A study of the effect of phosphorus doping on silicon nanocrystal formation

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Abstract

The original work presented in this thesis describes work done using simulations and experimental techniques for the investigation of the growth stages of silicon nanocrystals (Si-NCs) and the effect of phosphorus doping on the optical properties and size of Si-NCs. The model used to investigate the growth of Si-NCs and the effect of phosphorus on the size of Si-NCs is a simple Molecular Dynamics model employing a Monte Carlo (MC) method. The model was run on a desktop PC and the results were analyzed in Mathematica. The model uses a temperature dependent MC step that includes an activation energy, which is the barrier, needed to overcome for diffusion to occur. The model contains equations which govern the energetics of the atoms. When the atoms are allowed to diffuse, the equations give the probability of a jump of an atom from one lattice site to a random neighbouring site. The experimental work presented in this thesis employs photoluminescence (PL), X-TEM (cross-sectional TEM) and time resolved photoluminescence to investigate the structural properties of intrinsic Si-NCs and the optical properties of intrinsic and phosphorus doped Si-NCs. The samples were prepared by ion implantation and rapid thermal annealing using isothermal annealing.

The results presented in Chapter 2 show that a simple model as the one developed in this work can describe quite well the main stages of size evolution of Si-NCs. These stages are the accretion, the growth and the Ostwald Ripening. The activation energy of diffusion is determined by an Arrhenius relationship between the MC step time and the temperature. The number of isolated Silicon atoms can be then used to calculate the solubility of silicon in SiO$_2$. The value found is in reasonable agreement with previous experimental results. When phosphorus is introduced in the model it is found that the size of Si-NCs increases for all values of the binding energy ratio. This agrees with previous experimental results. Furthermore, it is found that the fraction of isolated silicon atoms increases with increasing annealing time in the presence of phosphorus.

The structural properties of intrinsic Si-NCs, investigated by X-TEM, reveal that there is a growth and Ostwald Ripening stage in the size evolution of Si-NCs. The optical properties show a PL enhancement of 50% in the case of phosphorus doped Si-NCs compared with intrinsic Si-NCs. Also it is found that the shift in peak energy is greater for phosphorus Si-NCs due to accelerated growth of Si-NCs. The time resolved PL experiments reveal that the PL enhancement is due to suppression of the dangling bond defects at the surface of Si-NCs. The fraction of phosphorus atoms that contains ionized substitutional donors increases for long anneal time. The PL Intensity quenching is due to the opening of an efficient, non-radiative, recombination path due to Auger recombination. The transition from defect passivation to free electron generation implies a threshold size which below that phosphorus passivates dangling bond defects at the surface of Si-NCs. The estimation found is in agreement with previous experimental results.
Declaration

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Publications

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1. Chapter 1: Introduction

1.1. Silicon Photonics

Research on Si-NCs has attracted much attention over the past few decades since the discovery by Canham et al[1] that porous silicon can emit very bright photoluminescence at room temperature (RT). This interest has continued with the very important report from Wolkin et al. [2] that luminescence from porous silicon is due to quantum confinement of silicon particles in the nanometre scale. The authors of [2] have also observed that the bandgap energy of the particles scale inversely with respect to the mean nanocrystal size. Furthermore, they have reported the importance of oxygen and hydrogen surface bonds on the luminescence and structural properties of porous silicon. This very important discovery opened the route for much research in order to optimise the properties and eventually produce microelectronic, CMOS compatible, optoelectronic devices from low-dimensional silicon. These devices will be a revolution in the optoelectronics industry which nowadays is dominated by the production of devices from III-V and II-VI semiconductors, which although they are very efficient in light generation, nevertheless are very cost-inefficient. Another reason that has driven much research on the properties of low-dimensional silicon (LD-Si) is the prospect of integrating light emitting devices that are CMOS compatible in current microelectronic circuits. This will increase the speed of data transmission by a few orders of magnitude and eliminate any RC delays associated with optical interconnects between transistors. Therefore, field is called silicon photonics since it is directly related to the integration of photonics with LD-Si.

