les conséquences de l’irradiation d’ion sur l’émission provenant des nanocristaux. La diminution de l’émission et sa sensibilité aux doses d’irradiation sont consistentes avec un processus d’amorphisation des nanocristaux du à l’irradiation. Ce phénomène est du à l’accumulation préférentielle de défauts non-radiatifs à l’interface nanocristaux/SiO₂. Ce processus est indépendant de l’énergie d’irradiation, montrant que le taux de production de défauts du aux pertes d’énergie electronique est plus faible que celui du aux pertes d’énergies nucleaires.

Le chapitre 6: démontre la cinétique de la passivation thermale d’hydrogène. Le chauffage à 500°C pour une heure dans un environnement de gaz (H₂+N₂) est suffisant pour passer la totalité des nanocristaux de silicium présent. La diffusion de H₂ dans SiO₂ étant un mécanisme rapide, la passivation des liaisons pendantes par H₂ est en fait le facteur limitant le processus de passivation, et une énergie d’activation de \(-0.19 \pm 0.02\) eV est obtenue. Bien que la passivation ne modifie pas l’absorption optique, l’émission augmente fortement et s’accompagne d’un déplacement vers les longueurs d’ondes élevées. L’hydrogénation ne favorise pas un renouveau de croissance pour les nanocristaux et ne peut donc pas être la cause du déplacement de l’émission vers les longueurs d’ondes élevées. L’augmentation d’intensité de l’émission ressort d’une diminution du taux de recombinaison non-radiative, du à la passivation des liaisons pendantes à la surface des nanocristaux par l’hydrogène. Cela mène aussi a une augmentation du temps de vie \( \tau \), a temperature ambiante.

Le chapitre 7: regarde en détails les effets de l’hydrogénation sur les propriétés optiques des nanocristaux de silicium. Une étude sur l’influence de la taille des nanocristaux montre que l’augmentation d’intensité ainsi que le déplacement dans la partie rouge du spectre présentent une dépendance lineaire, augmentant avec la taille. Une augmentation disproportionnée de l’émission à longueurs d’ondes élevées, donc du aux larges nanocristaux, explique tel phénomène. Le phénomène de passivation est plus efficace pour les larges nanocristaux, déplaçant l’émission vers les longueurs d’ondes élevées, comme le montre le spectrum de luminescence en fonction du temps, ou un deuxième pic dans la région des hautes longueurs d’ondes apparait après le processus d’hydrogénation. Le temps de vie augmente aussi après l’hydrogénation, en ayant la même dependence sur la taille des nanocristaux observée précédemment pour les caractéristiques de l’émission, étant plus important pour les longues longueurs d’ondes. Toutes les données expérimentales montrees dans ce chapitre s’accordent avec le modèle propose.
En dernier, *le chapitre 8* est une courte discussion sur les possibilités d’utilisation des nanocristaux de Silicium pour des applications optoelectroniques.

**References**


CHAPTER 2

LIGHT EMISSION
FROM
SILICON NANOCRYSTALS
(Literature review)
This chapter discusses some of the basics aspects of Si nanocrystals, including their properties and fabrication, optical absorption, luminescence and luminescence decay. An introduction to the quantum confinement theory is also given. The intention of this chapter is to provide the reader with adequate background knowledge for the discussion of experimental results presented in Chapters 4-8.

2.1 Preparation Technique

Following the electrochemical technique for fabricating porous silicon, many other methods were developed to make Si nanostructures. These include: Plasma Enhanced Chemical Vapour Deposition (PECVD) [1-4], evaporation [5], sol-gel process [6], glass-melt reaction [7], crystallization of amorphous silicon [8], laser ablation [9, 10], silicon and SiO₂ radio-frequency (rf) cosputtering [11, 12], reactive ion-etching [13] and ion implantation followed by high temperature annealing [14-18]. Photoluminescence has been observed from samples prepared by all such methods, albeit at different intensities.

The ability to manufacture luminescent Si by methods that are compatible with current Si microelectronics technology would provide new possibilities in optoelectronics. Among all the techniques listed previously, PECVD and ion implantation seem to be the most appropriate. Both are low-temperature processes that do not involve wet-chemical processing and both are currently being widely used in microelectronics manufacturing.

Ion implantation of Si into silica glass or SiO₂ layers has well known advantages, such as cleanliness of the procedure, good control of Si concentration and distribution, and produces films that have excellent chemical and mechanical stability. In this technique, high dose Si ion implantation is used to produce a supersaturated solid solution of Si in the SiO₂ substrate film. Subsequent thermal annealing induces the SiOₓ (x<2) matrix to decompose into a two-phase system consisting of Si nanocrystals (nc-Si) embedded in amorphous SiO₂. The aggregation behaviour is determined by the local temperature during ion implantation and by electronic, thermal and structural properties of the glass and the ion species. The structure, size and size distribution of clusters depend on the ion species and on their reactivity with the substrate, and for a given
substrate, on the various preparation parameters. The nanocrystal size and density can be controlled by the ion implantation and thermal annealing conditions.

Atomic displacements and electronic excitations caused by the implantation process lead to the formation of structural defects in the SiO₂ matrix [19] which show luminescence in the visible region. The nature of these radiation-induced-defects consist mainly of paramagnetic defects associated with O-deficient centres, such as the E' centre (O=Si•), the P_b centre (also called D), the neutral O vacancy (NOV) (O ≡ Si-Si ≡ O) and the nonbridging oxygen hole center (NBOHC). It has been shown that the predominant defect is controlled by the electronegative nature of the implants [20]. Electropositive implants (e.g. Si) produce Si-Si homobonds, which are basically oxygen vacancy type defects, while electronegative implants (e.g. O) generate oxygen-interstitial-type defects. The NOV and NBOHC defect centres luminesce around 470 nm and 650 nm respectively [21, 22]. The post-annealing process at high temperature, as well as initiating the nucleation and growth of the nanocrystals, reduces the defect concentration in the SiO₂ [22-24], with their related PL observed to disappear for temperatures ~ 800-900°C [18, 25].

It is well known that the luminescence observed from porous Si can be tuned from the near infra-red into the blue/green part of the spectrum by changing the preparation conditions [26]. The optical properties of Si nanocrystals fabricated by ion implantation and annealing are also sensitive to implantation parameters such as temperature, energy and dose of the implant as well as temperature and ambient of the anneal [14, 15, 27-29].

2.2 Quantum Confinement Theory

Band edge luminescence in bulk Si is very weak due to its indirect bandgap (~ 1.12 eV). The blue-shift of the emission as well as the increase in quantum efficiency for porous Si relative to bulk Si have been explained in terms of quantum confined states in reduced size structures (e.g. small crystallites). A useful reference for discussing such effects is the Bohr radius \( a_B \), as quantum confinement effects arise when the exciton Bohr radius \( a_{be} \) is of the order or larger than the size of the confined system. The exciton Bohr radius is given by \( a_{be} = a_B \times \epsilon m_e/\mu \), with \( \epsilon \), the dielectric constant and \( \mu \), the effective mass of the exciton equal to \( m_e m_h/(m_e+m_h) \), with \( m_e \) and
\(m_h\) being the effective mass of electron and hole respectively. For Si, the exciton Bohr radius is \(\sim 4.9\) nm [30]. Three distinct categories of confinement can be identified depending on the size of the nanocrystal compared to the Bohr exciton radius [31]. Weak confinement is observed when the radius \(R\) of the nanocrystal is greater than the bulk exciton Bohr radius \(a_{be}\). Moderate confinement arise when the size of the nanocrystal and \(a_{be}\) are roughly equivalent, and strong confinement arises when the size of the nanocrystal is smaller than \(a_{be}\).

The bandgap of Si increases as a result of quantum confinement (fig. 2.1), resulting in a blue-shift of the PL emission [32]. The PL intensity also increases as the crystallite dimensions are reduced due to an increase in the probability for radiative transitions [30]. This arises from the spatial localisation of carriers and the corresponding delocalisation in momentum space which results in a spread of the electron and hole wave functions in \(k\) space showing a weak overlap, leading to relaxation of the crystal momentum conserving selection rules [33, 34]. This mixing of \(k\) states increases the oscillator strength and results in the nanocrystals having optical properties intermediate between an indirect gap and a direct gap material [35, 36].

Theoretical calculations of the electronic band structure of quantum confined semiconductors have been performed either by semi-empirical calculations [35, 37] or first principle calculations [38, 39]. In both cases, it is assumed that the dangling bonds at the surface of the nanocrystals are saturated with hydrogen, otherwise the bandgap would be masked by surface states. The tight binding (TB) calculations assume that parameters known from bulk Si (e.g. lattice parameter, interatomic distance) still apply for the nanocrystals [35, 37]. Although such results have been compared to experimental data in a favourable way by Proot [37], that reliability has been questioned [40]. Calculations based on density functional theory (DFT) within the local density approximation (LDA) [41, 42] appear to give a good description of both the valence and conduction band compared to the TB method which only works well for the valence band.

However the LDA approach only provides a good description of the band structure for the ground state. Calculations for excited states underestimate the bulk Si bandgap, giving a value of \(\sim 0.6\) eV [43]. Most work favours the effective mass
approximation theory (EMA) [31, 39, 44-46]. This assumes an infinite potential barrier at the boundary of the nanocrystal accompanied by an envelop wave function of the electron-hole pair.

\[ d_1 < d_2 \]

\[ E_{c} \]

\[ E_{V} \]

\[ E_{g1} > E_{g2} \]

\[ E_{g,bulk} \]

**Figure 2.1:** The quantum confinement influence on the effective band-gap in small structures. \( d \) represents the diameter of the nanocrystal, while \( E_g \) correspond to its bandgap.

An important relationship to be determined from theory is the dependence of the energy bandgap upon the size of the nanocrystals. The EMA model predicts a \( 1/d^2 \) dependence, while TB calculations predict a dependence of the order of \( 1/d^{1.39} \), going on to \( 1/d^2 \) for large crystallite sizes [37]. An estimate of the oscillator strength as a function of size is also important since it provides information about the luminescence intensity. Delley et al. [38] showed that the oscillator strength exhibits a sharp dependence on size, with Khurgin et al. [44] obtaining a \( 1/d^6 \) dependence and Sanders et al [36] a \( 1/d^5 \) dependence. Clearly, these calculations [36] suggest that smaller particles contribute significantly more to the luminescence than larger particles. To obtain a reasonable fit to experimental data with this model, the size distribution has to be included [44], and improvements in fitting experimental spectra have been reported by Lu [47], Ranjan [45] and Trwoga [31]. Still, an overestimate of the bandgap by the EMA model was reported for clusters smaller than 2 nm [31].
Quantum confinement is thus expected to increase the bandgap and oscillator strength of small crystallites. However, the high PL efficiency of porous Si is not only due to quantum confinement effects but also to a low non-radiative recombination rate that results from the restricted volume available to the carriers [35, 48]. The probability of finding an impurity or a defect is low due to the small number of atoms in the crystallite (<10^5) [49]. Vial *et al* [49] pointed out that nanocrystals have such small volume and surface area (10^{-19} cm^3 and 10^{-12} cm^2, respectively) that the probability of finding non-radiative recombination centres inside or at the surface of the nanocrystal is very small even for Si of modest doping. The increase in emission efficiency is therefore partly due to quantum confinement effects, but mainly due to a reduction in non-radiative recombination [50]. The passivation of non-radiative recombination centres will also be shown to be an important aspect of maximising the luminescence from ion-implanted samples.

### 2.3 Optical properties

Optical absorption and photoluminescence measurements are common tools to study the optical properties of semiconductors. Such measurements provide information about the nature and structure of the semiconductor band structure, and are therefore able to provide information about the effects of quantum confinement. For an ensemble of nanocrystals, the analysis is made less straightforward by the size distribution of the crystallites. This tends to smear out characteristic features in the spectra, making it difficult to extract precise information.

#### 2.3.1 Absorption

Optical absorption experiments give a quantitative measurement of the absorption edge as they only depend on the volume properties. They allow a more direct characterisation of the intrinsic structure of nanocrystals.

There are two mechanisms responsible for absorption in ion implanted nanocrystals systems. The first source of absorption is defects created during ion implantation. For fused silica, they are known as the B_2 (neutral oxygen vacancy), E' (oxygen vacancy), peroxy and homobonds centres, exhibiting broad absorption bands at 248 nm, 214 nm, 165 nm and 163 nm, respectively [51, 52]. The second source of absorption is the presence of Si crystallites and their interactions with the substrate. For
wavelengths below 250 nm, the absorption is mainly due to the irradiation-induced defects, while above this value, the absorption spectrum is determined primarily by the optical properties of the Si nanocrystals. The absorption due to the E’ defect totally disappears after an anneal at 600-900°C, while the $B_2$ absorption band is still slightly present [52], though to a lesser extent than that prior to annealing.

Optical absorption spectra of Si nanocrystals produced by ion implantation generally contain no features characteristic of transitions between discrete states. Bulk Si also exhibits a fairly simple absorption spectrum with only two main features corresponding to the indirect bandgap at 1.12 eV and to the direct bandgap at 3.3 eV. The fact that no such features are observed for nanocrystals is presumably a consequence of the wide distribution of bandgaps which result from the nanocrystal size distribution.

![Electronic band structure of silicon](image)

**Figure 2.2:** Electronic band structure of silicon (from F. Herman and J. P. Van Dyke, unpublished)

In principal, the direct or indirect nature of the fundamental bandgap can be determined from a measurement of the absorption coefficient versus photon energy.

The absorption coefficient near the absorption edge can be expressed as:
\[(\alpha \ast E) = A \ast (\hbar w - E_g)^n \]  

(2.1)

where \(\hbar w\) is the photon energy, \(E_g\) is the bandgap and \(A\) is a constant [53]. Depending on the nature of the transitions, \(n\) takes different values:

- \(n=1/2\): allowed direct transitions
- \(n=3/2\): forbidden direct transitions
- \(n=2\): indirect transitions.

This equation is generally used to determine the value of the energy bandgap \(E_g\), of nanocrystals using a value of \(n=2\). A plot of \(\sqrt{\alpha \ast E}\) versus the energy \((\hbar w)\) is called a Tauc plot and should give a straight line which intercepts the X axis at the energy bandgap value (fig. 2.3). From this analysis, an average size of the nanocrystals is also frequently derived [14]. However, such analysis of the optical absorption data can lead to misinterpretation and needs to be used carefully. For example, Dowd [54] has shown that scattering losses due to Rayleigh scattering from randomly dispersed Ge atoms (or small Ge clusters in a silica matrix) can be misinterpreted as absorptive losses and give unrealistic values for \(E_g\).

![Figure 2.3:](image)

**Figure 2.3:** Tauc plot of the optical absorption of a sample irradiated with 400 keV, 4x10^{17} Si.cm^{-2} Si ions, annealed at 1100°C in N\(_2\). The straight line fit will give the value of the energy bandgap, consisting of the intercept of the line fit with the energy axis (X).
One of the more controversial aspects of quantum confinement in indirect bandgap nanocrystals is the change in nature of the bandgap, from indirect to direct as the particle size decreases. Several papers have used optical absorption data to show that the nature of the bandgap actually remains indirect for Si nanocrystals [55, 56]. Evidence for an increase in the bandgap was observed as a shift in the absorption edge to higher energies as the size decreases [55-57]. Interestingly, the shift in the absorption edge is reported to be much greater than that observed for PL emission.

2.3.2 Luminescence

2.3.2.1 Room Temperature

Ranjan et al [45] and Chen et al [58] have attempted to model the PL emission from an ensemble of nanocrystals. They assume a Gaussian nanocrystal size distribution \( P(d) \), given by:

\[
P(d) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{(d-d_0)^2}{2\sigma^2}\right) \quad (2.2)
\]

where \( d \) is the cluster diameter, \( d_o \) the mean particle diameter, and \( \sigma \) is the standard deviation of the size distribution. The variation of the oscillator strength \( f \), with the crystallite diameter \( d \) is usually assumed to have a power law of the form [44]:

\[
f \propto d^{-\beta} \quad (2.3)
\]

where the value of \( \beta \) can take a wide range of values (2<\(\beta\)<6) depending on the model employed [31, 36, 44]. The value of 2.25 has been shown to provide reasonable agreement with experimental data and will be used in this work. The energy shift due to quantum confinement is assumed to have a simple "particle in a box" form:

\[
\Delta E = \frac{c}{d^2} \quad (2.4)
\]

with \( c = 485.816 \text{ eV/Å}^2 \). Expressing the size distribution, equation 2.2, in terms of the bandgap energy, equation 2.4 gives the distribution of particles with a particular bandgap:
\[ P(\Delta E) = \frac{K}{\Delta E^3} \times \exp \left\{ -\frac{1}{2} \left( \frac{d_o}{\sigma} \right)^2 \left[ \left( \frac{\Delta E_o}{\Delta E} \right)^2 - 1 \right] \right\} \]  

(2.5)

where \( K \) is a normalisation constant, and \( \Delta E_o \) is the energy gap for crystallites with a mean size \( d_o \). The PL spectrum \( S(\Delta E) \) is then given by the product of this distribution function and the oscillator strength:

\[ S(\Delta E) = P(\Delta E) \times f(\Delta E) \]  

(2.6)

or

\[ S(\Delta E) = \frac{K}{\Delta E^{1.825}} \times \exp \left\{ -\frac{1}{2\sigma^2} \left[ \frac{22.041}{\Delta E^2} - d_o \right]^2 \right\} \]  

(2.7)

By comparing this model with experimental PL data, \( d_o \) and \( \sigma \) can be estimated. The expression of the full width at half maximum (FWHM) is given by [46]:

\[ \Delta E_{FWHM} = 4\Delta E_o \times \left( \frac{(d_o/\sigma)}{(d_o/\sigma)^2 - 2} \right) \]  

(2.8)

The mean energy of the up-shift \( \Delta E_o \) and the location of the PL peak \( \Delta E_p \) \([=h\nu - (E_g - E_b)\)] with \( E_b \) and \( h\nu \) the binding energy of the exciton and the photon energy, respectively are not identical, due to the statistical distribution in nanocrystals size.

From looking at the maxima condition for the equation 2.7 (derivative of the equation set to 0), the PL peak position \( \Delta E_p \) is given by [46]:

\[ \Delta E_p = \Delta E_o \left( 1 - 10 \times \left( \frac{\sigma}{d_o} \right)^2 \right) \]  

(2.9)

Depending on the values of \( d_o \) and \( \sigma \), the peak position can be red-shifted or blue-shifted relative to the emission expected from a particle of average size. A down-shift
(meaning $\Delta E_p < \Delta E_o$) has been seen to give reasonable values of exciton binding energies [45, 46].

Whilst this model is fairly simplistic, taking no account of the size dependence of the nanocrystal absorption cross section, it does provide a reasonable fit to experimental data and gives realistic estimates of the mean nanocrystal diameter, as confirmed by TEM [59]. Figure 2.4 shows the energy bandgap as a function of size, determined from either theoretical or experimental analysis by various groups. As can be seen, the data is consistent with an increase of the bandgap with increasing nanocrystal size due to the carrier confinement.

![Figure 2.4: Theoretical and experimental values for band gap in Si nanocrystals (after Delerue et al [35]). Dashed and solid lines represent theoretical values with and without excitonic correction.](image)

2.3.2.2 Temperature Dependence

In both porous Si and Si nanocrystal systems, the PL intensity increases with decreasing temperature, before reaching a maximum in the temperature range between 90 and 130K, and then decreases as the temperature decreases further [60, 61]. This behaviour has been explained by exciton singlet-triplet exchange splitting in Si nanocrystals. The model was first used to explain the behaviour of the PL of porous Si
[62, 63], and later for nanocrystals. The confined excitonic states are split by an energy \( \Delta \) due to the enhanced exchange interaction between the electron and the hole. The lower level corresponds to a triplet state which is three-fold degenerate, and the upper level to a singlet state. Radiative transitions from the lower triplet state are forbidden in the dipole approximation so electrons must be thermally excited to the singlet state in order to recombine radiatively. The temperature dependence of the radiative exciton lifetime \( \tau_{rad} \) results from the thermal balance between the occupation of the singlet and triplet states [62], and is given by:

\[
\tau_{rad} = \tau_T \frac{3 + \exp\left(\frac{-\Delta E}{kT}\right)}{3 + \tau_T/\tau_S \exp\left(\frac{-\Delta E}{kT}\right)}
\]

with \( \tau_T \) and \( \tau_S \) the triplet and singlet lifetime, respectively, \( kT \) the thermal energy and \( \Delta E(r) \), the energy splitting of the excitonic levels. A schematic diagram of the energy levels corresponding to this model is shown in fig. 2.5. At low temperatures (T=15K), only the triplet state is populated therefore radiative recombination is weak. At higher temperatures (15K<T<130K), the singlet state becomes populated and the radiative rate increases. As the temperature keeps increasing, non-radiative recombination becomes more and more significant, leading to a decrease in the PL intensity.

\[\Delta E(r)\left\{\begin{array}{c}
\text{Singlet (Allowed)}
\end{array}\right.\]

\[\begin{array}{c}
\text{Triplet (Forbidden)}
\end{array}\]

\[\tau_S \text{ (fast)} \quad \tau_T \text{ (slow)}\]

Figure 2.5: Schematic diagram of the excitonic level splitting due to electron-hole exchange interaction for Si nanocrystals.

It is important to note that the singlet-triplet splitting depends on the size of the nanocrystals, as it is affected by quantum confinement. For smaller nanocrystals, a
bigger splitting is expected due to a strong quantum confinement, leading to a maximum PL intensity at higher temperature than for bigger nanocrystals [61]. Values of $\Delta E(r)$ were found to increase from 8.4 meV up to 16.5 meV for corresponding nanocrystal sizes of ~5.5 - 2nm [59]. For bulk Si, the value of $\Delta E(r)$ is less than 0.15 meV [64].