Many optical devices have been realized while others are still under research and development for guiding, modulating, generating and amplifying light using silicon photonics. Examples of such devices are optical waveguides, optical ring microcavities, optical amplifiers, light-emitting diodes (LEDs) and solar cells. A review of the recent results on these type of devices is presented by Daldosso and Pavesi in [3]. Much discussion in reference [3] is given to the issue of optical gain properties in Si-NCs and to the sensitization of Erbium ions from Si-NC. Although, much progress has been made over the past few years to optimise the properties of Si-NCs that will enable CMOS compatible devices to be made, there is still a great
desire for a laser that will not be electrically pumped. Optical gain in Si-NCs has been observed for the first time by Pavesi et al [4] using ion-implanted silicon rich silica by the widely known variable stripe method[5, 6]. Furthermore, a few years later the first silicon laser was developed using stimulated Raman scattering[7], however this kind of laser needs to be externally pumped by another laser and hence it does not solve the need for a silicon laser achieving optical gain fabricated in a CMOS compatible way.

1.2. Silicon nanocrystals

After the discovery of bright luminescence from porous silicon, much research was done on the luminescent and structural properties of silicon nanocrystals (Si-NCs) prepared by doping silica films with excess silicon and the subsequent annealing to form nanocrystals (NCs) and remove any damage incurred by the preparation method. Various methods have been used to produce silicon nanocrystal ensembles such as PECVD (plasma enhanced chemical vapour deposition), ion implantation, laser ablation, magnetron co-sputtering and pyrolysis. It is generally accepted that luminescence from Si-NCs is due to quantum confinement of silicon nanoparticles in a silica matrix[8, 9]. Quantum confinement arises from electron-hole pairs (excitons) in a matrix of different bandgap (e.g. silicon dioxide or bulk silicon) that are spatially confined so that their mean average size is smaller than the exciton Bohr radius. In this case the semiconductor nanoparticles become low or even zero-dimensional particles with properties different to bulk, quantum wells and quantum wires. These nanoparticles are widely known as quantum dots (QDs). In QDs, the density of states (DOS) is modified, so that now the DOS is described by delta functions[10].

![Figure 1-1: From left to right: DOS Vs. Energy plots for bulk semiconductor, quantum well, quantum wire and quantum dot. Adapted after [10]](image-url)
This means that the semiconductor material that QDs are made of will emit in discrete energies for each nanoparticle. Figure 1-1 shows plots of the DOS, \( D(E) \), versus Energy, \( E \), for bulk semiconductors, quantum well, quantum wire and quantum dot. The degree of confinement is also shown, showing 0D for QDs.

1.3. **Light emission from indirect bandgap semiconductors**

Direct bandgap semiconductors (e.g. GaAs, InGaAs, CdSe) that mainly consist of III-V or II-VI materials have the bottom of the conduction band aligned with top of the valence band in momentum space (i.e. at the same wavevector). This makes recombination of confined excitons very easy at RT with radiative recombination rates very high. Therefore, direct bandgap semiconductors exhibit very strong light emission with quantum efficiency (QE) approaching as high as 99% in some cases. Quantum efficiency, in photoluminescence terms, can be defined as the ratio of photons out of a material over the total photons absorbed.

![Figure 1-2: Energy diagram of silicon. The various arrows indicate the various recombination paths for an excited electron.](image)

In the case of indirect bandgap semiconductors such as Si, direct recombination is forbidden since the bottom of conduction band is at a different wavevector than the top of valence band. The only way for an exciton to recombine radiatively is via phonon assisted processes. Although this is very unlikely to occur for pure silicon
(or rather is a very slow process), when Si is quantum confined to a few nanometers then the properties of Si-NCs change from its bulk counterpart. Kovalev et al. have demonstrated theoretically that the k-conservation rule that governs direct bandgap semiconductors radiative emission can be broken[11]. Since, Si has an indirect bandgap it has very important implications for light emission from Si-NCs. The basic idea is that the spatial confinement introduces a large uncertainty in the particles momentum and this relaxes momentum selection rule and allows it to emit photons in the VIS-NIR range of spectrum. It also shifts band edge due to quantum confinement and allows the emission energy to be increased significantly from that of bulk silicon.

1.3.1 Quantum confinement in silicon-nanoclusters

Quantum mechanics has been fundamental to the understanding of the semiconducting properties. The fundamental concepts behind Quantum mechanics are enshrined in Heisenberg’s uncertainty principle and Schroendinger’s equation[12]. These equation lead to the important concepts relevant for the exploitation of the optical and electronic properties of semiconductor quantum dots[13] with the scope to develop applications that will revolutionize nano-photonics. It is important to understand the context of quantum confinement applied to semiconductor quantum dots, in our case especially for Si-NCs.

Quantum confinement is the alteration of the physical and electronic properties of a material down to the nano-meter scale that arise specifically due to spatial confinement of the electronic wave-function in at least one dimension. When carriers are confined in real space, their associated wave-function spread in momentum space, which is expected as it arises from Heisenberg’s uncertainty principle, expressed mathematically as:

\[ \Delta p_x \Delta x \geq \hbar \]  

(1-1)

Physically this means that when a carrier (e.g. electron) is localized to a region in space \( \Delta x \) then there is an uncertainty in the momentum of the carrier (\( \Delta p_x \)) which is given by \( \hbar/\Delta x \). Now, when the degree of confinement increases the k-conservation rule breaks and there is an increased probability that a carrier in an excited electronic
state will relax to the ground state radiatively. Schrödinger’s equations (not given here but a detailed analysis can be found in [14]) can be used to find solutions of allowed k-states in a semiconductor and it can be shown that the allowed k-states for a confined particle in which the wavefunction boundary conditions are applied are given by:

\[ k_n = \frac{n\pi}{d}; n = 1,2,3 \ldots \]  

(1-2)

In Equation (1-2) \( k_n \) is the wave-vector and \( d \) is the diameter of the QD (or confined particle). The effective Bohr radius is a measure of quantum confinement, meaning that any particle with confined to a region below this size will experience quantum confinement effects. This includes electrons, holes and excitons.

An exciton is a bound state of electron and hole which are attracted by electrostatic Coulomb force [15]. It can exist in our case in semiconductors and it is able to transport energy without having a charge. An exciton can form by the absorption of a photon in a semiconductor. This will excite an electron from the valence band to the conduction band. It will leave behind a positively charged hole. The electron in the conduction band is then attracted to the hole in the valence band by repulsive Coulomb forces. These forces are created due to the large number of electrons near the electron and hole. The recombination of the electron and hole represent the decay of the exciton. Excitons are typically observed just below the bandgap energy and they are the main mechanism in semiconductors for light emission at low temperatures.

The values of Bohr radii of bound electrons, holes and excitons in semiconductors are given by Equations (1-3), (1-4) and (1-5) respectively:

\[ a_e = \frac{4\pi\hbar^2\varepsilon_r\varepsilon_0}{m_e^*e^2} \]  

(1-3)

\[ a_h = \frac{4\pi\hbar^2\varepsilon_r\varepsilon_0}{m_h^*e^2} \]  

(1-4)

\[ a_b = \frac{4\pi\hbar^2\varepsilon_r\varepsilon_0}{\mu e^2} \]  

(1-5)

In Equations (1-3), (1-4) and (1-5) \( m_e^*, m_h^* \) is the effective mass of electron and hole respectively, \( \mu \) is reduced mass and \( \varepsilon_r \) is the relative permittivity. The values for
electron, hole and exciton Bohr radii in silicon have been calculated as 3.19nm, 2.11nm and 5.3nm respectively [16]. In the case of Si-NCs we are interested in the exciton Bohr radius since in Si-NCs we have a system of confined excitons with increased probability of radiative recombination.

Furthermore, the allowed energy states for a quantum confined exciton system are given by [16]:

\[ E_n = \frac{\hbar^2 k^2_n}{2m_e^*} = \left( \frac{\hbar^2}{2m_e^*} \right) \left( \frac{n^2 \pi^2}{d^2} \right) \]  

(1-6)

In Equation (1-6) \( k_n \) is the wave-vector, \( m_e^* \) is the electron effective mass and \( d \) is the diameter of the QD. Note that Equation (1-6) is only valid for very-small nanoclusters. For \( n=1 \), we obtain the confinement energy \( \Delta E \) which is a measure of the increase of conduction band energy of the material relative to the bulk material, according to equation (1-7):

\[ E_{\text{confined}}^{CB} = E_{\text{bulk}}^{CB} + \Delta E = E_{\text{bulk}}^{CB} + \left( \frac{\hbar^2}{2m_e^*} \right) \left( \frac{\pi^2}{d^2} \right) \]  

(1-7)