2.3.3 Time-Resolved Photoluminescence

Crystalline silicon has long radiative lifetimes due to its indirect gap. As a consequence, excitons have time to diffuse in the semiconductor volume and find non-radiative centres rather than to recombine radiatively. This is exactly the case for porous Si, for which the luminescence lifetime has been extensively studied [62, 65-67]. For porous Si the luminescence decay has two components, a fast one (ns) and a slow one (μs) [62]. The slow decay component is associated with the visible IR PL of porous Si [68], and is consistent with the lifetime expected for radiative transitions in an indirect bandgap semiconductor.

2.3.3.1 Room Temperature

Stretched exponential decay of the luminescence signal is commonly observed for Si nanocrystals in an oxide matrix, porous Si and other materials that are disordered or inhomogeneous on the microscopic scale [69, 70]. The PL intensity is therefore given by [71,72]:

$$I(t) = I_o * \exp\left(-\frac{t}{\tau}\right)^{\beta}$$  \hspace{1cm} (2.11)

with $I(t)$ being the time dependent luminescence intensity, $I_o$, the intensity at $t=0$, $\tau$, the effective decay time and $\beta$, a dispersion exponent with a value between 0 and 1. The constant $\beta$ represents a measure of the departure from the isolated nanocrystal picture, and depends directly on the diffusion of the carriers. The fact that $\beta$ is less than 1 refers to the existence of a broad distribution of lifetimes, whether the relaxation process is radiative or non-radiative. In the case of non-interacting nanocrystals that can only decay radiatively, a single exponential decay is expected, which leads to $\beta=1$. For porous Si and Si nanocrystals systems, the broad distribution of lifetimes is the result of either an energy distribution of localised states [73, 74] or a dispersive motion of the excited carriers in a disordered network of nanocrystallites [65, 71]. Therefore, the
recombination dynamics for porous Si and for Si nanocrystals systems are determined by the recombination taking place on site and by the interactions between neighbouring nanocrystallites, or between nanocrystallites and the oxide matrix (defect sites).

Three different paths for carrier recombination are generally considered in the nanocrystal system: radiative recombination, non radiative recombination, and hopping. Those three possibilities appear in the decay lifetime as:

\[
\frac{1}{\tau} = \frac{1}{\tau_{\text{rad}}} + \frac{1}{\tau_{\text{nr}}} + \frac{1}{\tau_{\text{hop}}} \quad (2.12)
\]

This shows that exciton motion reduces the decay lifetime. So, a reduction in the exciton motion results in a longer decay lifetime and a value of \( \beta \) closer to 1.

The dependence of \( \tau \) and \( \beta \) on a wide range of parameters has been studied for the case of porous Si [30, 49, 60, 71, 72]. Of significance for this study is the fact that the lifetime is longer at longer wavelength [62, 66], and hence for bigger nanocrystals, and that both \( \tau \) and \( \beta \) decrease as the excitation intensity \( J_{\text{exc}} \) increases. These latter effects are believed to arise from saturation of non-radiative recombination paths and a decrease in \( \tau_{\text{hop}} \); and in the case of \( \beta \) from an increase in the motion of excitons to neighbouring nanocrystals.

### 2.3.3.2 Temperature Dependence

The PL decay time is strongly temperature dependent at all wavelengths, and three different regimes can be identified [72]. At low temperatures (T< 60K), the variation is primarily due to changes in radiative processes, i.e. processes taking place in the nanocrystals themselves (also called temporary traps). Suemoto et al. [60] have shown that the temperature dependence of the radiative lifetime can be extracted from the initial PL amplitude following the laser pulse, and from the near exponential gradient of the PL decay at long times, which is assumed to represent radiatively dominated decay. These two measures agree well and demonstrate that the increase in the decay lifetime below the intensity maximum is due to a variation in the radiative lifetime [66]. At high temperature (T>200K), the recombination is dominated by rapid on-site non radiative processes [75], whilst at intermediate temperatures, namely for
60K < T < 200K, it is due to the thermally activated release of carriers from temporary traps, and carrier hopping dominates, as the diffusion is restricted only by the silicon crystallite network geometry [76].

The temperature dependence of the lifetime, $\tau$, shows a simple continuous decrease with increasing temperature. For low temperatures, only the slow (dipole forbidden) triplet state is populated so $\tau \sim \tau_{\text{rad}}$ (excitonic recombination at the nanocrystals sites), and values of $\tau$ are quite high, in the order of ms at 4K [66, 72]. As the temperature is raised, the upper fast singlet state is increasingly populated and the lifetime decreases. At higher temperatures, competing non-radiative recombinations results in low values for $\tau$, of the order of 20-50 μs for Hooft et al [66] and Pavesi [65].

The temperature dependence of $\beta$ is somewhat more complex. For low temperatures, trapping at the nanocrystals dominates, and $\beta$ values are low. Increasing the temperature will thermally activate the detrapping process and therefore $\beta$ will increase [66, 72]. At higher temperatures, the diffusion is limited by the structure of the network of nanocrystals, so that the hopping process governs $\beta$, which is independent of temperature.

Equation (2.10) has been used to fit experimental data and to obtain estimates for the energy splitting $\Delta E$ and the ratio of the radiative rates to the non-radiative rates [77, 78]. This fitting requires a wide temperature range, usually from temperatures less than 50K up to 300K to be able to obtain a proper fit. It gives values for the exchange splitting which are consistent with expectations, as mentioned previously [59].

### 2.4 Passivation

Hydrogen has been extensively studied in amorphous and crystalline silicon systems [79] mainly because of its strong effect on the optical and electrical properties of semiconductors in general, as well as its presence in nearly any step of processing of Si.

An important characteristic of semiconductors concerns the influence of the surface on optical and electrical properties, and the need to embed semiconductor
clusters into a passivating medium. The quantum efficiency of light emission is very sensitive to the surface chemistry, particularly with regard to the amount of oxygen [49, 80, 81] and hydrogen [82, 83] on the surface. Surface termination modifies the electronic properties and different luminescence characteristics have been reported depending on whether a H-terminated surface or an oxidised-surface are considered [82, 84]. The H-terminated emission is red-shifted and less intense than O-passivated emission, due to the surface states being situated deeper in the bandgap. However there are conflicting reports about the efficacy of O in this regard, with some work reporting degradation [85] and others enhancement [49, 86] of the luminescence after oxidation.

Wolkin et al [32] have recently reported that an oxide may actually not provide good passivation for small crystallites. They have shown that when a Si nanocrystallite is passivated by oxygen, a stabilized electronic state is formed on Si=O covalent bonds, which act as electron traps, for nanocrystals smaller than 3nm. Figure 2.6 shows the electronic states in nanocrystals as a function of cluster size.

![Figure 2.6:](image)

Three zones are observed: zone I for free excitonic recombination, zone II where the electron is localised on a Si=O bond, while the hole is free, and zone III where both the electron and hole are trapped at the Si=O bond. Wolkin et al have shown good agreement between their model and experimental data.
The role of hydrogen at the interface of Si/SiO₂ is of particular interest due to its ability to passivate defects. Interface states in the c-Si/SiO₂ system are the result of a large mismatch in bond length (~7% or more) [87] and variations in surface stoichiometry (SiOₓ) [88]. One important Si/SiO₂ interface charge trap is called the Pb centre, which is a specific dangling bond type of defect, represented by -Si≡Si₃. Electrical measurements [89] have indicated that these defects are the dominant interfacial charge traps that make the Si/SiO₂ system less than ideal in device applications. These defects are also thought to act as non-radiative recombination centres and therefore to reduce the luminescence efficiency of nanocrystals. H passivation of such non-radiative defects can therefore have a significant effect on the luminescence efficiency.

The introduction of hydrogen can be achieved in several different ways, namely: ion implantation of either hydrogen [79] or deuterium [90, 91]; remote plasma hydrogenation [92]; radio-frequency (rf) plasma [93], and annealing in a hydrogen ambient [94]. The efficiency of electronic defect passivation by hydrogen is strongly dependent upon the method of its incorporation into the system as well as on its bonding configurations [92].

It has been known for a long time that Pb centres can be passivated by annealing in molecular hydrogen via the reaction:

\[ Pb + H₂ → HPb + H \]  \hspace{1cm} (2.13)

This reaction is thermally activated with an activation energy of 1.66 eV ± 0.06 eV [95]. The passivation process is believed to involve the binding of a hydrogen atom to the trivalent silicon atom, resulting in the formation of a diamagnetic, neutral defect symbolized as HPb. It has been reported that Pb centres can be passivated with H₂ above approximately 200°C [96, 97]. Although various mechanisms can account for the way in which the passivation of Pb centres with molecular hydrogen proceeds, most experimental results [96] agree with the following kinetic equation:

\[ \frac{d[Pb]}{dt} = -k_f[H₂][Pb] \]  \hspace{1cm} (2.14)
This equation indicates that the rate at which $P_i$ centres are passivated is proportional to the volume concentration of $H_2$ at the interface $[H_2]$, the surface density of $P_i$ centres $[P_i]$ and the forward rate constant $k_f$, which is temperature dependent. Previous work by Brower [95, 96, 98, 99] on the diffusion of $H_2$ in silica shows that the kinetic reaction agrees with a passivation process in which the $H_2$ molecule chemically reacts directly with the $P_i$ centre. The hydrogen is believed to reach the region of the interface by the diffusion of $H_2$ through the oxide [96, 100]. Shelby [100] has plotted the diffusion constant of $D_2$ and $H_2$ in bulk silica between 278K and 356K by using the following equation for the diffusion constant for chemically inert atoms or molecules in glasses:

$$D = D_o * T * exp \left( \frac{E_a}{kT} \right)$$  \hspace{1cm} (2.15)

The activation energy for the diffusion of $H_2$ in silica is 0.386 eV, and the value of $D_o$ is $3.1 \times 10^{-7}$ cm$^2$/K.s for temperatures between 278K and 356K [96]. For room temperature, the value of $D = 2.08 \times 10^{-11}$ cm$^2$/s is obtained for $H_2$ using the equation (2.15). Their work also shows that it is improbable that the process of passivation proceeds as a consequence of the partial absorption of $H_2$ at a trap or misbonding in the SiO$_2$ with the release of an atomic H atom which subsequently either passivates a $P_i$ centre or is captured in the SiO$_2$.

An estimate of the diffusion length $X$ can be determined from:

$$X = \sqrt{D * t}$$  \hspace{1cm} (2.16)

where $t$ is the anneal time. Using equation (2.16) and the value of the diffusion constant for $H_2$ at room temperature of $D = 2.08 \times 10^{-11}$ cm$^2$/s, it can be shown that hydrogen diffuses through a 1 µm layer of SiO$_2$ in ~ 5 ms at room temperature. As the diffusion constant increases with increasing temperature (equation 2.15), it can be assumed that the diffusion of hydrogen is a fast process, and is not a limiting step in the passivation process.

The depassivation of $HP_b$ is also a common process and occurs in vacuum at temperatures in excess of 550°C following the reaction:
\[ HP_b \rightarrow Pb + H \] (2.17)

with an activation energy of \(2.56 \pm 0.06\) eV. For temperatures around 500-600°C, different processes also start to become significant, such as the reverse passivation reaction:

\[ H + HP_b \rightarrow Pb + H_2 \] (2.18)

and the reverse dissociation reaction:

\[ H + Pb \rightarrow HP_b \] (2.19)

Both of these reactions are exothermic and occur spontaneously if atomic hydrogen encounters either the \(HP_b\) or \(Pb\) centres.

The interest in studying hydrogen for a nanocrystal system comes from the fact that nanocrystals are characterised by a large surface/volume ratio. Therefore, a large concentration of surface structural defects (=Si- and ≡Si- O-) exists due to the splitting of the ≡Si-O-Si≡ bond during particle formation. Passivating such defect states will be beneficial for the luminescence efficiency, as non-radiative exciton recombination will be reduced, favouring radiative recombination from the Si nanocrystals. Such results have been scarcely reported for Si nanocrystals [91, 94, 101, 102], but they all demonstrated a strong increase in the luminescence efficiency from Si nanocrystals.

References


CHAPTER 3

EXPERIMENTAL TECHNIQUES
In this chapter, the two different preparation techniques used to form the silicon nanocrystals, namely *Ion Implantation* and *Helicon Activated Reactive Evaporation*, are described first. The optical characterisation techniques used were *Optical Absorption*, *Photoluminescence*, *Time-Resolved Photoluminescence* and *Fourier Transform Infrared Spectroscopy*, in order to study the effect of size reduction (quantum confinement) on the optical properties of silicon. All the optical characterization techniques used in this work are non-destructive and give information on the energy levels and bandgap of semiconductors in general. Finally, *Transmission Electron Microscopy* was used to obtain information on the structure of the nanocrystals as well as on their size distribution.

### 3.1 Processing Techniques

#### 3.1.1 Ion Implantation

The ion implantation experiments were all performed at the Australian National University (ANU), in the Department of Electronic Materials Engineering (EME), using a 1.7 MV National Electrostatics Corporation (NEC) Tandem Pelletron Accelerator (model 5SDH-4). A schematic diagram of the ion implanter is shown in figure 3.1.

The ion source is a SNICS II (Source of Negative Ions by Cesium Sputtering) type that can produce a large variety of negative ion beams from a solid material cathode. Vaporised cesium (Cs) is ionised and Cs\(^+\) ions are accelerated to the negatively biased (≤ 10 kV) cathode. The sputtered negative ions are attracted by a positively biased extractor (≤ 15 kV). The beam of negative ions is focused by an einzel lens and accelerated through a potential (≤ 80 kV), before being mass analysed by a 90° magnet. The mass selected negative ions are then injected into the accelerator, where they are accelerated towards a positive terminal situated at the center of the accelerator tank. At the terminal, electrons are stripped from the negative ions by the introduction of N\(_2\) (stripping) gas. The positive ions are then further accelerated towards the high energy end of the accelerator.

The energy to which ions can be accelerated ranges from 0.2 to > 10 MeV, depending on the charge state of the ion. For low energy implants (≤ 100 keV), the N\(_2\) stripper gas is turned off so that ions do not undergo charge exchange in passing
through the accelerator. The negative ions are then accelerated and subsequently
decelerated by the same amount through the terminal potential, exiting the accelerator
with the initial injection energy. The ions exiting the accelerator are focussed by a set of
electrostatic quadrupole lenses and are steered into the energy selection magnet, at
which the final selection of the implant species is made.

Samples are mounted onto a four-sided Ni block with vertical and rotational
movements. The samples are held onto the block by clamping. In this work,
implantation was always conducted at room temperature. A K-type thermocouple,
embedded inside the block, close to the surface, was used to measure the temperature.
The definition of the implant area on the target was achieved by electrostatically
scanning the ion beam in x and y directions across a beam-defining aperture placed ~ 30
cm upstream of the target. The loss of secondary electrons produced by ion irradiation
was minimised by a Cu cage surrounding the target, biased at ~ 300 V. Accurate
dosimetry measurements were obtained with a capacitative-based charge integrator.

In this work, the samples were irradiated with a beam of $^{28}$Si ions. The depth
profile of the implant was estimated using the TRIM (transport of ions in matter) code
[1]. For a single energy implant, the implanted Si distribution has an approximately
Gaussian shape [2], so that nucleation occurs preferentially around the peak in the
implant depth profile. The standard samples were irradiated with 400 keV Si$^+$ ions. The
depth profile obtained from TRIM is shown in figure 3.2. The distribution extends from
~ 200 nm to 900 nm, with a peak projected range of ~ 670 nm. The peak of excess Si
concentration corresponds to $1.4 \times 10^{22}$ at/cm$^3$, for a dose of $3 \times 10^{17}$ Si.cm$^{-2}$ for the single
implant and $7 \times 10^{17}$ Si.cm$^{-2}$ for the multiple implant. The range of fluences implanted
was from $5 \times 10^{15}$ Si.cm$^{-2}$ up to $6 \times 10^{17}$ Si.cm$^{-2}$, which corresponds to an excess of Si ions
in the SiO$_2$ matrix of 0.25 at. % up to 30 at. %.

Multiple implants were also conducted at room temperature, keeping the peak
concentration of excess Si introduced comparable with the single implant samples.
Details of the multiple implants energies and concentrations are given in table 3.2.
Figure 3.1: Schematic of the 1.7 MV Tandem Pelletron Ion Implanter.
Table 3.1: Details of the single implant at 400 keV

<table>
<thead>
<tr>
<th>Dose (Si.cm(^{-2}))</th>
<th>Peak Concentration (%)</th>
<th>Range (nm)</th>
<th>Width (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6x10(^{16})</td>
<td>3</td>
<td>655</td>
<td>265</td>
</tr>
<tr>
<td>1x10(^{17})</td>
<td>5</td>
<td>650</td>
<td>255</td>
</tr>
<tr>
<td>2x10(^{17})</td>
<td>10</td>
<td>655</td>
<td>250</td>
</tr>
<tr>
<td>3x10(^{17})</td>
<td>14</td>
<td>650</td>
<td>255</td>
</tr>
<tr>
<td>4x10(^{17})</td>
<td>19</td>
<td>655</td>
<td>280</td>
</tr>
<tr>
<td>6x10(^{17})</td>
<td>29</td>
<td>650</td>
<td>260</td>
</tr>
</tbody>
</table>

Table 3.2: Details of the five sequential implants performed to make the multiple implant samples.

<table>
<thead>
<tr>
<th>Energy (keV)</th>
<th>MI 3</th>
<th>MI 2</th>
<th>MI 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>8.4x10(^{16})</td>
<td>1.62x10(^{17})</td>
<td>2.4x10(^{17})</td>
</tr>
<tr>
<td>300</td>
<td>8.2x10(^{16})</td>
<td>1.45x10(^{17})</td>
<td>2.2x10(^{17})</td>
</tr>
<tr>
<td>200</td>
<td>4.2x10(^{16})</td>
<td>8.1x10(^{16})</td>
<td>1x10(^{17})</td>
</tr>
<tr>
<td>150</td>
<td>3.4x10(^{16})</td>
<td>5.1x10(^{16})</td>
<td>8x10(^{16})</td>
</tr>
<tr>
<td>100</td>
<td>2.5x10(^{16})</td>
<td>4.4x10(^{16})</td>
<td>6x10(^{16})</td>
</tr>
<tr>
<td><strong>Total Dose (Si.cm(^{-2}))</strong></td>
<td><strong>2.67x10(^{17})</strong></td>
<td><strong>4.83x10(^{17})</strong></td>
<td><strong>7x10(^{17})</strong></td>
</tr>
</tbody>
</table>
3.1.2 Helicon Activated Reactive Evaporation (HARE)

The Helicon Activated Reactive Evaporation (HARE) system is located in the Plasma Research Laboratories, at the Research School of Physical Sciences and Engineering, at the Australian National University.

The HARE [3] is a plasma-assisted reactive evaporation device that combines an evaporation source (electron-beam evaporator) and a high density plasma source (helicon plasma source), in a configuration in which the evaporant is transported through the plasma source. Plasma enhancement of a simple electron-beam vapour deposition system can have a number of desirable effects. Through the ionization process, the plasma delivers an energetic flux of particles to the substrate, assisting the bonding of the coating material and the film uniformity. The energetic particle flux can be controlled by applying a bias (dc or rf) to the substrate. The plasma has the additional effect of assisting chemical reactions by dissociating the gas phase, thus enhancing the reactivity of the gas. In the present case, e-beam evaporation of silicon was combined with plasma activation of a reactive argon-oxygen atmosphere. The silicon vapour evaporated from a crucible is partially ionized as it passes through the helicon plasma.
source before condensing on the substrate. The plasma also enhances the reactivity of the atmosphere by ionizing and dissociating oxygen molecules and produces ion bombardment of the growing film to hinder columnar growth. In this way, high quality silica films can be grown at very low temperatures (typically below 200°C). Importantly, the technique is also capable of producing hydrogen-free films because unlike plasma-enhanced chemical vapour deposition (PECVD), which typically relies on the decomposition of \( \text{SiH}_4 \) and \( \text{N}_2\text{O} \), it employs hydrogen-free materials. This is important for photonic device applications where H-related absorption can be a limitation [4] and for photoluminescence studies, where the presence of H is known to strongly influence the luminescence intensity [5].

The experimental set up is shown in fig. 3.3. It consists of three distinct zones. The bottom chamber houses the electron-beam gun and the turbo-molecular pump. The top chamber is equipped with a substrate holder, vacuum gauges and gas inlet. A movable shutter is located in front of the substrate. The two chambers are connected by a section containing a glass tube, around which a helicon rf antenna is located, defining the actual plasma source region. Two electromagnetic coils surrounding the source tube provide the static axial magnetic field necessary for the efficient generation of the plasma. The top chamber is also equipped with an electromagnetic coil to control the plasma diffusing from the source. All gases are introduced in the top chamber. A differential pumping effect is created between the electron beam chamber and the rest of the system by the presence of a plate with an orifice located at the bottom of the glass tube.

Oxygen deficient silica films were grown at ~ 90nm/minute in the HARE reactor. In the present work, silicon was evaporated by electron beam heating into an argon-oxygen plasma generated by applying 400W RF power to the antenna at 13.56MHz. The argon flow rate was kept constant at 3sccm (corresponding to a pressure of 0.3mTorr in the process chamber), while the oxygen flow was varied to obtain films with a range of stoichiometries. During deposition the pressure in the process chamber was 0.5 mTorr and the sample temperature was typically less than 200°C [3]. The thickness of the films was subsequently checked by ellipsometry and a prism coupler, and was typically ~ 500 nm. For our work, films were grown with an excess Si ranging from 4% up to 60%.
3.1.3 Furnace Annealing

Annealing was performed in a quartz tube furnace (Lindberg) under a flowing gas ambient. The gas was fed through a two stage, moisture-removing cartridge containing pellets of anhydrous CaSO₄ and silica gel before being supplied to the quartz tube system. For each anneal, the temperature ramp up and cool down processes were performed with no gas flowing, followed by a stabilisation period of ~ 2h with flowing gas. All high temperature (1000°C, 1100°C) anneals were isochronal (1h) and were
performed in a N$_2$ ambient. The samples were placed in a quartz boat, which was inserted in the furnace tube.