This can be extended to include the Coulomb and correlation energy terms yielding equation (1-8) which is a reasonable approximation of the bandgap [17] energy as a function of radius size for the quantum confined particle:

\[ E_{\text{confined}}^g = E_{\text{bulk}}^g + \Delta E = E_{\text{bulk}}^g + \left( \frac{\hbar^2 \pi^2}{2 d^2} \right) \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \left( \frac{1.786 e^2}{\varepsilon d} \right) + 0.284 E_R \]  

(1-8)

In Equation (1-8), the first term is the bandgap of the bulk material, the second term is the energy dependence due to quantum confinement effect, the third term is a correlation effect that effectively describes the Coulomb potential between a hole and an electron and the last term includes the Rydberg energy, \( E_R \), for a bulk semiconductor given by [18]:

\[ E_R = \left( \frac{\varepsilon_0}{2\varepsilon^2 m_e^*(\frac{1}{m_e^*} + \frac{1}{m_h^*})\hbar^2} \right) = 13.56 \left( \frac{\varepsilon_0}{\varepsilon r m_e^*(\frac{1}{m_e^*} + \frac{1}{m_h^*})} \right) (eV) \]  

(1-9)

In equation 1-9 \( \varepsilon \) is the electronic charge, \( m_e \) is the electronic charge, \( \varepsilon_0 \) is the permittivity of free space and \( \varepsilon_r \) is the relative permittivity.
The Coulomb energy term arises from the Coulomb law of electrostatics. This law says that any two charged particles will experience a force equal to [19]:

\[ F = \frac{k_e q_1 q_2}{r^2} \]  \hspace{1cm} (1-10)

In the above equation \( q_1 \) is the charge of the first particle, \( q_2 \) is the charge of the second particle, \( k_e \) is the Coulomb constant, \( r \) is the distance between the particles and \( F \) is the force between the particles. Now this can be transformed into a potential which takes the form:

\[ V = \frac{k_e q_1 q_2}{r} \]  \hspace{1cm} (1-11)

In the above equation the symbols have the same meaning as before and \( V \) is the Coulomb potential. So in the case of electrons and holes there is Coulomb interaction between them given by the Coulomb potential. Their charges now are both \( e \) and this gives rise to the Coulomb term in equation 1-8.

The Rydberg or correlation term is related to the Rydberg constant given by [20]:

\[ R_{\infty} = \frac{m_e e^4}{8\varepsilon_0^2 \hbar^3 c} \]  \hspace{1cm} (1-12)

In the above equation \( m_e \) is the rest mass of the electron, \( h \) is the Planck’s constant, \( c \) is the speed of light, \( e \) is the electronic charge and \( \varepsilon_0 \) is the permittivity of free space. This formula is then multiplied by some extra terms and then equation 1-9 is derived. The Rydberg energy corresponds to the energy of a photon whose wavenumber is the Rydberg constant, that is the ionization energy of the hydrogen atom[20]. Ionization energy is the energy needed to remove an electron from the bandgap to the vacuum.

Figure 1-3 (modified after [21]) represents the quantum confinement effect for Si-NCs. In Figure 1-3, three different Si-NCs are shown \( d_1 > d_2 > d_3 \), yielding bandgap energies for the first energy state such that \( E_{g1} > E_{g2} > E_{g3} \).
1.4. Phase Transformations and Phase Separation Phenomena

A phase separation phenomenon is when a mixture of substances undergoes physical changes so that its substances are separated to their different phases. A phase is defined as a thermodynamic system where all the physical properties of a material are uniform. These properties may include chemical composition and density. The phases of a mixture can be described as different states of matter such as gas, liquid, solid and plasma. A mixture can undergo phase transitions which is a transformation from one state of matter to another. A classic example of phase transition is the
freezing of water to form ice. This represents a first order-transition since it involves latent heat. Latent heat is the energy released or absorbed by a body in a constant-temperature process. Hence, during a first order transition the thermodynamic system, or body, will either absorb or release an amount of energy. Phase transformations and phase separation are important phenomena for alloys and metals, such as the iron. A description of the phase transformation and phase separation phenomena in metals and alloys is provided by Porter and Easterling [22]. Phase separation or segregation in matrices, such as SiO$_2$, containing silicon in excess is an important process in the formation of Silicon Nanocrystals (Si-NCs). This process is similar to the segregation of a meta-stable alloy as described by Porter and Easterling [22].

**1.5. First-order phase transitions**

In general, the formation of Si-NCs from a supersaturated solid solution of silicon (Si) atoms is described as a first-order phase transition. In this case Si is considered the impurity atom and it is found in supersaturation since the critical concentration for nucleation and growth to occur is exceeded. The SiO$_2$ is considered the substrate or otherwise the matrix where the precipitation process will take place. The phase diagram in Figure 1-4 describes the various transitions that could take place in a substrate-impurity atom system. As shown in Figure 1-4, when the composition of the impurity atoms increases in the substrate, as is done with ion implantation, there are three possible cases:

- **Arrow 1:** If the temperature is too high and/or the concentration of the impurity atoms too low no Si-NCs will form and the system will not undergo a phase transition.
- **Arrow 2:** If the temperature and concentration of impurity is enough to make a transition in the metastable region, the system will undergo precipitation via nucleation and growth.
- **Arrow 3:** For very high concentrations of the impurity atom the composition will be too big and the system will undergo a first-order phase transition via spinodal decomposition.
The kinetics of the first-order phase transitions have been studied extensively by simulations using Monte-Carlo (MC) methods[23-25]. These simulations were used also to test the classical nucleation theory as well. A review of the first-order phase transitions including nucleation theory, spinodal decomposition, cluster growth and MC studies of first-order phase transitions was published by Gunton et al. [26]

### 1.6. Homogeneous Nucleation

The precipitation of Si-NC in Silicon Rich Oxide (SRO) is assumed that it evolves in the same manner as the nucleation and growth of solid clusters in a liquid. The classical nucleation theory was first developed by Volmer and Weber [27] and Becker and Döring[28]. Here, we will not go into details of the theory developed by these authors but describe briefly the homogeneous nucleation of Si-NCs in a matrix which usually is a liquid but in our case it is SiO$_2$. The formation of Si-NCs is essentially dependent on the reduction of the Gibbs free energy. The following equation describes the change in free energy of a binary alloy[22]:

$$\Delta G = -V\Delta G_v + A\gamma$$  \hspace{1cm} (1-13)
In Equation 1-13 $\Delta G$ is the free energy, $V$ is the volume of the Si precipitate, $\Delta G_v$ is the volume free energy, $A$ is the SiO$_2$/Si-NC interfacial area and $\gamma$ is the interfacial energy. Assuming that the precipitates of Si-NC are perfectly spherical, Equation 1-13 can be written as:

$$
\Delta G = -\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma 
$$

Equation 1-14

In Equation 1-14 $r$ is the Si-NC radius. When these two components are plotted we get Figure 1-5.

As the interfacial and volume energies compete with each other because of the order of each ($\propto r^2$ and $\propto r^3$ respectively) a maximum in the free energy forms. At this maximum the critical free energy is $\Delta G_c$ and critical radius is $r_c$. By taking the derivative of Equation 1-14 and setting it to zero one obtains:

$$
r_c = \frac{2\gamma}{\Delta G_v} 
$$

Equation 1-15

By substituting equation 1-15 into equation 1-14 one gets the following equation:

$$
\Delta G_c = \frac{16\pi \gamma^3}{3\Delta G_v^2} 
$$

Equation 1-16

Figure 1-5: Free energy as a function of the radius of Si-NCs. Adapted after [22]
Equation 1-16 shows that the critical free energy above which nucleation of clusters occurs is inversely proportional to the volume free energy. The volume free energy is proportional to the number of excess Si atoms hence the bigger the volume fraction of Si the lower the critical free energy will be. When Si atoms are added by ion implantation in SiO$_2$ and the material is annealed, the atoms move by diffusion and form very small clusters. When the cluster size is greater than the critical radius for nucleation, then these clusters are serving as nucleation clusters and possible clusters that will grow later. There is also the possibility of increasing the free energy by removing clusters smaller than the critical radius but this is not possible during an ion implantation procedure.