The hydrogen passivation anneals were also performed for 1h, in forming gas (5% H$_2$ + 95% N$_2$). Upon completion of the anneal, the samples were withdrawn into the cold zone and allowed to cool down for 2 minutes under flowing forming gas prior to removal from the quartz tube.

3.2 Optical Characterisation Techniques

3.2.1 Optical Absorption (OA)

In the absorption process, a photon excites an electron from a lower energy state to a higher energy state. Therefore, by illuminating with light and studying the changes in the transmitted radiation, information can in principle be obtained about all the possible transitions in a semiconductor.

The optical absorption measurements were conducted in the Laser Physics Center, at the Research School of Physical Sciences, at the Australian University, on a UV 3101 PC Shimadzu model scanning spectrophotometer operating from UV (190 nm) up to NIR (3200 nm). This spectrophotometer is a two beam system: one beam goes through a reference sample, while another parallel beam goes through the sample under study. The signal from the reference sample is then subtracted from the signal of the studied sample. Any absorption due to the substrate will therefore be eliminated, and the final measurement represents the true absorption from the implanted layer. In the present case, the reference sample consisted of an un-implanted fused silica slide. The optical absorption measurements relate directly to the implantation-induced disorder (as-implanted samples) and to the Si nanocrystals in the silica matrix (annealed samples).

The spectrophotometer was used in the Absorbance mode, where light was passed through the sample, and the amount of light exiting from the sample was measured as a function of the wavelength. The absorption equation is given by:

\[ I(v) = I_0 \cdot \exp(-\alpha d) \]  

(3.1)
\(I(\nu)\) being the intensity measured after exiting the sample, \(I_0\) the initial intensity entering the sample, \(\alpha\) the absorption coefficient and \(d\) the thickness of the sample. The absorbance is given by:

\[
Abs = -\log_{10}\left(\frac{I(\nu)}{I_0}\right)
\]

(3.2)

All measurements were made at room temperature and corrected by a baseline measurement. The baseline correction was performed by using two un-implanted slides of fused silica.

### 3.2.2 Fourier Transform Infra-Red Spectroscopy

Infra-red spectroscopy provides a powerful tool for the investigation of molecular structure [7]. It is based on the fact that atoms of any molecule are constantly oscillating about their equilibrium positions. These oscillations have high frequencies of the same order of magnitude as infra-red radiation. Therefore, if these vibrating molecules are irradiated with infra-red photons, all or part of the incident radiation will be absorbed, provided the frequencies match. Therefore, an analysis of an infra-red spectrum constitutes an analysis of the mechanics of the molecule studied. More importantly for the present studies, absorption bands occurring at certain frequencies can be correlated with certain bonds or atomic groups within the molecule, eg. Si-O, Si-H, etc. The analysis of the positions, symmetries and relative intensities of observed peaks provides much useful information about the molecule structure. Table 3.3 lists all the main peak positions useful for our studies, mainly related to Si-Si, Si-O and Si-H bonds.

Figure 3.4 illustrates a typical FTIR spectrometer. It contains an IR source, a Michelson interferometer, a sample stage and an IR detector. Software is employed to perform Fourier transform analyses and data manipulation. The interferometer is an optical device that splits a beam of light into two beams, making one light beam travel a different distance than the other, resulting in an optical path difference between the two beams, called \(\delta\). IR radiation from the source is split into two equal components by the beam splitter, and then reflected back by the two mirrors. One of the mirror moves away from its zero path length position at a constant velocity, while the second one is stationary, to produce the optical path difference. The two reflected beams interfere, such that the intensity of the IR beam interacting with the sample is modulated as a function of \(\delta\). The fundamental measurement obtained by an FTIR is a plot of light
intensity versus $\delta$, which is called an interferogram (fig. 3.5). The complete interferogram is a superposition of the detector response to all IR wavelengths, which contain information about the wavenumber and intensity of the radiation. The IR spectrum is the Fourier transform of the interferogram. Smith gives a complete description of the FTIR technique in ref [7].

<table>
<thead>
<tr>
<th>Mode</th>
<th>Frequency (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-O-Si</td>
<td></td>
</tr>
<tr>
<td>Rocking</td>
<td>475</td>
</tr>
<tr>
<td>Bending</td>
<td>820</td>
</tr>
<tr>
<td>Stretching</td>
<td>1080 - 1140</td>
</tr>
<tr>
<td>H-SiO$_3$</td>
<td></td>
</tr>
<tr>
<td>Bending</td>
<td>880</td>
</tr>
<tr>
<td>Stretching</td>
<td>2250</td>
</tr>
<tr>
<td>Si-OH</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3400</td>
</tr>
<tr>
<td>H-Si(O$_2$Si)</td>
<td></td>
</tr>
<tr>
<td>Bending</td>
<td>2200</td>
</tr>
<tr>
<td>Stretching</td>
<td>840</td>
</tr>
<tr>
<td>H-Si(OS$_2$I)</td>
<td></td>
</tr>
<tr>
<td>Stretching</td>
<td>2080</td>
</tr>
<tr>
<td>Si-H</td>
<td></td>
</tr>
<tr>
<td>Rocking</td>
<td>660</td>
</tr>
<tr>
<td>Bending</td>
<td>950</td>
</tr>
<tr>
<td>Stretching</td>
<td>2080 - 2250</td>
</tr>
<tr>
<td>Si-Si</td>
<td></td>
</tr>
<tr>
<td>Stretching</td>
<td>620</td>
</tr>
</tbody>
</table>

Fourier Transform Infrared measurements were conducted at room temperature using a Nicolet IMPACT 400 model spectrometer operating over the wavenumber range 400 – 4000 cm$^{-1}$. The FTIR set up was located in the Plasma Research Laboratories, in the Research School of Physical Sciences and Engineering, at the Australian National University.

### 3.2.3 Photoluminescence (PL)

Continuous wave (CW) photoluminescence (PL) is a standard technique for optical characterisation that provides information on the energy levels and bandgap of semiconductors. It is a very powerful and non-destructive technique for studying the intrinsic properties of semiconductors.
Figure 3.4: Schematic of a typical infrared spectrometer.

Figure 3.5: The Infrared spectrum (right) is the Fourier transform of the interferogram (left).
A typical PL spectrum consists of the measurement of the radiative emission intensity as a function of wavelength. In the case of a semiconductor, an electron can be excited up to the conduction band, leaving a hole in the valence band. These photoexcited carriers recombine to generate photons with characteristic energies related to the bandgap.

The luminescence can be the result of:
- Near band-gap transition: recombination of exciton or electron-hole pair.
- Shallow impurity transition: recombination of related shallow donor and/or acceptor levels.
- Deep level transition: recombination at deep impurities or defects sites.

By using different light energies (above or below bandgap), different energy levels may be probed. Typically, in standard PL measurements, light with an energy higher than the bandgap is used and near bandgap transition takes place.

For an indirect semiconductor, the emission of a photon from band to band transitions can only take place with the simultaneous emission of a momentum conserving phonon (fig. 3.6). This process therefore has a lower probability than the zero phonon-transitions allowed in direct band-gap semiconductors.

The PL apparatus was located in the Department of Electronic Materials Engineering, in the Research School of Physical Sciences and Engineering, at the Australian National University. The excitation source consisted of an argon ion laser, with an excitation wavelength of 488 nm (2.54 eV). The spot size on the sample was around 200-500 µm in diameter. The PL emission was collected using a lens to focus the light into a quartz light pipe. This was passed through a single grating monochromator (Digikrom model DK480) and detected with a GaAs photomultiplier tube (Hamamatsu R943-02). Standard lock-in detection techniques were used to maximise the signal-to-noise ratio. The sensitivity of the GaAs photomultiplier decreases rapidly for wavelengths above 850-900 nm. All spectra were then corrected for the spectral response of the system, by comparing with the response to a black body source. The spectrum obtained by a white light source was recorded, as well as the temperature of its filament (by using a pyrometer). Using the theoretical equation for a black body source, the relevant spectrum was finally obtained and used as a calibration for the system.
Figure 3.6: Illustration of indirect and direct recombination in a semiconductor

All PL measurements were conducted at room temperature and, where the spectra extended beyond 850 nm, the distribution was fitted with a Gaussian distribution in order to estimate integrated intensities. This assumes that the spectra are approximately symmetrical.

3.2.4 Time-Resolved Photoluminescence (TRPL)

The study of PL decay dynamics provides direct information about the luminescence (carrier recombination) mechanisms in nanoparticles, as well as information on the local environment surrounding the nanocrystals [6]. After a short (~100 ns) excitation pulse, the PL decay observed for a nanocrystal system has a stretched exponential behaviour given by equation 2.11.

Time Resolved Photoluminescence (TRPL) measurements were performed at the Department of Electronics, at KTH, Royal Institute of Technology, in Sweden. The apparatus was configured for measurements at room temperature (RT) as well as liquid nitrogen temperature (LT). TRPL measurements were performed using a frequency-doubled or -tripled yttrium-aluminum-garnet (YAG) laser (532 or 355 nm). The pulse
length was ~ 100 ns and the repetition rate 45 Hz or 20 Hz. The emitted PL was dispersed by a CVI 1/8 m double monochromator and detected by a cooled GaAs photomultiplier tube (PMT). PL transients were stored and averaged by a digital oscilloscope followed by computer readout. The data were then corrected for the spectral response of the system, as calibrated using a blackbody source.

3.3 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) is a very useful tool for obtaining information on the structure of the nanocrystals as well as on their size distribution. Unfortunately, because of the small Z-contrast between Si and SiO₂, nanocrystals with very small sizes are difficult to detect with TEM.

For a complete description of TEM imaging and diffraction refer to [8]. Only the sample preparation will be described in this section. TEM imaging was carried out by David Lwellyn at the Australian National University, in the Department of Earth Sciences, on a Philips CM 300, operating at 300 kV.

Cross-sectional TEM Sample Preparation

Fused silica samples were ultrasonically cut into 4 x 5 mm rectangles. Similar sizes silicon wafers were also cut to be used as reference samples. Using a mix of GATAN G-1 epoxy and hardener, the fused silica sample was sandwiched between the silicon wafers and glued together (fig. 3.7 left). The sample stack was then heated to 100°C for 5 minutes to cure the glue. A 3 mm diameter circular disc was ultrasonically cut from the sample stack, and inserted in a copper tube. Small slices of about 1 mm thickness were then cut with a diamond saw. At this stage, the sample consisted of a thin circular copper ring with the fused silica positioned in the middle of the ring, surrounded by silicon wafers (fig. 3.7 right). The sample was mechanically polished using a series of progressively finer SiC wet-dry sandpapers to a thickness of ~ 150 μm. Once polished, the sample was dimpled to a thickness of ~ 50 μm in the center. Ion beam thinning was then employed to achieve a thickness of electron transparency, and was conducted in a GATAN Model 600 Duomill Ar ion mill, operating with 4 keV Ar ion beam, with the Ar ion beam oriented at 15° to the sample surface.
Figure 3.7: TEM sample preparation schematic.

References


CHAPTER 4

SILICON NANOCRYSTALS
SYNTHESIS
AND
LUMINESCENCE
The properties of Si nanocrystals are highly dependent on the preparation conditions [1], and considerable effort has been devoted to studies of the dependencies of the PL of Si nanocrystals on processing parameters [2-5]. Naturally, the size of the Si nanocrystals has a particularly significant effect on the PL emission and correlations between nanocrystal size distribution and luminescence have added to the understanding of the luminescence mechanism. Photoluminescence spectra for as-implanted and annealed samples highlight the general features of visible light emission in the Si implanted silica system.

This chapter presents results from an investigation of the luminescence properties of Si nanocrystals produced by ion implantation.

4.1 Luminescence of as-implanted samples

As-implanted samples exhibit broad PL emission in the visible range due to radiation damage in silica [6-8]. The emission peaks approximately at 700 nm, as shown in fig. 4.1 and no significant shift of the peak position is observed as a function of irradiation dose. The PL emission peak intensity is a complex function of ion dose, increasing with dose up to $6 \times 10^{16} \text{ Si.cm}^{-2}$ before decreasing at higher doses, as shown in fig. 4.2. The initial intensity increase is consistent with an increase in the concentration of optically active defects with increasing irradiation dose. However, such an effect might be expected to saturate at higher doses rather than decrease. That the intensity decreases suggests that either the nature of the defects is altered by subsequent irradiation or that competing relaxation paths are created (non radiative defects centres) [10]. Indeed, such results have been reported by Devine [9] and Kim et al [11].

The multiple implant (MI) samples exhibit the same behaviour as the single implant (SI) samples (see the PL spectrum in fig. 4.1b). Although the range of doses for the MI samples is limited to doses above the "critical" dose, the reduction of the PL intensity is consistent with that observed for the single implant samples when normalised to the excess Si concentration. Indeed, the maximum corresponds to an excess Si of 3 at. % in both cases.
Figure 4.1: Room temperature PL spectra of as-implanted a) single implant and b) multiple implants samples. The numbers given in the legend represents the total implant dose multiplied by $10^{17}$ Si.cm$^{-2}$. 
Figure 4.2: Peak emission intensity as a function of implant dose, for as-implanted single implant (●) and multiple implants (♦) samples. The lines are a guide to the eye only.

The optical absorption data are shown in fig. 4.3, as a function of dose. The most common defects visible on an optical absorption spectra consist of the E' centre (~ 214 nm) and the B\textsubscript{2} defect (~ 248 nm, arrowed in fig. 4.3). In the present case, only the absorption related to the B\textsubscript{2} defect is visible.

Figure 4.3: Optical absorption spectra of as-implanted samples, as a function of implant dose.
Interestingly, the photoluminescence from HARE samples shows similar characteristics to the PL observed from implanted samples. Figure 4.4 shows PL spectra for as-deposited HARE samples having nominal excess Si concentrations of 4, 8 and 20 at. %, and for an as-implanted sample with a peak excess Si content of 10 at. %. The spectra from the 8 at % HARE sample and the 10 at. % implanted sample both show a broad emission peak centred around 670-720 nm.

![Figure 4.4: Room temperature PL spectra from as-deposited HARE samples having excess Si concentrations of 4, 8, and 20 at. % and from an as-implanted sample with an excess Si concentration of 10 at %. Note that the spectrum from the implanted sample is divided by a factor of 6.](image)

The stronger defect emission for the implanted samples presumably results from the destructive character of the ion implantation technique compared to the deposition technique. The implantation of Si into a stoichiometric SiO₂ destroys Si-O bonds and produces oxygen-deficient-type-defects. ESR studies have also shown that paramagnetic defects, such as the E' centre, are produced. In the case of the HARE technique, less bonds are broken, and the off ratio of Si content to O content leads to oxygen vacancy-type defects as well as Si dangling bonds (non radiative defect). This is also shown in the FTIR spectra of as-deposited samples, in fig. 4.5. Three peaks are evident in the spectra, which span the wavenumber range from 400 cm⁻¹ to 1600 cm⁻¹. The main absorption peak, located at 1075 cm⁻¹, is associated with the Si-O-Si stretching mode, whilst those at 820 cm⁻¹ and 475 cm⁻¹ correspond to bending and rocking modes, respectively. The absorption decreases with increasing Si fraction due to
the lower fraction of Si-O-Si bonds. The frequency of the main peak also shifts from 1075 cm\(^{-1}\) (stoichiometric SiO\(_2\)) to 970 cm\(^{-1}\) (60 at % excess Si) as the excess Si concentration increases, consistent with the increasing probability for Si-Si bonds and associated changes in the Si-O-Si stretching frequency [12]. Finally, the presence of the long tail at larger wavelengths for the PL spectrum of the HARE sample probably refers to an early growth of nanocrystals for high excess Si concentrations.

![Figure 4.5: FTIR spectra of as-deposited HARE samples with excess Si of 4%, 8%, 20% and 60%.

4.2 Optical Properties of Nanocrystals

4.2.1 Absorption

Figure 4.6a shows the optical absorption data for as-implanted and annealed samples for a dose of 1x10\(^{17}\) Si.cm\(^{-2}\), which corresponds to ~ 6 at. % excess Si in the SiO\(_2\) matrix. As mentioned previously, the spectrum for the as-implanted sample shows a clear absorption peak at 248 nm, due to the B\(_2\) defect. This peak is not evident after annealing at 1100\(^{\circ}\)C, consistent with the defects being removed or reduced below detection limit [7, 8]. The absorption density also increases upon annealing due to the presence of Si nanocrystals. The dose dependence of this optical absorption is shown in fig. 4.6b. The absorption edge shifts to lower energies (shorter wavelength) as the dose (particle size) increases. Fig. 4.6b also shows that the absorption density increases with dose, as the density of nanocrystals increases.
Figure 4.6: Optical absorption spectra for a) a sample implanted with an implant dose of $1 \times 10^{17} \text{Si.cm}^{-2}$, as-implanted (—) and annealed at $1100^\circ\text{C}$ in $\text{N}_2$ (—), and b) for samples implanted at various doses, annealed at $1100^\circ\text{C}$ in $\text{N}_2$. 

B$_2$ defect
From the optical absorption data, the energy bandgap can be calculated by using the TAUC plot (see figures 2.3 and 4.8). Figure 4.7 shows the dependence of the extracted bandgap energy as a function of dose, obtained by such technique. The extracted bandgap is observed to decrease with increasing dose (particle size), consistent with expectations from the quantum confinement model [4]. The values obtained for the bandgap energy are quite high compared to the indirect bandgap of 1.12 eV for bulk Si, and are consistent with particles of diameter ~ 3nm.

![Energy bandgap obtained by using the TAUC plot of the optical absorption as a function of implant dose, for samples annealed at 1100°C in N₂.](image)

Figure 4.7: Energy bandgap obtained by using the TAUC plot of the optical absorption as a function of implant dose, for samples annealed at 1100°C in N₂.

Figure 4.8a shows the optical absorption for a SI sample and for a MI sample having the same peak concentration of excess Si of ~ 1.3\times10^{22} \text{Si.cm}^{-3}, while fig. 4.8b shows the corresponding Tauc plot. The optical absorption spectra have the same shape, with an absorption edge shifted towards higher energy for the MI sample. The MI sample exhibits stronger absorption in the longer wavelengths region, and in total exhibits a higher absorption density than the SI sample. Figure 4.9 shows the values of the extracted energy bandgap for both SI and MI samples, as a function of peak concentration of excess Si ions. As seen previously, the trend is consistent with a quantum confinement model, and is similar for both sets of samples. However, the MI set of samples exhibit lower values of energy bandgap, suggesting larger nanocrystals, compared to the SI samples.
Figure 4.8: a) Optical absorption for a single (—) and a multiple (—) implant sample with the same peak concentration of excess Si of $1.3 \times 10^{22}$ cm$^{-3}$, annealed at 1100°C in N$_2$. b) Tauc plot of the absorption spectra shown in a) with the (—) curve corresponding to scattering loss $\sim 1/\lambda^4$. 
Figure 4.9: Energy bandgap obtained by using the TAUC plot of the optical absorption as a function of peak concentration for a single (♦) and multiple (◼) implant sample, annealed at 1100°C/N₂.

Figure 4.10 shows FTIR spectra for annealed HARE samples. For as-deposited samples, it was seen that the frequency of the main absorption peak of the Si-O-Si bonds shifted with increasing excess Si concentration, reflecting the variations in the stoichiometry of the SiO₂ matrix.

Figure 4.10: FTIR spectra of HARE samples with excess Si of 4%, 8%, 20% and 60%, annealed at 1100°C in N₂.

After annealing, the relative magnitude of the main absorption peaks observed in the as-deposited spectra remain unchanged, reflecting the fact that the stoichiometry is
unchanged by annealing (i.e. there is no further oxidation of the excess Si), but the peaks now show a much smaller shift with increasing Si content. This is consistent with formation of Si precipitates since their formation returns the surrounding material to stoichiometric SiO₂.

4.2.2 Photoluminescence

Figure 4.11 compares the PL spectra of as-implanted and annealed samples. The as-implanted sample exhibits defect-related luminescence centered around 660 nm. As the anneal temperature is increased from 300°C to 700°C to 1100°C, the defect peak slowly decreases (already at 300°C). Eventually it disappears and another peak starts emerging at approximately 770 nm, increasing in intensity and red-shifting as the temperature is raised. This strong PL emission is correlated with the presence of Si nanocrystals [13, 14]. It has been reported previously that the growth of the Si nanocrystals, though starting around 700°C- 800°C [15], requires a minimum temperature of ~ 950°C to form crystalline nanostructure [15]. A high annealing temperature enables a better removal of defects [7, 16]. The Si nanocrystal-related emission is fairly broad, with a FWHM ~ 300 nm, and strong. These characteristics are believed to be due to the quantum confinement effect which results in a widening of the bandgap and a decrease in non-radiative emission compared to bulk silicon [17].

![Figure 4.11: Room temperature PL spectra of a sample implanted with a dose of 3x10^{17} Si.cm^{-2}, as-implanted (x3), annealed at 300°C (x3), at 700°C (x3) and at 1100°C in N₂.](image-url)
Typical PL spectra are shown in fig. 4.12, while the integrated intensities as a function of implant dose are shown in fig. 4.13a. The red-shift at higher doses can be correlated with an increase in particle size [4, 18] (fig. 4.13b). As the size decreases, the bandgap increases giving emission at shorter wavelengths (widening of the bandgap).

![Figure 4.12: Room temperature PL spectra from implanted samples annealed at 1100°C in N₂. The numbers given in the legend represents the implant dose multiplied by 10^{17} Si.cm⁻².](image)

The integrated intensity has a more complex behaviour, increasing for doses up to 2x10^{17} Si.cm⁻² and decreasing for higher doses. The initial increase in intensity is consistent with the expected increase in nanocrystal concentration, as can be seen in recent work which involves "atomistic" simulations of Si nanocrystals kinetics behaviour [19, 20]. The reason for the reduction in intensity at higher concentrations is less clear, however, there are several possibilities. For example: a) the decreasing transition probability for larger crystallites, b) the increasing probability for nanocrystal-nanocrystal interactions and the possibility of energy transfer to non-radiative crystallites, and c) the increasing probability for defects in larger crystallites. The oscillator strength can be shown [21] to scale approximately at d^{2.25}, where d is the nanocrystal diameter. Hence a doubling in particle size is expected to result in a ~ 4-5 fold reduction in emission intensity [21]. Energy transfer between closely spaced nanocrystals is very likely and will usually be from small to large nanocrystals [22]. Since it is known that a large fraction of the large nanocrystals are optically inactive [22], such energy transfer is expected to reduce the total emission intensity. Since the
dipole-dipole interaction scales with $r^{-6}$ [23] where $r$ is the inter-particle separation, a rapid decrease in emission intensity is predicted with increasing particle concentration (the average distance between neighbour nanocrystals decreases accordingly [19]). Finally, the probability of a crystallite containing a defect is expected to scale with the crystal volume, producing a reduction in intensity that scales with $r^{-3}$, while the influence of interface defects between the crystallite and surrounding oxide would scale with $r^{-2}$. It is unlikely that such small particles encompass volume defects [24-26], but as shown by previous work [27, 28], the surface defects do play an important role in reducing the emission. Comparison with these models requires detailed particle sizing information and is complicated by the broad size distribution of nanocrystallites present in the samples.

The PL emission from the sample with a dose of $6 \times 10^{17}$ Si.cm$^{-2}$ shows anomalous behaviour. The peak position is blue-shifted compared to the peak position of the sample with a dose of $4 \times 10^{17}$ Si.cm$^{-2}$, while its intensity increases. A PL spectrum taken with a different system has shown the existence of emission at wavelengths up to 1 μm. C. Bonafos et al [20] have studied the kinetics of Si nanocrystal growth by coupling TEM measurements and "atomistic" simulations. They found good agreement for low super-saturation samples (<10 at %), while the experimental values are much higher than the theoretical calculations for the high super-saturation case (>20 at. %). They believe that for the highest volume fractions, the growth rate is increased by a "proximity" effect among the particles [20], which would increase the size of big nanocrystals at the expense of smaller ones, a process which resembles the Ostwald ripening process [30, 31]. Such a ripening process could account for the blue-shift and the increase in intensity observed, both of which would result from a decrease in size of the nanocrystals. For our study, because the PL detection is limited to 850nm, the contribution of the large nanocrystals is not apparent and the spectrum represents only the emission from smaller crystallites.

It is important to note that the peak emission of Si nanocrystals is ~ 800 nm (1.55 eV), which indeed is higher than the Si indirect bandgap energy value of 1.12 eV.
Figure 4.13: a) PL integrated intensity and b) PL peak position, as a function of implant dose, for samples annealed at 1100°C in N₂. The lines are a guide to the eye only.
Figure 4.14 is a plot of the energy bandgap obtained from optical absorption data and by the PL data as a function of dose. It is obvious that the PL occurs at significantly lower energies and that the dependence of the bandgap is stronger for the absorption data than for the PL [4]. The optical absorption data encompasses all the nanocrystals present in the sample, while the PL data is only showing the contribution of a small portion of the nanocrystals present in the sample. Some energy loss occurs in the electronic processes from the absorption to light emission [32]. The site for the photo-generation of carriers is different from the one where the radiative recombination of carriers takes place [32, 33]. The notion of surface states and their probable role in the PL emission is introduced to try to explain the PL emission weak dependence as well as its energy range.

It is important to remember that the interpretation of the optical absorption data to obtain the energy bandgap may not be reliable, due to the scattering of light from small particles of Si in glass [34].

![Figure 4.14: Average value of the nanocrystals energy bandgap obtained by the analysis of the optical absorption data (♦) and the PL data (•), as a function of implant dose, for samples annealed at 1100°C in N₂. The lines are a guide to the eye only.](image)

The PL spectra from a single implant (SI) sample and a multiple implant (MI) sample having the same peak concentration of excess Si (~ 1.3x10²² Si.cm⁻³), annealed at 1100°C in N₂, are shown in fig. 4.15. No differences in the peak position and the width of the emission are noticeable. The only difference is the fact that the integrated
intensity is about 3 times stronger for the MI sample compare to the SI sample. This can be explained by the number of nanocrystals being larger for the MI sample, as the total dose of Si introduced represents a dose of ~ 7x10^{17} Si.cm^{-2} (with the same peak concentration of excess Si ions).

Figure 4.15: Room temperature PL spectra of a SI (—) and a MI sample (—) implanted with a peak concentration of 1.3x10^{22} cm^{-3}, annealed at 1100°C in N₂. The SI sample spectrum is normalised to the MI sample spectrum.

The optical absorption data suggested that the MI sample contained bigger nanocrystals than the SI sample. The fact that the PL emission spectra are exactly the same leads to a suspicion about the interpretation of the optical absorption data analysis, as an increase in nanocrystals size would result in a red-shift of the PL peak position. The discrepancy between the PL data and the optical absorption data is believed to arise from the fact that the optical absorption data includes a significant component due to scattering losses. As the implant dose for the MI sample is higher than for the SI sample, the number of nanocrystals has increased and would be expected to give a stronger scattering loss for the MI sample, explaining the stronger absorption data for the MI samples. The scattering loss would also explain the fact that smaller energy bandgaps were obtained for the MI samples compared to the SI samples, when the peak concentration of excess Si have been kept constant (so that the average size is the same).

Only two HARE samples show PL emission in the 800 nm range after high temperature annealing. The emission from the 20% excess Si sample is a lot weaker and
red-shifted compared to the emission from the 8% excess Si sample (fig. 4.16).

![Figure 4.16: Room temperature PL spectra of a HARE sample with 8% (—) and 20% excess Si (—) and an implanted sample (—) with 10at. % excess Si, annealed at 1100°C in N₂.](image.png)

The red-shift is due to the increase in size of the nanocrystals [4], and the decrease in intensity is expected for larger crystallites (for the same reasons stated previously for the implanted samples). Figure 4.17 shows that the emission intensities of the HARE sample containing 8at % excess Si and the ion-implanted sample containing 10at. % excess Si are quite similar. The spectrum from the HARE sample is slightly red-shifted relative to the implanted sample, suggesting slightly larger nanocrystals in this case. The HARE sample has an 8at % Si excess throughout its 500 nm thickness, corresponding to a total excess areal density of 2.6x10¹⁷ Si.cm⁻², slightly higher than that of the implanted sample which was implanted with 2x10¹⁷ Si.cm⁻². Implanted samples have a skewed Gaussian distribution of excess Si with a peak excess concentration of 10at % and a FWHM of approximately 400 nm. A considerable fraction of the implanted volume therefore has an excess Si concentration less than 8at %. The higher average concentration in the HARE sample would favour the formation of larger nanocrystals, consistent with the observed red-shift. No decrease in the width of the PL peak was observed for HARE samples.
Figure 4.17: Integrated emission intensity as a function of excess Si introduced, for HARE samples (•) and implanted samples (♦), annealed at 1100°C in N₂. The line is a guide to the eye only.

4.2.2.1 Theoretical Modelling of the PL spectrum

It is useful to model the PL emission spectrum in order to understand its dependencies. Several models have been proposed [21, 35] which try to take into account the size distribution of the nanocrystals as well as the quantum confinement effect. In this section, the model proposed in ref. [21] was used with a Gaussian size distribution of the nanocrystals and the equations given in Chapter 2. The result of the fit can be seen in fig. 4.18a, where the experimental PL spectra is the full line and the theoretical fit appears as a dashed line. For an annealed sample implanted with $3 \times 10^{17}$ Si.cm$^{-2}$, the values obtained with such a fit for the average diameter $d$ and the standard deviation $\sigma$ are $d = 3.14$ nm and $\sigma = 0.51$ nm, and the corresponding size distribution $P(\Delta E)$ is shown in fig. 4.18b. The overall fit to the experimental PL spectrum is not very good, especially for the high energy and low energy tails [36]. However, the extracted size distribution has been shown to be consistent with TEM observations [34, 50]. The high energy emission corresponds to the emission from small nanocrystals. It has been shown recently [37] that for nanocrystals smaller than 2nm, PL emission may result from new electronic states due to the presence of Si=O bonds, and therefore no longer follows quantum confinement predictions. This emission is independent of nanocrystal size. This effect may explain some of the differences between the experimental PL peak and the theoretical fit for small nanocrystals, as this phenomena hasn't been taken into
Figure 4.18:  

a) Theoretical fit of the PL spectrum of a sample implanted with a dose of $3 \times 10^{17}$ Si.cm$^{-2}$, annealed at 1100°C in N$_2$, using equation 2.7.

b) Size distribution of nanocrystals for a SI sample (—) and a MI sample (—), annealed at 1100°C in N$_2$, using equation 2.2 and the parameters obtained by the theoretical fit of the PL data by equation 2.7.
account in the theoretical model. With the values of \( d \) and \( \sigma \) obtained by the fit, the full width at half maximum (FWHM) can be calculated by using the equation 2.16. For this sample, the FWHM is \(~ 290 \text{ meV}\). The experimental spectrum gives a FWHM around 305 meV. Another parameter that can be deduced from the fit as well is the relationship between the peak position \( \Delta E_p \) and the mean energy shift \( \Delta E_o \) due to the quantum confinement (equation 2.17). It shows that \( \Delta E_p = 0.72 \times \Delta E_o \), which indeed translates a red-shift of the PL peak position compared to the value of \( \Delta E_o \). It results in an exciton binding energy of the order of 50 meV, by simply using the relationship \( E_b = E_g + \Delta E_p - h\nu_p \). The value of 50 meV agrees quite well with the findings of others [36, 38], being lower than the theoretical value of 80 meV found by Takagahara [39]. The nanocrystals sizes are given by the size distribution \( P(\Delta E) \) to range from 1.5 nm up to 5 nm, which agrees with previous reports of a theoretical fit to experimental data that resembles the experimental data shown here [39, 40].

The parameters obtained by the fit of the PL data are given in table 4.1 for the range of implant doses studied. From the average size of the nanocrystals and the volume fraction of nanocrystals present, one can obtain the average distance between the nanocrystals as well as their density. Since the average size and density increase with dose, the average inter-nanocrystal distance is seen to decrease. Those facts are valid for doses up to a dose of \( 4 \times 10^{17} \text{ Si.cm}^{-2} \), as explained previously. The calculation of the inter-nanocrystal distance assumes that all the excess Si introduced in the SiO\(_2\) matrix contributes to form the nanocrystal responsible for the PL peak observed. This assumption is quite appropriate for most samples. The implant dose of \( 6 \times 10^{17} \text{ Si.cm}^{-2} \) is anomalous as previously discussed.

By fitting the emission peak of the MI sample with the previous equation (2.16), the values obtained for \( d \) and \( \sigma \) agree very well with the values obtained for the SI sample, as shown in table 4.1. The size distribution shows no significant differences from the one calculated for a SI sample, as can be seen in fig 4.18b.

The PL spectrum of the HARE sample was also fitted with the same equation. The values obtained are \( d = 3.12 \text{ nm} \) and \( \sigma = 0.50 \text{ nm} \), which agree well with the values obtained for the corresponding implanted sample.
Table 4.1: Various parameters obtained by theoretical fitting of the PL data for various implant dose, for single and multiple implants.

<table>
<thead>
<tr>
<th>Dose (Si.cm(^{-2}))</th>
<th>Mean Diameter (nm)</th>
<th>Standard Deviation (nm)</th>
<th>Mean Distance (nm)</th>
<th>Density (cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>6x10(^{16})</td>
<td>2.96</td>
<td>0.39</td>
<td>9.61</td>
<td>2.67x10(^{17})</td>
</tr>
<tr>
<td>1x10(^{17})</td>
<td>3.02</td>
<td>0.43</td>
<td>7.35</td>
<td>4.16x10(^{17})</td>
</tr>
<tr>
<td>2x10(^{17})</td>
<td>3.10</td>
<td>0.49</td>
<td>4.71</td>
<td>7.70x10(^{17})</td>
</tr>
<tr>
<td>3x10(^{17})</td>
<td>3.14</td>
<td>0.51</td>
<td>3.47</td>
<td>1.08x10(^{18})</td>
</tr>
<tr>
<td>4x10(^{17})</td>
<td>3.16</td>
<td>0.53</td>
<td>2.54</td>
<td>1.44x10(^{18})</td>
</tr>
<tr>
<td>6x10(^{17})</td>
<td>3.07</td>
<td>0.50</td>
<td>1.34</td>
<td>2.39x10(^{18})</td>
</tr>
<tr>
<td>MI 3</td>
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<td>0.45</td>
<td>7.48</td>
<td>4.16x10(^{17})</td>
</tr>
<tr>
<td>MI 2</td>
<td>3.12</td>
<td>0.49</td>
<td>4.74</td>
<td>7.70x10(^{17})</td>
</tr>
<tr>
<td>MI 1</td>
<td>3.15</td>
<td>0.51</td>
<td>3.48</td>
<td>1.08x10(^{18})</td>
</tr>
</tbody>
</table>

4.2.2.2 Temperature Dependence

In this section, the samples were excited with an excitation wavelength of 355 nm (3.50 eV) by a YAG laser. The temperature study extends from 70K up to 290K (room temperature). It is known that the PL intensity does not follow a monotonic variation with increasing temperature [41]. Figure 4.19 shows the intensity variation of a sample implanted with a dose of 4x10\(^{17}\) Si.cm\(^{-2}\), annealed at 1100\(^{\circ}\)C in N\(_2\). When the temperature is raised, the peak intensity increases with temperature up to 80K and decreases for higher temperatures.

The variation of the Si bandgap with temperature has been investigated in detail, and is known to be dominated by temperature-dependent electron-phonon interactions [42]. The decrease in bandgap for bulk Si is around 50 meV for the temperature range of 100K-300K, and can be described by the following equation:

\[
E_g(T) = E_g(0) - S\langle h\nu \rangle \left( \coth \left( \frac{\langle h\nu \rangle}{2kT} \right) - 1 \right) \tag{4.1}
\]
with $E_g(0)$ being 1.17 eV, $S$ equal to 1.49 and $\langle \hbar w \rangle$ is 25.5 meV (average phonon energy), which are values obtained in [42]. The theoretical temperature dependence of the bandgap for bulk Si is compared to the decrease of the bandgap energy for a sample with a dose of $1 \times 10^{17}$ Si.cm$^{-2}$ in figure 4.20. As can be seen a good agreement exists between both data sets [43, 44].

![Figure 4.19: PL spectra of a sample implanted with a dose of $4 \times 10^{17}$ Si.cm$^{-2}$, annealed at 1100°C in N$_2$, at various temperatures.](image)

The temperature dependence of the PL intensity has been explained by exciton singlet-triplet exchange splitting in Si nanocrystals [41, 45]. At low temperature, only the triplet state is populated resulting in a small amount of radiative recombination which explains the small emission intensity. As the temperature is increased, the singlet state becomes populated and the amount of radiative recombination increases, up to a certain temperature where the non radiative recombination processes become significant. This results in a quenching of the emission intensity at higher temperature [46].

The temperature dependence on the PL emission has been investigated for a range of doses from $1 \times 10^{17}$ Si.cm$^{-2}$ up to $6 \times 10^{17}$ Si.cm$^{-2}$. The dependence of the PL intensity is plotted in fig 4.21a for doses of $2 \times 10^{17}$ Si.cm$^{-2}$, $4 \times 10^{17}$ Si.cm$^{-2}$ and $6 \times 10^{17}$ Si.cm$^{-2}$. It is clear that the behaviour is somewhat different for the different samples. All exhibit a
maxima of emission intensity followed by a decrease as the temperature increases. The
temperature at which the intensity maxima is observed varies with implantation dose,
being 90K for the dose of 2x10^{17} \text{Si.cm}^{-2}, 80K for the dose of 4x10^{17} \text{Si.cm}^{-2} and 110K
for a dose of 6x10^{17} \text{Si.cm}^{-2}. These results are consistent with the exciton singlet-triplet
exchange splitting model since the exciton singlet-triplet splitting is predicted to be
larger in smaller nanocrystals. Therefore, the intensity maxima should occur at higher
temperatures for lower implantation doses. The case of the 6x10^{17} \text{Si.cm}^{-2} dose is again anomalous as mentioned previously in section 4.2.

![Figure 4.20:](image)

Figure 4.20: Theoretical fit of the PL peak position variation (■) as a function of
temperature, for a sample implanted with 1x10^{17} \text{Si.cm}^{-2}, annealed at 1100°C in
\text{N}_2. The theoretical fit was done using equation 4.1.

If the emission intensity is now plotted as a function of implant dose for each
temperature studied, the trend previously observed at room temperature stays the same
independent of the temperature. Figure 4.22 shows an increase of intensity up to a dose
of 2x10^{17} \text{Si.cm}^{-2}, and a decrease as the dose keeps increasing up to 4x10^{17} \text{Si.cm}^{-2}.
Therefore, all nanocrystals sizes that contribute to the PL spectrum actually exhibit the
same temperature dependence, as the dose dependence of the PL does not change with
temperature [22, 47].
Figure 4.21: a) Integrated emission intensity and b) PL peak position as a function of temperatures, for samples implanted with 2x10^{17} Si.cm^{-2} (●), 4x10^{17} Si.cm^{-2} (■) and 6x10^{17} Si.cm^{-2} (♦), annealed at 1100°C in N₂. The lines are a guide to the eye only.
Figure 4.22: Integrated emission intensity as a function of implant dose, for samples annealed at 1100°C in N₂, for temperatures of 90K (♦), 150K (●), 200K (■) and 290K (▲). The lines are a guide to the eye only.

The HARE sample with 8at % excess silicon exhibits similar behaviour as the implanted sample with a dose of 3x10¹⁷ Si.cm⁻², as observed previously.

4.2.2.3 Excitation Intensity Dependence

For these measurements, an excitation wavelength of 355 nm (3.49 eV) was used with a YAG laser as the excitation source. The power of the beam was varied by setting a transmission filter in front of the sample and changing its transmission coefficient. Transmission coefficients of 100 %, 68 %, 22 %, 8 % and 1 % were used for the excitation power dependence study. The corresponding value for the pump power of the laser have not been calculated as the aim here was to show if a saturation phenomena was taking place. Figure 4.23a shows the dependence of the intensity for the wavelengths where the peak emission is observed, while fig. 4.23b shows the dependence of the integrated intensity, as a function of transmission coefficient, for various doses.

The same trend was observed by Credo et al. in their experiments measuring the luminescence saturation of a single nanoparticle [48]. All doses show exactly the same behaviour, reaching saturation for the same pump power (transmission coefficient).
Figure 4.23: PL intensity (a) for peak wavelength emission for a sample implanted with 1x10^17 Si.cm^2, annealed at 1100°C in N_2, and (b) for various implant dose, annealed at 1100°C in N_2, as a function of transmission coefficient (%) at room temperature. The lines are a guide to the eye only.

The peak position is seen to blue-shift with increasing excitation intensity (fig. 4.24), shifting the emission from large nanocrystals (long wavelengths) to small nanocrystals (short wavelengths). This shift to higher energies means that the low energy side of the PL band is more easily saturated [49]. This is consistent with the fact that large nanocrystals have a bigger absorption cross-section and will therefore saturate faster than small nanocrystals. The population of smaller nanocrystals tend to be saturated at much higher pump powers than that of large nanocrystals [50].
4.2.3 Luminescence Decay

Luminescence decay give insight into the radiative and the non-radiative emission rates, as well as the influence of the environment on the recombination mechanism taking place.

4.2.3.1 Room Temperature

Figure 4.25 shows typical time-resolved photoluminescence signals as a function of wavelength. Two important results can be obtained from these measurements. Firstly, the PL decay exhibits a non exponential behaviour. Indeed it is described by the stretched exponential equation (equation 2.11). This result agrees with previous work on Si nanocrystals [51] and can generally be explained by the same theory utilised for porous Si [52]. It has been shown that the non exponential profile of the decay curves can be interpreted by a broad distribution of lifetimes. Such broad distributions are believed to be the result of a diffusive motion of the excited carriers [47]. For the case of porous Si, this is referred to as a trap-controlled hopping process [53] of excitons between nearby nanocrystals. The disordered environment created by the nanocrystals in the SiO$_2$ matrix causes a distribution of capture and/or release times for activated emission from temporary traps (nanocrystals).
The main feature of the time-resolved PL signals shown in fig. 4.25 is a reduction of the decay with decreasing wavelength. This decrease in PL decay lifetime is naturally explained by quantum confinement [54], since this leads to an increase of the bandgap leading to a shorter wavelength emission. But it also increases the oscillator strength of radiative transitions (as the oscillator strength varies as $1/d^{2.25}$ with $d$ being the diameter of the nanocrystal, which results in a decrease of the radiative lifetime. The reduction in the decay time across the PL band is evidence for inhomogeneous broadening of the emission spectrum.

Values of BETA ($\beta$) and TAU ($\tau$) can be obtained by fitting the stretched exponential equation to the decay curves (see section 2.3.3.1). The decay lifetimes are found to be in the $\mu$s range as expected for an indirect bandgap semiconductor. Their dependence on the observation energy is shown in fig. 4.26a and 4.26b, for a range of doses from $1 \times 10^{17}$ Si.cm$^{-2}$ to $6 \times 10^{17}$ Si.cm$^{-2}$. All doses follow the same trend, which is a decrease of $\tau$ and $\beta$ with increasing energy. $\beta$ values actually show a slight decrease over the energy range observed, and agree quite well with results from other groups [52, 55, 56]. Linnros et al [51] reports a constant value of 0.68 for their nanocrystals, although the trend exhibited was similar to those shown.