1.7. Growth, Ostwald Ripening and Coalescence

The Si-NC growth is the stage that takes place after the nucleation has finished. An important equation for the growth of Si-NCs is the Gibbs-Thomson equation (GT) given in equation 1-17:

$$c^{GT}(R) = c_\infty \exp\left(\frac{R_c}{R}\right)$$  

(1-17)

In equation 1-17, $c^{GT}(R)$ is the Gibbs-Thomson concentration, $c_\infty$ is the Si equilibrium concentration at a flat phase boundary, i.e. for $R \to \infty$ and $R_c$ is the capillary length defined by equation 1-18[29]:

$$R_c = 2\sigma V_a \beta$$  

(1-18)

In equation 1-18 $\sigma$ is the surface tension, $V_a$ is the atomic volume and $\beta = \frac{1}{k_B T}$, where $k_B$ is Boltzmann’s constant and $T$ is the temperature. The consequences of equation 1-18 are that when the average concentration of Si is greater than $c^{GT}$, i.e. $\bar{c} > c^{GT}$, the Si-NC will grow and can be considered as a sink for Si atoms. However, if $\bar{c} < c^{GT}$ the Si-NC will be a source to other Si-NC and will not grow. The Si-NCs will then continue to grow by diffusion of Si atoms to Si-NCs until a particle radius distribution is achieved which contains Si-NCs of a range of different sizes. It is important to note that this distribution is usually represented by a log-normal fit as it will be shown in the results section and also from previous papers of our results[30]. Of course, these results include late process such as Ostwald
Ripening but even for early stages of growth the size distribution can be fitted well with a log-normal distribution.

The next stage that takes place is Ostwald ripening. In this stage isolated Si-NCs are diffusonally interacting between them which drive the surface energy of the Si-NC/SiO$_2$ interface to a minimum. This will end in smaller Si-NCs shrinking and larger Si-NCs growing even more, consuming the smaller ones. The classical works of Lifshitz and Slyozov[31] as well as Wagner[32] describe the Ostwald ripening process and basically all work on Ostwald ripening references these results. The process described formed the well-known LSW (Lifshitz Slyozov Wagner) theory of Ostwald ripening. It is important to understand that the LSW theory is valid for vanishing volume of the minority phase. Various authors tried to challenge this with developing Ostwald ripening for non-vanishing volumes of the minority phase[33, 34]. It was found that at late stages the growth exponent of the time evolution was confirmed and results of differed authors differed between them. MC simulations of the kinetic Ising model in two and three dimensions[35-39] yielded growth exponents lower than 1/3 predicted by LSW work. The authors commented that this could be because of insufficient runs of the simulations that affected the average values obtained for the scaling function and other parameters in their work. Huse suggested a modification and some additions to the classical work of LSW which agrees well with some experimental results[40]. In order to understand LSW theory we start by assuming that in a vanishing volume of the minority phase the different Si-NCs do not interact with each other. In diffusion controlled Ostwald ripening it is correct to say that the critical radius above which Si-NCs will grow is the same as the average ensemble size. This gives the following equation that was derived in LSW theory[29] for the critical radius:

$$\langle R \rangle(t) = \langle R \rangle_0 \left( 1 + \frac{t}{\tau_{diff}} \right)^{1/3}$$  \hspace{1cm} (1-19)

In equation (1-19), $\langle R \rangle(t)$ is the critical radius, $\langle R \rangle_0$ is the initial critical radius, $t$ is the time and $\tau_{diff} = \frac{9(R_0)^3}{4\epsilon_0DV_dR_c}$, where $D$ is the diffusion rate of Si.

Coalescence is the process where in very high densities of Si the Si-NCs formed touch each other and their sizes increases. In the model and the results used in this
work coalescence will not be taken into account because it is not applicable for the sample fabricated in our case.

1.8. Ion Implantation

Ion implantation was used to prepare all the samples studied which are presented in this thesis. The samples were prepared using ion-implantation of silicon and in Chapter 3 of phosphorus in silica thin films. The samples were prepared with collaborators in the group of Professor Gwilliam in the Surrey Ion Beam Centre. Ion implantation involves using a high energetic beam of ions that are implanted in silica so that the properties of the original matrix are now modified. Ion beam formation and the control of the ion trajectory are accomplished using a particle accelerator, which is shown in Figure 1-6.