Figure 4.25: Room temperature decay luminescence spectra for a sample implanted with a dose of $3 \times 10^{17}$ Si.cm$^{-2}$, annealed at 1100°C in N$_2$, for various observation wavelengths.
Figure 4.26: a) Decay lifetime $\tau$ and b) Disorder parameter $\beta$, as a function of observation energy, at room temperature, for various samples annealed at 1100°C in N$_2$. The numbers given in the legend represents the implant dose multiplied by $10^{17}$ Si.cm$^{-2}$. The lines are a guide to the eye only.
A plot of decay rate (inverse of lifetime) versus photon energy is shown in fig. 4.27, for a dose of $3 \times 10^{17}$ Si.cm$^{-2}$. Since at room temperature, non-radiative recombination dominates [57], the decay luminescence spectrum illustrates more precisely the dependence of non-radiative recombination on the photon energy $E$. The decay rate given by $\tau = 1/W_{NR}$ follows well the equation:

$$W_{NR} = A \exp \left( \frac{E}{E_a} \right)$$  \hspace{1cm} (4.2)

The exponential dependence of $\tau$ on observation energy has been interpreted as evidence for an escape of the carriers from the nanocrystals, where they were confined, into the surrounding SiO$_2$ matrix [47, 52]. It has been suggested that the escape of carriers is likely to be a tunneling process to silicon oxide regions which is then followed by non-radiative recombinations [57]. Equation 4.2 accounts well for the experimental results of decay rates, with a value of $E_a = 0.28$ eV obtained for porous Si [57] and Si nanocrystals [51], or a value of 0.32 eV [52] for samples of different porosities. In our case, the values obtained for $E_a$ vary between $0.26 \pm 0.06$ eV (low dose) and $0.36 \pm 0.02$ eV (high dose), which is in excellent agreement with the data for porous Si.

![Graph](image.png)

**Figure 4.27:** Non-radiative decay rate as a function of observation energy at room temperature, for a sample implanted with a dose of $3 \times 10^{17}$ Si.cm$^{-2}$, annealed at 1100°C in N$_2$.

The dependence of $\beta$ on the $h\nu_{\text{obs}}$ is explained by the inter-nanocrystal energy barrier also being dependent on the bandgap of the nanocrystals [55, 56]. Recently, it
has been shown by Suemoto et al [58] that the escape process is a combination of tunnelling through, and thermal activation over a barrier. More details will be given in the temperature dependent, section 4.2.3.2.

For high doses ($\geq 2 \times 10^{17}$ Si.cm$^{-2}$), the decay rate becomes faster and $\tau$ approaches lowerer values as can be seen in fig. 4.28a, where the high doses are all on the same exponential, compare to the dose of $1 \times 10^{17}$ Si.cm$^{-2}$. This result has been reported earlier for porous Si sample with different porosities [52], but also recently for Si nanocrystals prepared by implantation [59]. For high doses, the density of nanocrystals present is quite high, and therefore the spacing between nanocrystals is reduced, favouring tunneling of excitons through the thin oxide, increasing the exciton motion. On the other hand, for low doses ($1 \times 10^{17}$ Si.cm$^{-2}$), the recombination is only affected by the properties of isolated nanocrystals whose energies correspond to the observation energy, and is totally independent of the surroundings. The excitons are then more localized. The existence of slightly lower values of $\beta$ for the high dose samples agrees with the model of an increased exciton motion due to a better interconnected network of nanocrystals (fig. 4.28b). In this study, it can be seen that the low dose regime consists of doses $< 1 \times 10^{17}$ Si.cm$^{-2}$. The fact that the highest dose of $6 \times 10^{17}$ Si.cm$^{-2}$ behave similarly to a low dose sample is due again to the bimodal character of its PL spectrum mentioned previously.

A comparison of PL decay for different doses was examined at an observation wavelength of 800 nm (the PL peak emission position). In this case, the average size of the nanocrystals is the same for all doses as the observation energy is fixed at 1.55 eV, only the density of nanocrystals is different between the samples. The value of $\tau$ decreases as the dose increases up to $4 \times 10^{17}$ Si.cm$^{-2}$, as can be seen in figure 4.29a. This relates to the escape of carriers being more important for a well interconnected network of nanocrystals, suggesting that as the density of nanocrystals increases, the distance between neighbouring nanocrystals facilitates tunneling of the excitons into the oxide matrix [57]. For higher hopping probabilities, the target nanocrystals are emptied faster due to a competing loss of excitons caused by hopping, therefore the value of $\tau_{\text{hop}}$ decreases, which leads to a reduction of $\tau$ [47]. The behaviour of $\beta$ in fig. 4.29b shows a decrease as a function of dose [59], as the total density of nanocrystals increases to create a better inter-connected network.
Figure 4.29: a) Decay lifetime $\tau$ and b) Disorder parameter $\beta$, as a function of implant dose, for an observation energy of 1.55 eV (800 nm) at room temperature, for annealed samples.
The same type of study was conducted for the HARE sample containing 8\% excess Si. The HARE sample was compared to an implanted sample of dose of 2\times10^{17} \text{Si.cm}^{-2} (excess Si \approx 12\text{at. \%}). The PL decay curve also exhibits a non-exponential behaviour, well fitted by the stretched exponential used previously. The values of $\beta$ and $\tau$ obtained with the fit are shown in fig. 4.30a and 4.30b, as a function of observation energy. Again, both sets of samples exhibit similar behaviour, a decrease of the decay lifetime as the observation energy increases.

**Figure 4.30:** a) Decay lifetime $\tau$ and b) Disorder parameter $\beta$, as a function of observation energy, at room temperature, for the 8\% excess Si HARE sample (triangle) and the sample implanted with 10at. \% excess Si (circle), annealed at 1100°C in N$_2$. The lines are a guide to the eye only.
The $\tau$ values are fairly close, although it can be noticed that the HARE $\tau$ values are lower than the implanted $\tau$ values. As the HARE sample is known to contain slightly bigger nanocrystals (total concentration $\sim 2.6\times10^{17}$ Si.cm$^{-2}$), therefore lower values of $\tau$ are expected, as exciton motion will be more important in the HARE sample than in the implanted sample. The same remarks can be made for the $\beta$ values. A value of $E_a=0.33\pm0.01$ eV is also obtained when fitting an exponential behaviour to the dependence of $\tau$ on the observation energy. This value agrees well with the previous results on Si nanocrystals [51] and with the values obtained for the implanted Si nanocrystals (from 0.26 eV to 0.36 eV).

### 4.2.3.2 Temperature Dependence

The temperature dependence of both $\tau$ and $\beta$ can be explained by a combination of 3 regimes [47]. In this study, it will only be possible to discuss two regimes: the intermediate temperature regime for temperatures between 60K and 200K, and the high temperature regime for temperatures above 200K (as 70K was the lowest temperature studied).

The variation of $\tau$ with temperature shown in fig. 4.31a (for an observation energy of 1.55 eV) follows the expected trend: a high value of $\tau$ for low temperature as $\tau\sim\tau_{\text{rad}}$ followed by a decrease as the temperature increases due to an increase in hopping process and non-radiative recombinations. Looking at the variations of $\beta$ in fig. 4.31b, a small increase can be noticed from 70K up to 150K, followed by a saturation at higher temperatures. The small increase observed in the low temperature part of the graph can be explained by the thermally activated diffusion process of the carriers out of the nanocrystals. At high temperature, the structure of the nanocrystals network is the only limiting factor to the hopping of carriers and as a consequence $\beta$ is independent of temperature, like for a pure hopping mechanism. A range of results for the dependence of $\beta$ on the temperature have been reported [47, 52, 53, 60]. Some show a value of $\beta$ which is independent of temperature [60], while others report an initial increase for temperature up to 150K, followed by a saturation [52, 53] and finally others report an increase of $\beta$ for temperature up to 60K, a plateau for temperatures between 60K and 200K, followed by a rapid increase up to 1 [47]. An explanation for such discrepancies is given in work on Monte Carlo simulations by Roman et al [47]. Another important
fact is that the dependence of $\tau$ and $\beta$ are quite similar for all the doses studied. Again, the low dose samples (dose $< 1 \times 10^{17} \text{Si.cm}^{-2}$) and the sample of dose of $6 \times 10^{17} \text{Si.cm}^{-2}$ show higher values of $\tau$ throughout the temperature range, which is expected due to the lower local density of nanocrystals present reducing the exciton motion (the total density would be higher for $6 \times 10^{17} \text{Si.cm}^{-2}$ but the local one is roughly the same as for the dose of $1 \times 10^{17} \text{Si.cm}^{-2}$). In this case, it can actually be seen that as the dose increases, the values of $\tau$ actually decrease.

![Figure 4.31: Decay lifetime $\tau$ and Disorder parameter $\beta$, as a function of temperature, for an observation energy of 1.55 eV (800nm) for samples implanted with a dose of $1 \times 10^{17} \text{Si.cm}^{-2}$ (*), $2 \times 10^{17} \text{Si.cm}^{-2}$ (●), and $3 \times 10^{17} \text{Si.cm}^{-2}$ (▲), annealed at 1100°C in N2. The lines are a guide to the eye only.](image)

94
The variations of $\tau$ and $\beta$ as a function of observation energy are plotted in figures 4.32a and 4.32b for a dose of $3 \times 10^{17}$ Si.cm$^{-2}$, for all temperatures. The dependence of $\tau$ is roughly the same, not being altered by the temperature.

![Graph](image)

**Figure 4.32:** a) Decay lifetime $\tau$ and b) Disorder parameter $\beta$, as a function of observation energy, for a sample implanted with $3 \times 10^{17}$ Si.cm$^{-2}$, annealed at 1100°C in N$_2$, for various temperatures. The lines are a guide to the eye only.

Such dependence has been interpreted as escape of the carriers from the nanocrystals into the surrounding amorphous matrix by tunneling processes [57]. Pavesi [52] reported that the dependence got weaker as the temperature was lowered, and even disappeared for temperatures less than 70K. They attributed this effect to a thermally activated inter-nanocrystal hopping of excitons in addition to the simple excitonic
escape through barriers [61]. Thermal activation dominates as the temperature is increased above the intensity maximum, while the tunnelling becomes significant at very low temperatures, when the radiative lifetime is long. In our case, a small weakening of the dependence can be observed, without being pronounced. But the exponential law does not properly fit the experimental data any longer as the temperature is decreased. It also has to be noted that the temperature dependence observed in this study is already weaker than the dependence observed by Pavesi [52] for their porous Si samples. The dependence of $\beta$ on $h_{\text{obs}}$ does not show significant changes as the temperature is varied. As the temperature increases, the exciton motion is activated, and the fact that the inter-nanocrystal energy barrier depends on the size of the nanocrystals present explains the dependence of $\beta$ on $h_{\text{obs}}$ [52]. The same behaviour of $\tau$ and $\beta$ upon temperature variations have been observed for all the different doses studied and the explanations of those behaviours are still valid.

Figure 4.33 shows the dose dependence of $\tau$ for a range of temperatures, for an observation energy of 1.55 eV, which corresponds to the PL peak emission position (~800 nm). For all temperatures studied, the decay lifetime is seen to decrease constantly with increasing doses up to $4 \times 10^{17}$ Si.cm$^{-2}$.

![Figure 4.33: Decay lifetime $\tau$ as a function of implant dose, for an observation energy of 1.55 eV (800nm), for temperatures of 70K ($\bullet$), 150K ($\Delta$), 200K ($\ast$) and 290K ($\blacklozenge$). The lines are a guide to the eye only.](image-url)
The trend seen at room temperature is still valid at low temperatures, simply exhibiting higher values of \( \tau \) due to the radiative recombinations taking over from the non-radiative ones present at room temperature. The case of \( 6 \times 10^{17} \text{Si.cm}^{-2} \) again shows an increase in \( \tau \), due to its peculiar characteristics explained in section 4.2.2.

A comparison of the values of \( \tau \) obtained for the HARE sample and the implanted sample shows a similar behaviour as a function of temperature, and as a function of energy (eV). Slightly higher values are obtained for the implanted case, as smaller nanocrystals and smaller density of nanocrystals characterise this sample compare to the HARE sample.

### 4.3 Size Distribution of the Nanocrystals

The study of the size distribution of nanocrystals embedded in a silicon oxide matrix is made difficult by the small Z-contrast between Si and SiO\(_2\), which render the detection of nanocrystals with smaller sizes impossible by TEM. Another important fact is that TEM only provides structural information. Whether the nanocrystals are optically active or not can not be answered by using TEM imaging. TEM is usually used to correlate the size distribution of the nanocrystals with the theoretical predictions. It has been shown that small nanocrystals can be found at both edges of the implantation layer, while the large nanocrystals main concentration is situated in the centre of the implanted area [22].

Figures 4.35, 4.36 and 4.37 show TEM imaging for a sample implanted with a dose of \( 4 \times 10^{17} \text{Si.cm}^{-2} \), annealed at 1100\(^\circ\)C in N\(_2\). Figures 4.35 and 4.36 show bright field images, with fig. 4.35 showing the implanted layer and fig. 4.36 showing Si nanocrystals, while fig. 4.37 shows dark field images. The dark field images allow to increase the contrast between the crystalline nanocrystals and the amorphous SiO\(_2\) matrix. Unfortunately, none of the TEM studies conducted have enabled an extraction of the size distribution of the nanocrystals. The only information contained in those TEM images is that nanocrystals are indeed present in the SiO\(_2\) layer.
Figure 4.35: Bright field TEM image of the implanted layer of a sample implanted with a dose of $4 \times 10^{17}$ Si.cm$^{-2}$, annealed at 1100°C in N$_2$. 
Figure 4.35: Bright field TEM image of a sample implanted with $4 \times 10^{17}$ Si.cm$^{-2}$, annealed at 1100°C in N$_2$. The arrows show some nanocrystals.
Figure 4.36: Dark field TEM image of a sample implanted with $4 \times 10^{17}$ Si.cm$^{-2}$, annealed at 1100°C in N$_2$. 
4.4 Conclusion

It has been shown that Ion implantation can be used for fabricating Si nanocrystals embedded in a SiO₂ matrix. Nanocrystals fabricated by such a technique exhibit strong luminescence around ~ 800 nm at room temperature, depending on the implant dose.

The dose dependence of the PL emission shows a red-shift of the peak position as the dose (size) increases. The red-shift is a direct effect of the quantum confinement effect as small nanocrystals are expected to emit at lower wavelengths. The integrated intensity shows an initial increase as the dose increases attributed to the increase in nanocrystal density. For doses above 2x10¹⁷ Si.cm⁻², the intensity decreases. Such behaviour is believed to result from the relative contribution of competitive processes, such as nanocrystal-nanocrystal interactions and non-radiative recombination, is seen to increase with the density and size of nanocrystals. By using an effective mass approximation approach (EMA) for the theoretical model, it is possible to fit the experimental PL spectrum and obtain valuable information on the nanocrystal characteristics.

The bandgap energy can be obtained by a Tauc plot analysis of the optical absorption data, as well as by the theoretical fit to the PL data, and both analysis have shown general agreement with the trends predicted by the quantum confinement effect, showing an increase in bandgap energy as the implant dose decreases. But a large discrepancy in the values of the energy bandgap exists between both methods. Although it is known that the site for the photo-generation of carriers is different from the one where radiative recombination takes place [32,33], it has been shown that the interpretation of the optical absorption data may not be reliable, due to scattering of light from small Si particles [34]. This assumption has been strengthened by the data from the multiple implant samples, which, while exhibiting stronger optical absorption density, result in smaller values for the energy bandgap, while the PL data clearly showed no change in size distribution. The larger the implant dose, the stronger the scattering loss, as seen in the optical absorption data.
The PL emission of the sample with a high dose of $6 \times 10^{17}$ Si.cm$^{-2}$ shows a peculiar behaviour, with a blue-shift of the PL peak position and an increase in PL intensity. Such PL characteristics are the quantum confinement effects of a decrease in size of the nanocrystals. In fact, the emission spectrum from this sample extends well beyond the sensitive region of the PMT used in this work. Preliminary measurements using other system have shown the existence of an emission peak around 1000nm, and might be due to a bimodal nanocrystal size distribution. Such a distribution could result from an increase of the growth rate due to a "proximity" effect among the particles for high implant dose samples, as stated by Bonafos et al [20] in a study of growth kinetics of the nanocrystals. In this work, because the detection system is limited to 850 nm, the high dose sample should behave very similarly to a low dose sample, as only the emission from the small nanocrystals will be detectable.

The temperature dependence of the PL intensity agrees well with the model of thermally-induced transitions between excitonic singlet and triplet states in Si nanocrystals [11, 12]. Its size dependence was consistent with such a model. The shift of the peak position to higher wavelengths as the temperature increases is due to temperature-dependent bandgap electron-phonon interactions [42], commonly observed in bulk Si.

The decay lifetime of implanted Si nanocrystals is of the order of $\mu$s which is characteristic of an indirect bandgap. The dose dependence of the decay characteristics ($\tau$ and $\beta$) can be explained by the carrier migration/diffusion or so called trap-controlled-hopping mechanism [52]. Carriers escape from the confined zone where they are generated to migrate between neighbours, towards a less confined region, may become trapped for an extended period of time and thereafter may migrate to another nanocrystal or into the silicon oxide matrix, where recombination may take place. The recombination in turn may be either radiative or non-radiative, the latter being dominant at room temperature. The exponential dependence of decay lifetime with confinement energy (which increases with decreasing sizes) supports a tunnelling mechanism for the non-radiative escapes [52, 57]. This process is also dependent on the size of the nanocrystals as well as the density.
Low implant dose samples behave almost like a system of isolated nanocrystals, the luminescence being limited by the bandgap of the nanocrystals. High implant dose exhibit characteristics consistent with a highly interconnected network of nanocrystals in which the trap-controlled-hopping mechanism has a strong influence on the decay rate [59].

At low temperatures (< 70K), the trapping of carriers at nanocrystals sites being very effective, the decay characteristics are solely influenced by the intrinsic properties of the nanocrystals. As the temperature is raised, the hopping mechanism is initiated and the topology of the nanocrystals network is now the limiting factor for the decay luminescence. The temperature behaviours of $\tau$ and $\beta$ are consistent with the trap-controlled-hopping mechanism introduced for room temperature results.

The HARE samples exhibited the same behaviour as the implanted samples.

References


CHAPTER 5

THE EFFECT
OF
RADIATION DAMAGE
ON LUMINESCENCE
Irradiation-induced defects in SiO₂ play an important role in the semiconductor industry and have been extensively studied [1]. In this study, the influence of defects on the luminescent properties of Si nanocrystals is assessed by irradiating SiO₂ samples containing nanocrystals with low (400 keV) and high (3 MeV) energy Si ions. The magnitude and nature of the energy loss is very different for these two cases and this provides an opportunity to distinguish any differences associated with the energy loss mechanism. The thermal stability of irradiation induced changes is also examined.

5.1 Irradiation Conditions

It has been shown that defects can be created by both nuclear and electronic energy loss processes and that the rate of defect production is much higher for nuclear processes [1]. It is also known that nuclear energy loss will damage Si nanocrystals and that electronic energy loss will preferentially create damage in the SiO₂ matrix. Studying two cases with very different nuclear and electronic energy loss contributions should enable such contributions to be distinguished.

Samples containing nanocrystals were irradiated with either 400 keV or 3 MeV Si⁺ ions to doses in the range 0.05 - 1.0x10¹⁴ Si.cm⁻². The energy loss as a function of depth, obtained by the TRIM code, is shown in figures 5.1a and 5.1b for both energies. For 400 keV ions (fig. 5.1a), the nuclear and electronic energy losses are approximately equal at the peak of the nanocrystal distribution (700 nm) and correspond to 140 eV/nm. In contrast, the energy loss of 3 MeV ions (fig. 5.1b) is dominated by electronic energy loss (~1500 eV/nm, nuclear energy loss ~ 30 eV/nm). Although the total energy loss is 5.5 times greater for 3 MeV ions than for 400 keV ions, it is important to note that the nuclear energy loss is 4.7 times greater for 400 keV ions than for 3 MeV ions, while the electronic energy loss 11 times greater for 3 MeV ions than for 400 keV ions. The relative contribution of nuclear and electronic energy losses is therefore very different for the two cases.

5.2 Effect of Irradiation on Emission

5.2.1 Quenching of the Nanocrystal Emission

Figure 5.2 shows typical photoluminescence spectra from an implanted sample for each fabrication steps of the nanocrystals. The as-implanted sample exhibits two main
Figure 5.1: Nuclear (—) and Electronic (—) energy loss as a function of depth for an implant at a) 400 keV and b) 3 MeV, obtained by the TRIM code. The nuclear energy loss is multiplied by a factor of 10 for the 3 MeV case. The arrow represents the peak of the nanocrystal distribution.
peaks, a well-known defect peak at approximately 640 nm [2], due to radiation-induced defects [3, 4], and a second at approximately 780 nm, associated with Si nanocrystals [2, 5, 6]. Following annealing at 1100°C, the PL emission is dominated by the nanocrystal-based emission and is centred at 806 nm. The peak emission wavelength is consistent [7, 8] with emission from nanocrystals of mean diameter ~3 nm, giving a nanocrystal density of ~4x10^{17} cm^{-3}. The nanocrystal emission is further enhanced by annealing in forming gas, as previously reported [8] (such effect will be looked in detail in chapters 6 and 7). The increase in emission suggests that non-radiative defects remain after annealing at 1100°C, and have a significant effect on the emission intensity [4].

![Typical Photoluminescence spectra for a sample implanted with 1x10^{17} Si.cm^{-2}](image)

1) As-implanted (x3), 2) Annealed at 1100°C in N₂ (x3) and 3) Annealed at 1100°C in N₂ + 500°C in (N₂+H₂).

Irradiation reduces the nanocrystal emission at 802 nm and increases the defect emission at 640 nm (fig. 5.3). Figure 5.4 compares the PL intensities of the defect and nanocrystal emission peaks for samples irradiated with 3 MeV ions. For the lowest dose, 5x10^{12} Si.cm^{-2}, only the nanocrystal emission is present but its intensity is already reduced to ~4% of that measured for the un-irradiated sample. [This corresponds to ~20% of the un-passivated intensity]. Defect emission (640 nm) is only observed for doses ≥1x10^{13} Si.cm^{-2}. This suggests that irradiation creates two types of defects, the well known radiative centre which give rise to the emission at 640 nm and a non-radiative defect that quenches the nanocrystal emission. The nanocrystal emission continues to decrease for higher doses but saturates for doses ≥3x10^{13} Si.cm^{-2}.
Figure 5.3: PL spectra for a sample implanted to a dose of $1 \times 10^{17}$ Si.cm$^{-2}$, annealed at 1100°C in N$_2$ and subsequently irradiated with 3 MeV Si ions.

Figure 5.4: Sample implanted to a dose of $1 \times 10^{17}$ Si.cm$^{-2}$ and subsequently irradiated with 3 MeV Si ions. Peak emission intensity as a function of implant dose for nanocrystal emission at 780 nm (♦) and defect emission at 650 nm (▲). The lines are a guide to the eye only.

It has previously been shown [6] that Si nanocrystals can be amorphised at displacement rates of 0.1-0.2 dpa, more than two orders of magnitude lower than that required to amorphise bulk Si. For 400 keV Si ions this corresponds to a dose of between $3 \times 10^{13}$ Si.cm$^{-2}$ (~0.06 dpa) and $1 \times 10^{14}$ Si.cm$^{-2}$ (0.18 dpa), in the range where the nanocrystal emission saturates. The mode of amorphisation was attributed to the
accumulation of point defects at the Si-SiO₂ interface [6], a process which in its initial stages was speculated to cause the observed reduction in nanocrystal emission. The point defects were assumed to form non-radiative defect centres at the nanocrystal-SiO₂ interface, quenching the nanocrystal emission. The present results are consistent with this model.

Surprisingly, the reduction in nanocrystal emission and the increase in defect emission shows a similar dose dependence for both 400 keV and 3 MeV irradiations, as shown in fig. 5.5a and 5.5b, despite significant differences in the magnitude and mechanism of energy loss. For this to be the case, the defects responsible must be produced at similar rates in both cases. It has been shown [1] that defects are created more efficiently in SiO₂ by nuclear energy loss processes than by electronic energy loss processes. This can account for the present results if it is assumed that defect production is ~10 times lower for electronic than for nuclear energy loss. The fact that the 400 keV irradiation is dominated by nuclear energy loss means that, for the 3 MeV irradiation to affect the PL similarly to the 400 keV irradiation, its predominant electronic energy loss (~10 times the nuclear energy loss of 400 keV ions) has to be 10 times less effective for defects creation. This assumption is supported by ellipsometry measurements conducted on thermally grown SiO₂ after each step of the processing, shown in fig. 5.6.

Amorphous SiO₂ has a refractive index of ~ 1.46, which upon Si irradiation increases to 1.52, due to compaction of the SiO₂ matrix [9]. After annealing at 1100°C in N₂ to form the Si nanocrystals, the refractive index of the layer is reduced to a value intermediate between the initial and as-implanted values, due to relaxation of the SiO₂ network [1]. Subsequent irradiation of the Si nanocrystal/SiO₂ system with 400 keV (or 3 MeV) Si ions results again in compaction of the system, which increases as the irradiation dose increases, consistent with previous work [1, 9]. It is well known that compaction is due to nuclear and electronic energy loss, with nuclear energy loss being more effective than electronic energy loss [1, 11]. Since figure 5.6 shows that both energies reflect roughly similar increase in refractive index, it agrees with the previous assumption made that the defect production rate is about ~ 10 times lower for the electronic energy loss compared to the nuclear energy loss.

Another effect of irradiation on the PL emission of the nanocrystals, observed at
Figure 5.5: Peak emission intensity as a function of irradiation dose for nanocrystal emission at a) 780 nm and defect emission at b) 640 nm, for 400 keV (●) and 3 MeV (■) Si irradiation. The lines are a guide to the eye only.
802 nm, is a blue-shift of the emission correlated with the irradiation dose. For the lowest dose of $5 \times 10^{12}$ Si.cm$^{-2}$, no shift of the peak position is observed. As the irradiation dose increases, the blue-shift increases accordingly, so that for example, for a dose of $3 \times 10^{13}$ Si.cm$^{-2}$, the peak emission is now centred approximately at 770 nm. In fact, after irradiation for doses larger than $5 \times 10^{12}$ Si.cm$^{-2}$, the PL spectrum is very similar to the one obtained for the as-implanted sample, with the two peaks centred roughly at the same position. This emission shift is believed to be associated with the amorphisation process as well, as it shows the same dose dependence.

![Graph of refractive index vs. dose](image)

**Figure 5.6:** Refractive index measured by ellipsometry for amorphous SiO$_2$ ($\blacktriangle$), as-implanted with a dose of $1 \times 10^{17}$ Si.cm$^{-2}$ ($\times$), annealed at 1100°C in N$_2$ ($\bigstar$), and subsequently irradiated with 400 keV ($\bullet$) and 3 MeV ($\blacksquare$) Si ions, as a function of Si dose. The lines are a guide to the eye only.

All radiation-induced-damage have exhibited a dose dependence [9, 10], resulting in major differences in the damaged region behaviour following low or high ion dose irradiation [11].

### 6.2.2 Recovery of the Nanocrystal Emission

#### 6.2.2.1 Annealing Behaviour

Figures 5.7a and 5.7b show the effect of annealing on the intensity of the defect and nanocrystal emissions for samples irradiated to a dose of (a) $1 \times 10^{13}$ Si.cm$^{-2}$ and (b) $3 \times 10^{13}$ Si.cm$^{-2}$. As the temperature increases, the defect-related peak gradually decreases and the nanocrystal-related peak increases in intensity.
Figure 5.7: PL spectra for a sample implanted to a dose of $1 \times 10^{17}$ Si.cm$^{-2}$, annealed at 1100$^\circ$C in N$_2$, irradiated with 3 MeV Si ions to a dose of (a) $1 \times 10^{13}$ Si.cm$^{-2}$ and (b) $3 \times 10^{13}$ Si.cm$^{-2}$, and annealed in N$_2$, at the temperatures shown.
Figure 5.8: Peak emission intensity as a function of anneal temperature for defect emission (a) at 650 nm and nanocrystal emission at (b) 780 nm, for a sample implanted to a dose of $1 \times 10^{17}$ Si.cm$^{-2}$, annealed at 1100°C in N$_2$ and subsequently irradiated with 400 keV (●) and 3 MeV (■) Si ions to a dose of $1 \times 10^{13}$ Si.cm$^{-2}$. The lines are a guide to the eye only.
Again, the results show similar trends for samples damaged by 400 keV and 3 MeV ions. The defect emission is already reduced by annealing at 200°C and is eliminated by annealing to temperatures in the range 600–800°C (fig. 5.8a and 5.8b). The nanocrystal emission remains largely unaffected by annealing up to 600°C, but increases rapidly for temperatures between 800°C and 1000°C. Previous experiments [12] have shown that nanocrystals rendered amorphous by irradiation do not recrystallise below ~775°C. This would suggest that the recovery of the nanocrystal emission for temperatures in the range 600-800°C is associated with crystallisation, at least for samples irradiated to higher fluences. This is supported by the fact that recovery occurs at much lower temperatures (400–600°C) for samples irradiated to the lowest dose. The extent of recovery after annealing to 1000°C also depends on the irradiation dose, being greater for samples irradiated to lower doses. This supports evidence from H-passivation experiments that non-radiative defects remain after annealing at 1000°C.

The results are consistent with a previously proposed model [12] in which point defects produced by irradiation accumulate at the nanocrystal surface, leading to amorphisation at low displacement rates (0.1–0.2 dpa). These showed distinctly different temperature dependencies, with the defect emission eliminated by annealing to temperatures in the range 600–800°C, and the nanocrystal emission showing only partial recovery after annealing to 1000°C.

Annealing back in nitrogen also affects the peak position of the emission, as can be seen in fig. 5.9 for irradiation at 400 keV. The peak position red-shifts slowly back to its pre-irradiation value of 802 nm as the temperature increases. The recovery seems to happen for all doses for a temperature around 500°C, and is therefore independent of irradiation dose. An exception can be seen for the two highest doses of 1x10^{14} Si.cm^{-2} and 3x10^{13} Si.cm^{-2} where, for temperatures between 600°C and 800°C, the emission is now red-shifted compared to the pre-irradiation position of 802 nm. This red-shift is also dependent on the irradiation dose, as it is greatest for the highest dose. A possible explanation could be a slight growth of the nanocrystals during the recrystallisation process (a shift of 40 nm represents a growth of 0.3 nm [13], although this seems unlikely as a dose of 1x10^{14} Si.cm^{-2} represents ~ 0.005 % excess Si introduced (see table 4.2) and a temperature of at least ~ 800°C is usually required for growth of the nanocrystals [14]. An alternative explanation might be that the quality (better
crystallinity) of the larger crystals is improved by the amorphisation/recrystallisation process, which then results in a red-shift of the PL emission.

![Figure 5.9: Nanocrystal PL peak position as a function of anneal temperature for a sample implanted to a dose of $1 \times 10^{17}$ Si.cm$^{-2}$, annealed at 1100°C in N$_2$, and subsequently irradiated with 400 keV Si ions, with a dose of $5 \times 10^{12}$ Si.cm$^{-2}$ (♦), $1 \times 10^{13}$ Si.cm$^{-2}$ (■), $3 \times 10^{13}$ Si.cm$^{-2}$ (●) and $1 \times 10^{14}$ Si.cm$^{-2}$ (▲).](image)

**Figure 5.9:** Nanocrystal PL peak position as a function of anneal temperature for a sample implanted to a dose of $1 \times 10^{17}$ Si.cm$^{-2}$, annealed at 1100°C in N$_2$, and subsequently irradiated with 400 keV Si ions, with a dose of $5 \times 10^{12}$ Si.cm$^{-2}$ (♦), $1 \times 10^{13}$ Si.cm$^{-2}$ (■), $3 \times 10^{13}$ Si.cm$^{-2}$ (●) and $1 \times 10^{14}$ Si.cm$^{-2}$ (▲).

### 5.2.2.2 Annealing in Hydrogen ambient

After the annealing sequence conducted in N$_2$ ambient, another anneal at 500°C in forming gas was performed. The reason being that, prior to the second irradiation, the samples had been annealed at 500°C in forming gas, to passivate defects present in the Si-nanocrystals/SiO$_2$ system. Further irradiation might have caused the hydrogen introduced at such defect centres to actually be freed or to move to other defect sites, therefore having a lower impact on the PL intensity observed. Therefore, by reintroducing the hydrogen in the system, it will be possible to check if further passivation takes place, which will be another indication of the presence of defects after high temperature anneals.

As can be seen in figure 5.10, subsequent hydrogenation has a strong effect on the PL intensity. The extent of recovery is stronger for the low dose irradiation, and diminishes as the irradiation dose increases. Hydrogen increases the PL intensity by a factor of 2 to 3 in all cases, but does not restore the PL intensity to its pre-irradiation level. The extent of the recovery is less for the high dose case.
5.3 Irradiation-induced Defect Emission

In this section, amorphous SiO₂ substrates were subjected to the same irradiation energies as the Si nanocrystals/amorphous SiO₂ (a-SiO₂) system studied in the previous section. The motivation was to try to answer the following question: does the presence of the nanocrystals in the system prior to irradiation have any effect on the radiation damage caused in the SiO₂ matrix? Thermally grown SiO₂ wafers were irradiated with either 400 keV or 3 MeV Si ions at room temperature, for the same range of doses previously investigated.

Figure 5.11 shows the PL spectra after the 3 MeV irradiation, as a function of dose. Both previously observed peaks are present in this case, which leads to the conclusion that they are both defect-related emissions. In this case, the implanted doses being quite small, irradiation-induced nanocrystal growth as an explanation for the emission peak ~ 770 nm seems very unlikely. The oxygen-vacancy-defect-related emission at 640 nm exhibits the same behaviour as a function of dose, mainly an increase in intensity as the dose increases. For the dose range studied, the emission at 770 nm is actually saturated, and does not depend on irradiation dose.
For a better perception, the PL spectra of samples with and without nanocrystals are plotted on the same graph in figure 5.12, with normalised intensities. It is quite clear that the main difference lies in the emission peak at 770 nm, especially for low implantation dose, which is the case where the nanocrystal emission is less perturbed by the subsequent irradiation.

![Figure 5.11: PL spectra of amorphous thermally grown SiO$_2$ wafers, irradiated with 3 MeV Si ions.](image)

The thermal stability of the emission observed from the irradiated amorphous SiO$_2$ matrix has also been studied, by subjecting the samples to a further anneal in N$_2$ ambient for 1h, increasing the temperature from 200°C up to 800°C. As can be seen in fig. 5.13, for a dose of 1x10$^{13}$ Si.cm$^{-2}$, both peak intensities decrease rapidly for 200°C, and keep decreasing until the signal is barely observable. Both emissions are believed to be defect related. In the case where nanocrystals were present in the SiO$_2$ matrix prior to irradiation (section 5.2), the emission at 770 nm was probably a combination of defect-emission and nanocrystal emission, which would explain the shifting of the peak as a function of temperature and dose. The hydrogenation of the sample by annealing at 500°C in (H$_2$+N$_2$) was not conducted for those samples, as such process only affects the nanocrystals related emission [8].

Therefore, it can be deduced that the presence of pre-existing Si nanocrystals in the SiO$_2$ matrix does not modify the irradiation-induced damage contribution to the
Figure 5.12: PL spectrum of amorphous SiO$_2$ (—) and a sample implanted to a dose of $1 \times 10^{17}$ Si.cm$^{-2}$ annealed at 1100°C in N$_2$ + 500°C in (N$_2$+H$_2$) (—), irradiated with 3 MeV Si ions with a dose of (a) $5 \times 10^{12}$ Si.cm$^{-2}$ and (b) $3 \times 10^{13}$ Si.cm$^{-2}$. The intensities are normalised.
emission. The only effect observed is the modification of the nanocrystals themselves upon further irradiation, but the host matrix shows the same optical properties. Both energies again show exactly the same behaviour, which agrees well with the results stated in the previous section (5.2).

![PL spectra](image)

**Figure 5.13:** PL spectra of amorphous thermally grown SiO₂ wafer, irradiated with 3 MeV Si ions to a dose of 1x10¹³ Si.cm⁻², annealed in N₂, as a function of anneal temperature.

### 5.4 Conclusion

The role of irradiation-induced defects on the photoluminescence from Si nanocrystals was investigated by irradiating samples with low and high energy Si ions. The PL intensity was reduced by the irradiation and, unexpectedly, showed a similar dose dependence for both low and high irradiation energy, even though these ions had different dominant energy loss mechanisms. Electronic energy loss is expected to produce defects predominantly in the SiO₂ matrix or at the SiO₂/Si interface, and nuclear energy loss is expected to produce defects in both the SiO₂ and the Si nanocrystals. The fact that ions with either dominant electronic or nuclear energy loss exhibit the same dose dependence therefore suggests that the defect production rate for electronic energy loss is lower than for nuclear energy loss. The quenching of the nanocrystal emission and its sensitivity to dose for both sets of irradiation energies is consistent with the preferential accumulation of non-radiative defects at the nanocrystal-SiO₂ interface. Indeed, the fact that both sets of irradiation energies affect the
nanocrystals PL in a similar way, while only nuclear energy loss is known to damage nanocrystals, conveys that the damage creation is located at the interface of the nanocrystals and SiO$_2$. The existence of such defects was also supported by the annealing behaviour of the nanocrystal and defect emissions.

The nanocrystal related emission showed full recovery after annealing at temperatures of 1000°C in the case of low irradiation doses, while high dose irradiated samples showed a slight recovery. A red-shift of the peak emission was also observed in the case of high irradiation doses. It is believed that the quality of large nanocrystals is improved by the amorphisation/recrystallisation process due to the irradiation-annealing steps (reduction of non-radiative sites), giving rise to the shift in the emission towards longer wavelength (large nanocrystals).

Finally, it is interesting to note that the effect reported in this chapter can explain results reported by Franzo et al [17], which they appear to have misinterpreted as due to nanocrystal-Er interaction. In their case, Er implantation was carried out after the formation of Si nanocrystals, followed by annealing at ~ 900°C to remove the radiation damage cause by the Er implant. Their implantation doses were comparable to those in the present study, but Er being a heavier element than Si, the Er irradiation is expected to result in greater defect production. Following the second anneal, they observe a reduction in the Si nanocrystal emission with increasing Er concentration, while an emission peak around 1.54 μm increases correspondingly. The authors attribute the reduction in the nanocrystals emission to energy transfer between the nanocrystals and erbium ions [17]. In fact, the present work would suggest that the reduced Si nanocrystal emission is simply due to irradiation damage caused by the Er implant.

References


CHAPTER 6

HYDROGEN PASSIVATION
- MECHANISMS -
The introduction of hydrogen is known to passivate non-radiative defects and increase the PL intensity from nanocrystals. This chapter looks at the passivation process and its dependencies in an attempt to optimise and understand it.

### 6.1 The Passivation Process

Hydrogen passivation was achieved through thermal annealing. Samples were initially annealed at high temperature (1100°C) to form the nanocrystals, and the introduction of hydrogen was achieved by a subsequent anneal in forming gas (5%H₂ + 95%N₂). The most obvious consequence of H-passivation is illustrated in figure 6.1 which shows typical PL spectra before and after passivation, for a sample implanted to a dose of 1x10¹⁷ Si.cm⁻².

![Figure 6.1: Room temperature photoluminescence from Si implanted SiO₂ (1x10¹⁷ Si.cm⁻²) after annealing at 1100°C in N₂ and after an additional anneal at 500°C in (N₂+H₂).](image)

In this case, the PL intensity is increased by a factor of 4 after passivation, an effect that is attributed to the passivation of non-radiative surface states (P₆ centres) at the Si nanocrystal/SiO₂ interface [1, 2].
6.1.1 Temperature dependence

The temperature dependence of the passivation anneal was studied for temperatures up to 800°C by employing isochronal anneals of 1h duration. At higher temperatures, further growth of the silicon nanocrystals was observed.

The effect of annealing temperature was studied for two samples implanted with doses of $2 \times 10^{17}$ Si.cm$^{-2}$ and $4 \times 10^{17}$ Si.cm$^{-2}$ respectively. As shown in fig. 6.2, both samples behave similarly. As the temperature is raised from 20°C up to 500°C, the intensity of the PL (red-visible PL around 800 nm) increases, reaching a maximum value for temperatures in the range 500-600°C. Above 600°C, the PL intensity saturates. The fact that both the low and high dose samples behave similarly implies that the diffusion mechanism and kinetics are independent of the size distribution of the nanocrystals present in the matrix. The magnitude of the enhancement is much stronger for the high dose sample compared to the low dose one, a feature that will be discussed in more detail in Chapter 7. These data agree qualitatively with similar work by Brower [3, 4].

For temperatures up to ~ 500°C, passivation should be dominated by the reaction described by equation 2.13. At higher temperatures, around 500-600°C, both passivation (equation 2.13) and depassivation (equation 2.15) reactions are expected to compete but since the samples are cooled to room temperature in the hydrogen-rich ambient, the saturation level is maintained.

An Arrhenius plot of the data over a limited temperature range is shown in figure 6.3. A straight line was fitted through the data and an activation energy of $0.21 \pm 0.02$ eV determined for the passivation of non-radiative defects in our samples. (For the corresponding HARE sample, a value of $0.23 \pm 0.02$ eV is obtained). Similar values have previously been determined for lower energy implants [M. L. Brongersma, private communication].

All subsequent passivation anneals were conducted at a temperature of 500°C.
Figure 6.2: Increase in emission intensity as a function of the forming gas anneal temperature for a sample of dose of $2 \times 10^{17}$ Si.cm$^{-2}$ ($\bullet$) and $4 \times 10^{17}$ Si.cm$^{-2}$ ($\ast$), annealed at 1100°C in N$_2$.

Figure 6.3: Arrhenius plot of the PL intensity as a function of annealing temperature for the forming gas anneals at temperatures between 250°C and 500°C for a sample implanted with $2 \times 10^{17}$ Si.cm$^{-2}$ annealed at 1100°C in N$_2$. 
6.2.2 Time dependence

The time dependence of the passivation process was investigated at a temperature of 500°C. Figure 6.4 shows the PL intensity for samples implanted with doses of $2 \times 10^{17}$ Si.cm$^{-2}$ and $4 \times 10^{17}$ Si.cm$^{-2}$, as a function of annealing time. The intensity increases for annealing time up to 60 mins, and then saturates as the duration of the anneal is further increased.

![Figure 6.4: Increase in emission intensity as a function of annealing time in forming gas at 500°C, for a sample of dose of $2 \times 10^{17}$ Si.cm$^{-2}$ (♦), $4 \times 10^{17}$ Si.cm$^{-2}$ (•) and for a HARE sample of 8% excess Si (■). In all cases, nanocrystals were formed by annealing at 1100°C in N$_2$.](image)

The diffusion of hydrogen in the 1 μm thick SiO$_2$ layer is a fast process, requiring only a few ms to diffuse throughout the layer at room temperature (see chapter 2). Thus the rate-limiting step in the chemical kinetics of passivation of non-radiative defects is not the diffusion of H$_2$ to the defects but rather the direct reaction between H$_2$ and the defects [3, 4].

As noted in chapter 2, the reaction rate for the passivation reaction ($P_b + H_2 \rightarrow HP_b + H$) is given by:

$$\frac{d[P_b]}{dt} = -k_f[H_2][P_b]$$  \hspace{1cm} (6.1)
where \([P_b]\) is the defect concentration at the interface, \([H_2]\) is the hydrogen concentration and \(k_f\) is called the forward rate constant [4, 5]. The rate of passivation is directly proportional to the concentration of \(H_2\) at the interface as seen in equation (6.1) [4, 5]. In the present case, as the hydrogen diffusion is very fast, the concentration of \(H_2\) can be considered constant throughout the layer, therefore, the unpassivated defect concentration can be expressed as:

\[
[P_b] = [P_b]_0 \times \exp^{-\frac{1}{\tau_c}}
\]

with \([P_b]_0\) corresponding to the concentration of defects at \(t=0\), and \(\tau_c = k_f[H_2]\) being a characteristic annealing time. By fitting the data in fig. 6.4, values of \(\tau_c\) were estimated to be ~18 min.