![Figure 1-6: Schematic of a low energy (<10keV), high current (mA) ion-implanter, adapted from [21]](image)

The operation of the ion-implanter lies on the stripping of electrons in a plasma discharge from the source material from where they are extracted under vacuum with the assistance of a high-voltage pre-acceleration towards a mass analyzing magnet. The kinetic energy of an ion beam is given by equation 1-20:

\[ E = \frac{1}{2} mv^2 \]  

(1-20)
In equation 1-20, \( m \) is the total mass of all the isotopes contained in a specific ion beam and \( v \) is the speed of the ion beam in vacuum. The trajectory of the beam will depend according to equation (1-21):

\[
R = \frac{mv}{Bq}\tag{1-21}
\]

Equation (1-21) expresses the radius of curvature \( R \), which is a function of the mass of the ion beam, \( m \), its velocity, \( v \), the function of the magnetic field, \( B \), and the charge of the ions, \( q \). This means that if one implants a specific element containing different isotopes (e.g. Si) then different isotopes will deflect in different directions. In this way the desired isotope can be tuned to hit the desired point on the target by controlling the magnetic field to reject all the un-desired isotopes. The beam is accelerated towards the target and hits the target at a given energy. As the ions enter the target material their speed decreases and undergo a series of elastic (nuclear) and inelastic (electronic) scattering processes. These processes were originally described by Lindhard, Scharff and Schiott, best known as the LSS theory[41].

The energetic ions impinging on the target, which in our case is SiO\(_2\), lose their kinetic energy and come to rest after a series of collisions. An energetic ion on its path is slowed down by nuclear collisions and electronic scattering process. These are also known as elastic and inelastic interactions respectively. The energy loss per unit length can be written as:

\[
\frac{dE}{dx} = \left( \frac{dE}{dx} \right)_{nuc} + \left( \frac{dE}{dx} \right)_{el} = -\rho[S_{nuc}(E) + S_{el}(E)] = -\rho S(E) \tag{1-22}
\]

In the above equation \( \rho \) is the number density of atoms in the sample, \( S_{nuc}(E) \) is the nuclear stopping cross-section and \( S_{el}(E) \) is the electronic stopping cross-section. The nuclear energy loss can be thought to be a series of binary collisions in which the energy is transferred to the substrate atoms. This described in known as the binary collision approximation[42]. The nuclear stopping cross-section can be defined as[43]:

\[
S_{nuc}(E) = \int_{0}^{T_{max}} T d\sigma \tag{1-23}
\]

In this equation \( d\sigma \) is the scattering cross-section and \( T \) is the transferred energy by a collision. Now, \( d\sigma \) is dependent on the energy of the ion before collision and the
interatomic potential, hence it can be written as $d\sigma(E, V)$. The energy transferred from ion $M_1$ to atom $M_2$ is equal to:

$$T = \frac{1}{2} M_2 v_2^2 = \left( \frac{4 M_1 M_2}{(M_1 + M_2)^2} \right) E_0$$  \hspace{1cm} (1-24)

More details about the interatomic potential can be found in [42, 43]. It is found[44] that initially the nuclear stopping cross-section increases linearly until it reaches a maximum at some intermediate energy. It then decreases for high energies since the faster the ions become the less time they have to interact with target atoms. Furthermore, heavier atoms experience a larger energy loss per unit distance. The electronic stopping cross-section is found to be equal to[44]:

$$S_{et}(E) = k_e \sqrt{E}$$  \hspace{1cm} (1-25)

In the above equation $E$ is the energy of the incident ion and $k_e$ is a coefficient which is a weak function of atomic mass and atomic number. It is shown in [44] that for phosphorus and boron incident to Si, electronic stopping dominates for a large energy range of the incident ion. However, for heavy ions such as arsenic, nuclear stopping will dominate over most of the energy range. The implanted profile can be approximated along the angle of incidence as:

$$n(x) = \frac{s}{\sqrt{2\pi}\sigma_p} \exp \left[ -\frac{(x-R_p)^2}{2\sigma_p^2} \right]$$  \hspace{1cm} (1-26)

In the above equation $S$ is the ion dose per unit area, $x$ is the distance from the surface of the target on the side the ion is incident, $R_p$ is the projected range and $\sigma_p$ is the projected straggle which accounts for the statistical fluctuations in the projected range. When the $S_{nuc}(E)$ and $S_{et}(E)$ are known one can calculate the range $R$ by integrating the first equation of this section. Furthermore the $R_p$ and $\sigma_p$ can then be approximated as[44]:

$$R_p \cong \frac{R}{1+(M_2/3M_1)}$$  \hspace{1cm} (1-27)

$$\sigma_p \cong \frac{2}{3} \left( \sqrt{\frac{M_1 M_2}{M_1 + M_2}} \right) R_p$$  \hspace{1cm} (1-28)