No further increase of the PL efficiency is observed when a second anneal in forming gas is performed (1h anneals). It can therefore be assumed that the hydrogen has effectively passivated the non-radiative recombination pathways [6] during the first anneal, and that this is achieved after 1 hour at 500°C.

**6.2 Effect on the Optical properties**

Nanocrystals contain a large concentration of surface structural defects due to the splitting of \(\equiv Si-O-Si\equiv\) bonds during nanocrystal formation. In fact, non-radiative recombination has been reported to be the dominant process at room temperature [7, 8]. Passivating such defect states should therefore be beneficial for the luminescence efficiency, as non-radiative recombination will be reduced, favouring radiative recombination from the Si nanocrystals.

**6.2.1 Room Temperature Photoluminescence**

**6.2.1.1 Characteristics of the PL spectra**

The effect of hydrogen passivation on the PL emission for a sample implanted with a dose of \(3\times10^{17}\) Si.cm\(^{-2}\) is shown in fig. 6.5. This figure compares the PL spectra from a sample annealed at 1100°C in \(N_2\) ambient, before and after hydrogen passivation. (To enable ready comparison of peak positions, the spectrum from the unpassivated
sample is also shown scaled by a factor of five). The emission from the unpassivated sample exhibits a broad PL peak centred around 800 nm.

![Graph showing photoluminescence spectra](image)

**Figure 6.5:** Room temperature photoluminescence from Si implanted SiO$_2$ (3x10$^{17}$ Si.cm$^{-2}$) after annealing at 1100°C in N$_2$ and after an additional anneal at 500°C in (N$_2$+H$_2$). The unpassivated spectrum is also shown scaled by a factor of 5 for comparison.

The comparison of these spectra illustrates the most obvious consequence of hydrogen passivation which is a factor of five increase in emission intensity. This effect has been widely reported [1, 2, 9, 10] and is believed to result from the passivation of non-radiative defects at the nanocrystal/oxide interface (dangling bonds). Non radiative recombination is the dominant mechanism for carrier recombination at room temperature [7, 8], and therefore limits radiative emission. By passivating the non-radiative centres, the radiative recombination probability is enhanced, and is manifest as an increase in PL emission efficiency from Si nanocrystals. Only a small fraction of nanocrystals luminesce before hydrogen passivation, implying that most of them contain non radiative defects. This has been noted by other groups and discussed in terms of dark and bright nanocrystals [7]. Dark nanocrystals refer to nanocrystals which have at least one non-radiative defect, while bright nanocrystals consist of nanocrystals with no defects.

Also evident from figure 6.5 is a red-shift of the PL spectrum after passivation, which for the 3x10$^{17}$ cm$^{-2}$ implant shown, amounts to a shift of about 40 nm in the peak
emission wavelength. Since the emission peak is known to depend on particle size [11], a shift of this magnitude could result from the growth of nanocrystals during the 500°C passivation anneal. Indeed, such a shift would only require an increase in average crystallite size $\Delta R = R^*\Delta E_c/2(E-E_g)$ [12], assuming that the confinement energy $E_c$ ($E_c = E-E_g$) varies with $d^2$ where $d$ is the crystallite diameter ($E_g$ corresponds to the bandgap energy). On this basis, the spectral shift corresponds to an increase in size of $\sim0.3$ nm [12, 13]. However, for a sample annealed at 1100°C in N$_2$, a 500°C subsequent anneal in N$_2$ ambient does not produce such a shift (fig. 6.6), implying that crystal growth is not responsible for the red-shift observed. This is supported by the PL data from samples annealed in H$_2$ within the temperatures range 20-800°C. These spectra show that the red-shift reaches a maximum at a temperature of 500°C and remains constant for higher temperature anneals. The red-shift therefore appears to be correlated with the passivation process and is inconsistent with crystal growth. Further evidence for this assertion is provided by the optical absorption data, which exhibits no change upon hydrogenation. As the absorption mechanism takes place in the nanocrystals themselves [14], a change in size or structure (bandgap energy) would be expected to result in a change in the absorption spectrum.

![Figure 6.6: Room temperature photoluminescence spectra from Si implanted SiO$_2$ (2x10$^{17}$ Si.cm$^{-2}$) annealed at 1100°C in N$_2$, 1100°C in N$_2$ + 500°C in N$_2$ and 1100°C in N$_2$ + 500°C in forming gas (N$_2$+H$_2$).](image)

From the previous results, it can be inferred that neither the thermal treatment at 500°C nor the presence of hydrogen results in further growth of the nanocrystals. Cody
[15] also referred to the absence of changes of the characteristics of the optical absorption upon hydrogenation. They argue that the red-shift is a consequence of hydrogen on the emission mechanism itself, not on the structure of the nanocrystals, which agrees with previous results.

### 6.2.1.2 Reversibility-Stability

At room temperature, hydrogen is stable in the oxide. Fink reported no change in the hydrogen distribution in silica over long times, indicating that detrapping and out diffusion are not significant at RT [16]. A study of the stability of passivated samples over time agrees well with such reports. Samples were passivated by hydrogen and then stored in air at room temperature. PL measurements were conducted 6 months and 1 year later. The increase in PL intensity due to passivation remains unchanged. In contrast, heating at temperatures sufficiently high to detrap H leads to changes in the PL spectrum.

Both the intensity enhancement and the red-shift observed after passivation are reversible [2, 17], with PL spectra returning to their pre-passivation form when H is removed by subsequent annealing in N\textsubscript{2}. This occurs for temperatures above approximately 600°C, as shown in fig. 6.7, and is consistent with the release of H from Si-H bonds. Indeed, passivated Pb centres are known to dissociate in vacuum at temperature in excess of 550°C [18] following the dissociation equation (2.17) shown earlier.

That the effects are reversible demonstrates that these characteristics are a direct consequence of the hydrogen presence in the sample [19]. It also confirms that annealing in forming gas does not induce further growth of the crystallites and that the red-shift results from a change in the optically active size distribution [17], not the physical size distribution.

### 6.2.2 Luminescence Lifetime

Figures 6.8a and 6.8b show the effect of hydrogen passivation on the luminescence lifetime as a function of wavelength for a sample implanted with 3x10\textsuperscript{17} Si.cm\textsuperscript{-2}. Agreeing with previous results, the lifetime is longer at longer wavelengths [8, 20, 21], and has a non-exponential shape [20, 22, 23]. However, all the decay curves,
Figure 6.7: Integrated photoluminescence intensity (a) and peak wavelength (b) as a function of annealing temperature in N₂ for a passivated sample (2x10¹⁷ Si·cm⁻²) initially annealed at 1100°C in N₂ and 500°C in forming gas (N₂+H₂). The single point at T=20°C represents the value obtained from an unpassivated sample, i.e. one annealed at 1100°C in N₂.
irrespective of the wavelength, exhibit a slower decay rate after passivation. This increase is consistent with the passivation of non-radiative channels for carrier decay, therefore enhancing the radiative recombination [8] (intensities of the decay curves have been normalised, but the passivated sample does show an important increase in intensity as well as an increase in decay lifetime). Such results are consistent with equation 2.12 and have previously been observed for porous Si passivated by H [24, 25].

The luminescence lifetime increases from a 1/e value of 12 μs before passivation, to 23 μs after passivation, for an observation wavelength of 800 nm. This is particularly interesting since it implies that luminescence is being detected from nanocrystals that contain defects. For this to be the case, the lifetimes of the radiative and non-radiative channels must be comparable. An estimate of these lifetimes can be made from a rate equation [22] describing excitation and decay in a simple two-level energy scheme such as that shown below,

\[
\frac{dN}{dt} = R - \frac{N}{\tau_R} - \frac{N}{\tau_D} \tag{6.3}
\]

where \(N\) is the concentration of carriers in the upper energy level, \(R\) is the excitation rate, \(\tau_R\) is the lifetime of the radiative transition and \(\tau_D\) is the lifetime of the non-radiative channel. The measured lifetime, is then given by:

\[
\frac{1}{\tau} = \frac{1}{\tau_R} + \frac{1}{\tau_D} \tag{6.4}
\]

If after passivation, \(\tau_D\) is assumed to be infinite, i.e. no non-radiative defect-related recombination, then the measured luminescence lifetime is equal to the radiative lifetime of 23 μs. From the lifetime of the unpassivated material it follows that \(\tau_D\) is ~ 25 μs.
Figure 6.8: Luminescence lifetime measured at room temperature, for a sample implanted with 3x10^{17} Si.cm^{-2}, annealed at 1100°C in N₂, a) before and b) after H-passivation.
Lannoo et al [26] have mentioned that the non-radiative recombination is much faster than the perfect crystallite radiative recombination and that the presence of a dangling bond at the surface of a crystallite is enough to kill its visible luminescence above 1.1 eV (non-radiative recombination takes place). The present results suggest otherwise.

Using the stretched exponential equation to fit the data (see equation 2.11), the values obtained for the unpassivated sample are $\tau = 16.2 \, \mu s$ and $\beta = 0.62$, and for the corresponding passivated sample $\tau = 29.8 \, \mu s$ and $\beta = 0.64$. The values of $\tau$ ($\mu$s) are in agreement with the 1/e values. Regarding the $\beta$ values, there is little change effected by passivation. Variations in $\beta$ translate to a variation in the interconnected network of nanocrystals, which can be associated with a variation in the distance between nanocrystals. Therefore, such results for $\beta$ imply that there is no variation in the effective size or density of nanocrystals after hydrogenation.

The exponential dependence of $1/\tau=W_{NR}$ on the observation energy (wavelength) observed previously for unpassivated sample (equation 4.2) remains for passivated samples, as shown in fig. 6.9.

**Figure 6.9:** Non-radiative decay rate as a function of observation energy for a sample implanted with $3 \times 10^{17}$ Si.cm$^{-2}$, annealed at 1100°C in N$_2$, before (♦) and after (▲) H-passivation.
The value of $E_a$ obtained by fitting this equation to the experimental data is $0.33 \pm 0.06$ eV compared to the value of $E_a = 0.32 \pm 0.06$ eV obtained for unpassivated sample. Only the pre-factor, $A$, varies significantly, from $53 \text{ s}^{-1}$ to $33 \text{ s}^{-1}$ for the unpassivated and passivated sample, respectively.

Vial [8] has reported similar results for porous Si samples oxidised to various levels, with a value of $A$ of $40 \text{ s}^{-1}$ and $E_a = 0.28$ eV for highly oxidised samples. Using the model of escape of the carriers through oxide barriers, Vial et al [8] showed that the dependence of $E_a$ upon the barriers’ characteristics (height and width) is quite weak (square root) whereas the pre-factor, $A$, depends strongly on such parameters. It is also possible to obtain a value for the width of the oxide barriers using this model, which amounts to $4 \text{ nm}$ in the present case (before and after passivation). This agrees reasonably well with the value for the inter-nanocrystal separation of $3.47 \text{ nm}$ determined for this sample in Chapter 4 (see table 4.2), using theoretical fitting of the PL spectra.

### 6.3 Detection of Hydrogen in the samples

Fourier Transform Infrared (FTIR) spectroscopy was used to study thick thermally grown oxide samples implanted under the same conditions as fused silica substrates. Usually, the FTIR technique is sensitive to Si-H bonds and is well suited to quantitative analysis. Several peaks due to hydrogen in different configurations should be visible, such as: stretching (2090-2145 cm$^{-1}$), wagging (630-670 cm$^{-1}$) and scissor (910 cm$^{-1}$) Si-H$_n$ modes, as well as O$_2$-Si-H modes (880 and 2250 cm$^{-1}$) and the O$_2$-Si-H$_2$ (950 cm$^{-1}$) mode. However, for the present sample, no H-related absorption peaks were detected. The detection limit of the FTIR system was approximately $10^{19} \text{ cm}^{-2}$.

ERDA was also employed in an attempt to detect the H. For this technique, the fused silica substrates samples were used. Again, no H was detected. It is therefore believed that the H content in our sample is very low, less than 0.1 % which is the detection limit of ERDA.
6.4 Conclusion

Although the photoluminescence intensity from Si nanocrystals is quite strong, it has been shown that passivation by H results in a significant increase in emission intensity. Numerous experimental results (optical absorption data, decay rate, annealing studies, reversibility) have shown that no further growth of the nanocrystals was induced by thermal annealing in hydrogen at temperatures ~ 500°C. Therefore, the effects of this subsequent anneal on the optical efficiency of the Si nanocrystals is solely due to the presence of hydrogen.

The kinetics of the hydrogen passivation process were measured and shown to be independent of nanocrystals size or size distribution. Hydrogen passivation was found to be maximised following a one hour anneal at 500°C, with the diffusion of H₂ in the sample being a fast process. At this temperature, the passivation efficiency is a function of annealing time, reaching a maximum after approximately 60 mins. The passivation process was also shown to be reversible with H being removed from the samples at temperatures above 650-700°C. All hydrogenation effects are stable at room temperature.

This chapter showed the first report of hydrogenation-induced increase of decay lifetime for Si nanocrystals. Passivated samples exhibited a slower decay rate consistent with the passivation of non-radiative defects. Using the stretched exponential equation, values of τ were seen to increase upon hydrogenation compare to values of β which remained unchanged, suggesting no variation in the effective size or density of nanocrystals. The exponential dependence of 1/τ on the observation energy is commonly used for porous silicon to describe the tunneling process of the carriers from the nanocrystals to the oxide [8]. It was used here for a Si nanocrystal system and provided a good fit to the data. The hydrogenation was seen to only influence the pre-factor A, giving the same value of E_a for both unpassivated and passivated samples. Such results had only been shown before for oxidised porous silicon [8].

Another important result is the fact that the lifetimes of the radiative and non-radiative channels were found to be comparable, suggesting that luminescence can be detected from nanocrystals that contain defects. Such results imply that the presence of
a single dangling bond at the surface of a crystallite is not enough to favour non-radiative recombination instead of radiative one [26].

References


CHAPTER 7

HYDROGEN PASSIVATION
- PROPERTIES
AND
DEPENDENCIES -
The effects of H-passivation were found to vary with nanocrystal size and size distribution. This chapter examines these effects in detail.

7.1 Size Dependence of the Hydrogenation Effects

7.1.1 Photoluminescence features as a function of nanocrystal size

The effect of hydrogenation is illustrated in fig. 7.1a for a sample of $6 \times 10^{16}$ Si.cm$^{-2}$ that contains the smallest nanocrystals (mean size $\sim 2.96$ nm) for our study. The increase in emission intensity after passivation is of the order of 2.55. No changes in spectral shape are observed, consistent with uniform enhancement of the emission for all wavelengths (size). In contrast, figure 7.1b, for the high fluence sample of $4 \times 10^{17}$ Si.cm$^{-2}$ (i.e. a sample that contains nanocrystals of mean size $\sim 3.16$ nm and a broader distribution of nanocrystals), the emission intensity is increased by a factor of 6-7 accompanied by a red-shift in the spectral distribution ($\sim 50$ nm). The red-shift is particularly significant and appears to arise from a greater enhancement of long-wavelength emissions. This is illustrated in fig. 7.2, which shows the passivation-induced enhancement as a function of wavelength for samples implanted with $6 \times 10^{16}$ and $4 \times 10^{17}$ Si.cm$^{-2}$. For the low dose sample, the enhancement factor is approximately constant as previously discussed, however, for the high fluence sample the enhancement increases monotonically with increasing wavelength. Since longer wavelength emission is characteristic of larger nanocrystals, the data in fig. 7.1 is consistent with a disproportionate increase in the emission from larger nanocrystals following passivation. This implies that a greater fraction of these nanocrystals contain non-radiative defects prior to passivation. Such an effect is sensible since the number of defects might reasonably be expected to scale with either the volume or surface area of the nanocrystal, depending on the nature of the defect. Indeed, modelling of the PL emission spectra [1] on the assumption of an $r^2$ or $r^3$ dependence for the defect density shows that such models can reasonably account for the observed red-shifts. However, the probability of having volume recombination centres for crystallite size of a few nanometres is small, as reported by several groups [2-4]. Therefore, recombination centres at the surface are expected to be the dominant defects responsible for luminescence quenching, and therefore the defects passivated by H.
Figure 7.1: Room temperature photoluminescence from Si implanted SiO$_2$ with a fluence of a) $6 \times 10^{16}$ Si.cm$^{-2}$ and b) $4 \times 10^{17}$ Si.cm$^{-2}$, after annealing at 1100°C in N$_2$ and after an additional anneal at 500°C in (N$_2$+H$_2$). The unpassivated spectrum is also shown normalised to the passivated sample for comparison.
Figure 7.2: Passivation induced enhancement of PL emission as a function of emission wavelength for samples implanted with $6 \times 10^{16}$ Si.cm$^{-2}$ ($\rightarrow$) and $4 \times 10^{17}$ Si.cm$^{-2}$ ($\leftarrow$).

Figures 7.3a and 7.3b show the dose dependence of the integrated intensity and the peak position respectively before and after hydrogen passivation. The trends after passivation are similar to those prior to passivation. A slight difference can be noticed in the intensity dependence for the high dose regime ($2 \times 10^{17}$ Si.cm$^{-2}$ < dose < $4 \times 10^{17}$ Si.cm$^{-2}$) where the intensity seems to have reached a plateau. In this dose range, it was mentioned in chapter 4 that apart from the size effect, other factors affect the PL efficiency (i.e. nanocrystal-nanocrystal interactions, and non-radiative defect sites). Furthermore, it is also known that larger nanocrystal have a higher probability of containing non-radiative defect sites. Therefore, reducing the non-radiative recombinations strongly affects the PL intensity behaviour in the high dose regime.

As shown in figures 7.4a and 7.4b, both the intensity enhancement and red-shift increase with implant dose for doses above about $1 \times 10^{17}$ Si.cm$^{-2}$ up to $4 \times 10^{17}$ Si.cm$^{-2}$. The intensity enhancement ranges from 2.5 for the lowest dose to 6.8 for the highest dose, while the red-shift ranges from 0 to 70 nm over the same range. As mentioned previously in chapter 6, both these effects are reversible, demonstrating that they are not due to further growth of the nanocrystals, but to a change in the optically active size distribution.
Figure 7.3: a) Integrated emission intensity and b) Peak position of the emission as a function of implant dose for samples annealed at 1100°C in N₂ before (▲) and after (●) passivation. The lines are a guide to the eye only.
Figure 7.4: a) Increase in emission intensity and b) Red-shift of the PL peak position as a function of Si implanted dose. Samples were annealed at 1100°C in $N_2$ and subsequently annealed at 500°C in forming gas ($N_2+H_2$).
The spectral distortion caused by the disproportionate increase in emission from larger nanocrystals and the resulting red-shift in the emission spectra are expected to reflect both the average size and the size distribution of nanocrystals. For example, a smaller red-shift is expected from samples with a narrow crystal size distribution than from samples with a broad crystal size distribution, even if they have the same average nanocrystal size. The observation that there is no significant red-shift for low implant dose samples could therefore be interpreted as resulting from their narrower size distribution or from the assumption that the non-radiative defects are not relevant to the emission observed from the smallest nanocrystals [5, 6]. Similarly, a larger red-shift is expected when the average nanocrystal size and size distribution increase due to the increasingly disproportionate contribution from larger nanocrystals. Since both the average particle size and size dispersion increase with increasing dose, these observations are consistent with the assertion that larger nanocrystals are more likely to exhibit non-radiative recombination [5].

The sample implanted to a dose of $6 \times 10^{17}$ Si.cm$^{-2}$ shows a reduced red-shift and intensity increase compared to the sample implanted to a dose of $4 \times 10^{17}$ Si.cm$^{-2}$. This behaviour is unexpected but a bimodal particle size distribution could account for the results observed, as previously discussed (chapter 4).

**7.1.2 Luminescence Decay and Relaxation Time as a function of wavelength**

In order to assess how the PL decay time is affected by nanocrystal size before and after passivation, time-resolved PL transients were recorded at a range of different wavelengths. Figure 7.5 shows the spectral evolution, as derived from the transient data, for a sample implanted with $1 \times 10^{17}$ Si.cm$^{-2}$, before and after H-passivation. Importantly, no significant passivation-induced red-shift was observed for this sample, as the spectral shape look the same before and after passivation for each decay time studied. By way of comparison, fig. 7.6 shows PL transients for a sample implanted to $3 \times 10^{17}$ Si.cm$^{-2}$. In this case, passivation results in a significant red-shift of the PL spectrum, as well as an increase of the PL emission from large nanocrystals. This is correlated with the strong shoulder evident after passivation around 800-850 nm in fig. 7.6b, while being present to a lesser extent in fig. 7.6a, before passivation. The slower decay time for this long wavelength emission is consistent with it resulting from larger nanocrystals.
Room temperature photoluminescence from Si implanted SiO$_2$ with an implant dose of 1x10$^{17}$ Si.cm$^{-2}$, as a function of decay time, (a) after annealing at 1100°C in N$_2$, and (b) after an additional anneal at 500°C in forming gas (N$_2$+H$_2$). The arrow represents the peak position of the PL emission for CW excitation conditions.
Figure 7.6: Room temperature photoluminescence from Si implanted SiO$_2$ with an implant dose of 3x10$^{17}$ Si.cm$^{-2}$, as a function of time, (a) after annealing at 1100°C in N$_2$ and (b) after an additional anneal at 500°C in forming gas (N$_2$+H$_2$). The arrow represents the peak position of the PL emission for CW excitation conditions.
The passivation-induced red-shift is then clearly explained as arising from a disproportionate increase in the longer wavelength emission from larger nanocrystals.

Comparison of the data in figs. 7.5 and 7.6 also shows an increase in the lifetime after passivation as discussed in chapter 6, with a red-shift of the peak position as the decay time increases, both before and after passivation.

The dependency of the luminescence decay lifetime $\tau$ upon observation energy, at room temperature, is shown in figure 7.7 for a sample implanted with a dose of $4 \times 10^{17}$ Si.cm$^{-2}$. As the energy increases (wavelength decreases), the difference in $\tau$ values between passivated and unpassivated decreases. The variation of $\tau$ with observation energy is again consistent with a disproportionate increase in the emission from larger nanocrystals (smaller energy). Indeed, the largest change in $\tau$ is observed for the observation wavelength of 850 nm (large nanocrystals), consistent with the spectral evolution shown in fig. 7.6. All doses exhibit the same behaviour.

![Figure 7.7](image)

**Figure 7.7:** Decay lifetime as a function of observation energy, for a sample implanted with $4 \times 10^{17}$ Si.cm$^{-2}$, annealed at 1100°C in N$_2$ (♦) and after a subsequent anneal at 500°C in (N$_2$+H$_2$) (●). The lines are a guide to the eye only.

Figure 7.8 shows more clearly that the variation in $\tau$ upon hydrogenation is roughly constant over the dose range studied for a given wavelength. $\tau$ values obtained for a fixed wavelength only refer to the size of the nanocrystals (energy levels) and do not take into account the number of nanocrystals of such size. It is therefore expected to
obtain the same increase in $\tau$ values for a fixed wavelength throughout the dose range studied. The differences observed for the red-shift and the efficiency of the PL as the dose varies are simply due to the number of nanocrystals of each size present. For example, for a wavelength of 850 nm, which corresponds to large nanocrystals, the fact that a sample of $1 \times 10^{17}$ Si.cm$^{-2}$ will contain less large nanocrystals compared to a sample of $4 \times 10^{17}$ Si.cm$^{-2}$, means that the effect on large nanocrystals will be more important for the $4 \times 10^{17}$ Si.cm$^{-2}$. Therefore the red-shift and efficiency increase will be more important in the high dose sample than in the low dose sample.

Figure 7.8: Increase in emission lifetime upon hydrogenation as a function of implant dose, for an observation energy of 1.77 eV (700 nm) (●), 1.65 eV (750 nm) (■), 1.55 eV (800 nm) (▲) and 1.46 eV (850 nm) (♦).

The equation (6.5) describing the dependence of $\tau$ upon the observation energy at room temperature can be used to obtain the values of the pre-factor $A$ and of $E_a$ after passivation. Table 7.1 shows the values of $A$ and $E_a$ before and after passivation for all doses. It can be seen that all doses show a decrease in the $A$ value upon hydrogenation and that $E_a$ values are roughly constant as expected [7]. This is again due to the fact that the dependence of $E_a$ on the barrier characteristics is weak, while the prefactor $A$ depends on the inverse number of luminescent crystallites, number which increases upon hydrogenation (the non-radiative decay rate decreases as the decay lifetime increases due to an increase in luminescent crystallites).
Table 7.1: Values of $E_a$ and $A$ obtained by fitting the non-radiative decay rate experimental data with theory, before and after passivation.

<table>
<thead>
<tr>
<th>Dose (Si.cm$^{-2}$)</th>
<th>No Hydrogen</th>
<th>Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_a$(eV)</td>
<td>$A$ (ms$^{-1}$)</td>
</tr>
<tr>
<td>1x10$^{17}$</td>
<td>0.41</td>
<td>1.14</td>
</tr>
<tr>
<td>2x10$^{17}$</td>
<td>0.32</td>
<td>0.42</td>
</tr>
<tr>
<td>3x10$^{17}$</td>
<td>0.32</td>
<td>0.54</td>
</tr>
<tr>
<td>4x10$^{17}$</td>
<td>0.33</td>
<td>0.65</td>
</tr>
</tbody>
</table>

The increase in lifetime for Si nanocrystals as well as for porous Si has been explained as a passivation of dangling bonds situated at the surface of the nanocrystals [7, 8], reducing non-radiative recombination. Matsumoto et al [9] also mention a widening of the bandgap upon hydrogenation [10]. The increase in lifetime would then be due to a change in the origin of the luminescence, from surface states (dangling bonds) to quantum confined states (intrinsic to the nanocrystals size). Although a widening of the bandgap usually means a blue-shift of the PL peak position, in this case, as the emission from the surface states is a non-radiative emission and therefore no emission (or weak) was observed in the long wavelength range, the hydrogenation will result in a red-shift of the total emission by causing emission in the long wavelength range. This result also implies that the emission observed prior to hydrogenation is already blue-shifted compared to the expected emission (which consists of the emission taking place within the nanocrystals themselves if they were all equally efficient for light emission). It is important to remember that the emission from the small nanocrystals does not shift, as the preferred recombination path for small crystallites is not the surface states [5].

7.1.3 Photoluminescence Maxima

The dependence of the PL emission of Si nanocrystals upon temperature was examined in Chapter 4. An initial increase in intensity with increasing temperature is observed at low temperatures before reaching a maximum and then decreasing upon further rise in temperature. This behaviour has been explained by thermally-induced transitions between excitonic singlet and triplet states in Si nanocrystals [11, 12]. As the
energy splitting depends on the size of the nanocrystals, the temperature for which the maxima of the intensity was observed is lower for bigger nanocrystals. The temperature dependence of the PL emission is shown in fig. 7.9, before (fig. 7.9a) and after passivation (fig. 7.9b).

The initial increase in intensity is quite evident. But most importantly, the temperature for which the maximum intensity is observed seems to be shifted to lower temperatures after passivation for all samples. Apart from the sample implant with $6 \times 10^{17}$ Si.cm$^{-2}$, no intensity maximum is indeed observed in the temperature range starting at 70 K, suggesting the maximum appears at lower temperatures for passivated samples. The other possible explanation would be that the temperature dependence is monotonic. This alternative is implausible since it would require a change in the electronic structure of the nanocrystals. Therefore, it is concluded that the temperature maximum is shifted to lower temperatures by hydrogenation. The fact that it is actually the case for the sample implanted with $6 \times 10^{17}$ Si.cm$^{-2}$, which now exhibits a maximum in intensity for a temperature of 90 K instead of 110 K prior to hydrogenation is reinforcing the hypothesis made.

Quantum confinement affects both the bandgap and exciton splitting, increasing with decreasing size. Therefore, the maximum intensity will be observed at higher temperatures for smaller nanocrystals [12]. As hydrogen enhances the emission from larger nanocrystals disproportionately to the emission of the small ones [13], this effect will be translated into a lower temperature at which the intensity maximum is reached (smaller exciton singlet-triplet splitting), as can be seen in the data of figure 7.9.

7.2 Temperature Dependence of the Hydrogenation Effects

The temperature dependence does not show any variations in the behaviour of all the hydrogenation effects discussed previously. The temperature range studied starts at 70 K up to room temperature (290 K).

The size dependence of the red-shift and of the increase in intensity do not vary upon changes in temperature. The explanation lies in the fact that the dose (size)
Figure 7.9 Emission integrated intensity as a function of temperature for samples implanted with $2 \times 10^{17}$ Si.cm$^{-2}$ (●), $4 \times 10^{17}$ Si.cm$^{-2}$ (■) and $6 \times 10^{17}$ Si.cm$^{-2}$ (♦), annealed at 1100°C in N$_2$ a) before and b) after passivation. The lines are a guide to the eye only. The intensities are not comparable.
Figure 7.10: a) Increase in emission intensity and b) Red-shift of the peak position as a function of implant dose, for temperatures of 70K (▲), 90K (♦), 110K (●), and 290K (★). The lines are a guide to the eye only.
dependence of the PL intensity is not modified by the temperature (figures 4.12) and by the introduction of the hydrogen (figure 7.3a). Therefore, although the actual values of the increase in intensity are slightly different, the increase in intensity still follows the same trend for the dose dependence as the temperature is increased, as can be seen in figure 7.10a. For the red-shift (fig. 7.10b), although the temperature is known to introduce a blue-shift of the peak position as it decreases [14], such a blue-shift is observed for samples before and after passivation. It is also important to note that such a blue-shift upon a temperature decrease is not dependent on the size of the crystallites [15], as it is present in the emission for all doses, and the overall shape of the spectrum is still the same.

The increase in \( \tau \) observed upon hydrogen passivation is shown in figure 7.11 as a function of temperature (K) for a sample of \( 3 \times 10^{17} \text{ Si.cm}^{-2} \). As observed for the values of \( \tau \), before and after passivation, the increase in \( \tau \) is more important at low temperatures and decreases as the temperature increases.

![Figure 7.11: Increase in decay lifetime upon hydrogenation as a function of observation energy, at various temperatures, for a sample implanted with \( 3 \times 10^{17} \text{ Si.cm}^{-2} \), annealed at 1100°C in N\(_2\). The lines are a guide to the eye only.](image)

Another plot in fig. 7.12 shows the same behaviour for all doses as the temperature increases, for an observation wavelength of 800 nm (only 3 doses are shown in fig. 7.12 for clarity purposes). Again, all doses exhibit roughly the same values for the increase of \( \tau \).
The time dependence of the PL shows exactly the same characteristics as at room temperature. The only difference is that as the temperature is decreased, the PL intensity grows stronger and the features of the peak becomes more defined. At 70K, the second shoulder is more visible and can almost be considered as a second peak. As the intensity is a lot stronger, the signal is still visible up to 800 μs.

Figure 7.12: Increase in decay lifetime upon hydrogenation as a function of temperature for an observation energy of 1.55 eV (800 nm), for implant dose of 1x10^17 Si.cm² (▲), 2x10^17 Si.cm² (●), and 4x10^17 Si.cm² (■), annealed at 1100°C in N₂. The lines are a guide to the eye only.

7.3 Excitation Energy Dependence

The dose dependence of the red-shift is shown in figure 7.13 for excitation energies of 2.54 eV (488 nm) and of 3.49 eV (355 nm).

The values obtained for the red-shift are fairly close in both cases (within experimental errors), and its dose dependence is the same for both excitation energies. The peak emission (hence the red-shift) is constant with excitation energy and is therefore related to the intrinsic properties of the nanocrystals (bandgap).
Figure 7.13: Red-shift of the peak position upon hydrogenation as a function of implant dose for an excitation energy of 2.54 eV (●) and 3.55 eV (▲). The lines are a guide to the eye only.

7.4 Conclusion

The surface passivation of Si nanocrystals and porous Si has proven to be a critical parameter for the visible luminescence [2, 16, 17]. Hydrogen passivation results in a red-shift of the PL emission as well as an important increase in PL efficiency. An increase in decay lifetime \( \tau \) was also observed. Such hydrogenation effects exhibit a dose dependence, increasing with increasing implant dose. The various experimental data shown in this chapter agree with the model of a disproportionate enhancement of the emission from large nanocrystals.

A decrease in the temperature maxima for the PL intensity upon hydrogenation is also reported here for the first time. The temperature behaviour of the PL intensity is explained by thermally-induced transitions between excitonic singlet and triplet states in nanocrystals. As bigger nanocrystals require lesser temperatures to induce these optical transitions, due to a smaller splitting of the energy level, the hydrogenation therefore results in a decrease of the temperature for the PL intensity maxima. This effect is again reasonably explained by the disproportionate enhancement of emission efficiency from larger nanocrystals by the hydrogen passivation.
Both the increase in PL intensity and the red-shift of the PL peak position do not vary upon temperature and excitation energy changes. It is a good indication that such parameters depend only on the intrinsic properties of the nanocrystals (bandgap energy).

References


CHAPTER 8

SUMMARY & CONCLUSIONS
In this work, Si nanocrystals embedded in a SiO₂ matrix were fabricated by ion implantation followed by high temperature annealing. This thesis constitutes a study of the influence of the processing parameters on the nanocrystals and their optical properties.

The implantation of Si ions in a SiO₂ matrix results in two different types of emissions. The first one is observed around 650-700 nm and is related to irradiation-induced defects. The second emission appears after a high temperature anneal and is related to the formation of Si nanocrystals in the SiO₂ layer. The nanocrystal luminescence observed is strong and is centred around ~ 800 nm at room temperature, depending on the implant dose. A dose dependence of both PL emissions have been conducted at room temperature, and exhibit the same behaviour: an initial increase in intensity as the dose increases followed by a decrease in intensity above a critical implant dose. The initial increase in intensity is consistent with, for the defect-related emission, an increase in the concentration of optically active defects, and for the nanocrystal-related emission, an increase in the nanocrystals concentration, with increasing irradiation dose. The intensity decrease above a certain dose for the defect emission suggests either a saturation of the defect creation or the creation of competing non-radiative paths. Regarding the nanocrystal-related emission, such behaviour is consistent with an increase of competitive processes, like nanocrystal-nanocrystal interactions, or decrease in emission efficiency with size as the oscillator strength varies as 1/d². While the defect-related emission does not shift, the nanocrystal emission also exhibits a red-shift of its peak position as the implant dose increases. This red-shift is a direct effect of quantum confinement as small nanocrystals are expected to emit at shorter wavelengths. By using an effective mass approximation (EMA) approach for the theoretical model [1], it is possible to fit the experimental PL spectrum and obtain valuable information on the nanocrystal characteristics.

Optical absorption data have also been commonly used to obtain the average bandgap energy of the nanocrystals [2-4] by using the Tauc expression. The analysis of the optical absorption and of the PL emission have both shown good agreement with the quantum confinement effect, showing an increase in bandgap energy as the implant dose increases (size). But a large discrepancy in the values of the bandgap energy exists between both methods. Although it is known that the site for the photo-generation of carriers is different from that where their radiative recombination takes place, it has
been shown that the interpretation of the optical absorption data may not be reliable, due to scattering of light from small Si particles [5].

The decay lifetime of implanted Si nanocrystals exhibits the same stretched exponential behaviour as for porous Si. The decay lifetime is in the order of μs which is characteristic of an indirect bandgap. The dose dependence of the decay characteristics (τ and β) can be explained by the carrier migration/diffusion or the so called trap-controlled-hopping mechanism [6]. Carriers escape from the confined zone where they are generated to migrate between neighbours, towards a less confined region, may become trapped for an extended period of time and thereafter may migrate to another nanocrystal or into the silicon oxide matrix, where recombination may take place. The recombination in turn may be either radiative or non-radiative, the latter being dominant at room temperature. Such mechanisms are highly dependent on the density and size of the nanocrystals, as low implant dose samples behave almost like a system of isolated nanocrystals, the luminescence being limited by the bandgap of the nanocrystals, while high implant dose samples are the perfect example of a highly interconnected network of nanocrystals in which the trap-controlled-hopping mechanism has a strong influence on the decay rate.

At room temperature, as non-radiative recombination is dominant, the decay lifetime τ is representative of the non-radiative recombination rate (~ 1/τ). The exponential dependence of the decay lifetime τ with confinement energy, which increases with increasing confinement, supports a tunnelling mechanism for the non-radiative escape [6, 7]. This process is also dependent on the size of the nanocrystals as well as the density.

The temperature dependence of the PL emission and PL lifetime from ion implanted Si nanocrystals was studied for various implant doses. In general, the PL emission exhibits an initial increase in intensity with increasing temperature, reaching a maximum before decreasing upon further increase in temperature. This temperature dependence is well explained by thermally induced transitions between excitonic singlet and triplet states in Si nanocrystals [8, 9]. Its size dependence was explained by quantum confinement, as it reduces both the bandgap and the exciton splitting as the nanocrystal size decreases, resulting in an intensity maximum observed at lower temperatures for large nanocrystals (high implant dose). The shift of the peak position to higher wavelengths as the temperature increases is due to temperature-dependent
electron-phonon interactions [10] (commonly observed in bulk Si), as shown by a good fit between experimental data and theoretical calculations.

At low temperatures (< 70K), the trapping of carriers at nanocrystals sites being very effective, the decay characteristics are solely influenced by the nanocrystals intrinsic properties (bandgap). As the temperature is raised, the hopping mechanism is initiated and the topology of the nanocrystals network becomes the limiting factor for the decay luminescence. The temperature dependence of $\tau$ and $\beta$ are consistent with trap-controlled-hopping mechanism introduced for porous Si for room temperature results.

The role of irradiation-induced defects on the photoluminescence was investigated for a Si nanocrystal/SiO$_2$ system by irradiating samples with low and high energy Si ions. The case of low energy ion irradiation, representing high nuclear energy loss, was compared to the case of high energy ions irradiation, representing high electronic energy loss. As only nuclear energy loss creates damage in Si nanocrystals (while both nuclear and electronic energy loss damage the SiO$_2$ matrix), the fact that both cases exhibited similar quenching rate of the nanocrystal emission is in agreement with a model of preferential accumulation of non-radiative defects at the nanocrystals/SiO$_2$ interface.

The nanocrystal related emission showed full recovery after annealing at temperatures of ~ 1000°C in the case of low irradiation dose, while high dose irradiated samples showed only slight recovery. A red-shift of the peak emission was also observed in the case of high irradiation dose. It is believed that the quality (less defects) of large nanocrystals is improved by the amorphisation/recrystallisation process due to the irradiation-annealing steps (reduction of non-radiative sites), which would shift the emission towards higher wavelength (large nanocrystals).

Finally, further evidence of such phenomenon can be found in the study of Er implantation in Si nanocrystals system, reported recently by Franzo et al [11] as an energy transfer from the excitons confined in the nanocrystals to the erbium ions. The Si nanocrystal emission is observed to decrease with increasing Er implant concentration, while an emission peak around 1.54 $\mu$m increases correspondingly. The observed variations of the Si nanocrystal related emission correspond exactly to the quenching of Si nanocrystals emission due to irradiation damage induced by the high implantation
dose of Er ions, following an exact same dose dependence as the one observed in this work with Si ion implantation.

Although the photoluminescence intensity from Si nanocrystals is quite strong, it has been shown that surface passivation is a critical parameter for optimal visible luminescence. In this work, hydrogen passivation was carried out by performing a subsequent anneal in forming gas (5% H₂+95% N₂). The kinetics of such a process showed that passivation was maximised when an anneal of 1 hour duration was carried out at 500°C in hydrogen ambient. At this temperature, the passivation efficiency is a function of annealing time, reaching a maximum after approximately 60 mins. The diffusion of hydrogen in the SiO₂ layer is a fast process. The kinetics of the hydrogen passivation process were shown to be independent of nanocrystal size or size distribution. The passivation process was also shown to be reversible with H being removed from the samples at temperatures above 650-700°C. All hydrogenation effects are stable at room temperature.

Numerous experimental results (optical absorption data, decay rate, annealing studies, reversibility) have shown that no further growth of the nanocrystals was induced by thermal annealing in hydrogen at temperatures of ~ 500°C. Therefore, the effects of this subsequent anneal on the optical efficiency of the Si nanocrystals is solely due to the presence of hydrogen.

The photoluminescence from Si nanocrystals has been shown to increase significantly, as well as to shift to higher wavelengths, upon hydrogenation. The increase in PL intensity is due to the passivation of non-radiative defect sites present at the surface of the nanocrystals (dangling bonds) and has been reported by various groups [12-14]. The red-shift of the peak position is reported here for the first time, and is believed to be due to a disproportionate increase in efficiency from the larger nanocrystals. An increase in decay lifetime upon hydrogenation has also been observed and reported for the first time. Indeed, passivated samples exhibited a slower decay rate consistent with the passivation of non-radiative defects. Values of τ were seen to increase upon hydrogenation compare to values of β which remained unchanged, suggesting no variation in the effective size or density of nanocrystals.

The study of the dependence of the non-radiative decay rate as a function of observation energy showed that the data for both unpassivated and passivated samples can be well fitted by the theoretical equations for the tunnelling of carriers through an
oxide barrier. From the theoretical fit, it can be seen that the hydrogenation only influenced the pre-factor $A$ (being related to the number of passivated crystallites), while leaving the values of $E_a$ unchanged. Such results had only been reported before for oxidised porous silicon [7].

Finally, hydrogenation was also shown to influence the temperature dependence of the PL intensity. Passivated samples exhibit a PL intensity maxima for lower temperatures. This effect is again reasonably explained by the disproportionate enhancement of emission efficiency from larger nanocrystals by hydrogenation, as large nanocrystals will exhibit a smaller energy level splitting (weaker quantum confinement).

The effect of passivation on the nanocrystal luminescence exhibited a dose dependence, increasing with increasing fluence. A disproportionate enhancement of the emission from large nanocrystals is proposed to explain such size dependencies, and agrees well with all the previous experimental results.

Both the increase in PL intensity and the red-shift of the PL peak position do not vary upon temperature and excitation energy changes. This is a good indication that such parameters depend only on the intrinsic properties of the nanocrystals (energy bandgap).

A study of Si nanocrystals fabricated by a plasma deposition technique, called HARE (Helicon Activated Reactive Evaporation) was carried out along side the study of implanted Si nanocrystals. Such samples were found to exhibit similar optical properties to those of implanted nanocrystals. The only major difference was observed in the defect-related luminescence, where the HARE samples were seen to emit weak luminescence around 650 nm, probably due to the less destructive character of the plasma deposition compared to the ion implantation technique.

**Future Work**

Further work is required to reach a satisfactory description of the growth mechanism of nanocrystals. Recent work [15, 16] has modelled experimental TEM and PL data with some "atomistic" simulations. This work shows good agreement for small and average nanocrystals, while for larger nanocrystals, the experimental data results in larger sizes compared to the simulations. The possible interactions between nanocrystals
for high density system renders the growth process more complex, with possible "proximity effects" increasing the growth of the nanocrystals to the detriment of smaller ones [15,16]. The case of high excess Si concentration is still unclear, and might result in bimodal size distribution, as possibly seen here for the case of the implant of 6x10^{17} Si.cm^{-2} (~30% excess Si).

As well as studying the influence of the preparation conditions on the nanocrystals and their optical properties, this thesis has also shown that the surface passivation plays an important role in the mechanism of the luminescence observed. The extent of the influence of hydrogen on the luminescence observed from Si nanocrystals has been shown to be quite broad, with both decay characteristics and luminescence characteristics being affected, while the structure of the nanocrystals remained the same. Such hydrogenation effects, and specially their dependence on the size and the size distribution of the nanocrystals, are still not fully understood and need to be investigated further.

Finally, the broadness of the size distribution of nanocrystals is still an issue, rendering the analysis of optical data more complex and less detailed. Finding a method to decrease such broadness will be beneficial for the analysis of the optical data, as well as for the understanding of the PL mechanism. So far, the possible interactions taking place between nanocrystals of various size have been seen to highly influence the PL observed.

References


Publications