The concentration versus depth profile shows a tail which varies exponentially, i.e. deviates from the predicted Gaussian profile[44]. This is due to the ion-channelling effect which happens when the incident ions are aligned with the major crystallographic direction. This results to the ions following a path between the rows.
of atoms in a crystal. This means that the ions will not be brought close to atoms to experience nuclear stopping. It is then a consequence that these ions will only experience electronic stopping. There are many different techniques to minimize ion-channeling[44] and there are generally implemented in modern ion implantation. Nuclear stopping causes atoms to be displaced which they can displace other atoms in their turn and cause a tree of disorder. The material will be amorphous if the displaced atoms per unit volume are equal approximately to the atomic density of the material. The tree of disorder occurs close to the final position for lighter ions since for most of the path electronic stopping dominates and nuclear stopping becomes dominant only in the final stages of the ion movement. An estimation of the dose required for a crystalline material to become amorphous is given by the following equation:

\[ S = \frac{(10^2 \text{keV/cm}^2)R_p}{E_0} \]  

(1-29)

The line of disorder becomes a cluster of disorder for heavy ions since too many atoms are displaced and a cluster is created. Annealing is used for semiconductor materials in order to restore mobility, lifetime and other physical parameters that have been degraded by the disorder cluster and the implantation damage.

### 1.9. SiO\(_2\) film growth

Oxide growth is achieved using the technique of ‘wet’ thermal oxidation. Using this technique it was possible to obtain films of high temperature oxide (HTO) on either (100) silicon substrates or grown from a layer of Si on Al\(_2\)O\(_3\) substrates. In this case the oxidising agent was H\(_2\)O which was heated to 1000°C at 1 atmosphere and reacted with the wafers in the following manner:

\[ \text{Si(solid)} + 2\text{H}_2\text{O(gas)} \rightarrow \text{SiO}_2\text{(solid)} + \text{H}_2 \]  

(1-30)

An atomically flat interface is formed when the oxidising agent diffuses into silicon[45]. The next thing that happens is a layer by layer consumption of the uppermost parts of the silicon. The ratio of film growth to substrate consumption is a function of the ratio of the atomic densities of silicon and, given by:

\[ \frac{x_0}{x_{Si}} = \frac{N_{Si}}{N_0} \]  

(1-31)
In equation 1-31 \( x_0 \) is the thickness of the oxide formed, \( x_{Si} \) is the thickness of the Si substrate, \( N_{Si} \) is the atomic density of silicon and \( N_0 \) is the atomic density of silicon dioxide. When \( N_{Si} = 5 \times 10^{22} \text{ atoms/cm}^3 \) and \( N_0 = 2.3 \times 10^{22} \text{ molecules/cm}^3 \), then \( \frac{x_0}{x_{Si}} = 2.17 \). This is shown in the next figure.

![Figure 1-7](image.jpg)

**Figure 1-7:** Molecular dynamics simulation of (a) \( x_0 = 1 \text{nm} \), (b) \( x_0 = 3 \text{nm} \) and (c) \( x_0 = 5 \text{nm} \) oxide growth on Si (001). The red dotted line shows the original substrate. Image adapted after [45].

The best known model for the resulting film growth was reported in 1965 by Deal and Grove[46]. Reaction rates and film growth can be predicted with very good accuracy using this model. The rate of growth of the oxide layer depends on the following factors:

- The molecules per unit area per unit time of the oxidising agent (\( \text{O}_2 \) or \( \text{H}_2\text{O} \))
- The reaction rate of the oxidising agent-oxide and oxide-silicon interfaces
- The diffusion of the oxidizing agent through the initial oxide layer
- The solubility of the oxidizing agent in the oxide

In the Deal-Grove model the initial oxide layer, \( x_i \), is related to a growth of oxide layer, \( x_0 \), by the following equation:

\[
x_0^2 + Ax_0 = Bt + x_i^2 + Ax_i
\]  

(1-32)

The above equation can be rewritten as:

\[
x_0^2 + Ax_0 = B(t + \tau)
\]  

(1-33)

In equation 1-33 \( \tau \) is given by:

\[
\tau = \frac{(x_i^2 + Ax_i)}{B}
\]  

(1-34)
In equation 1-31 \( \tau \) is the shift in the oxidation time interval before the start of the reaction. The oxide thickness is then given as a function of time by:

\[
x_0(t) = \frac{A}{2} \sqrt{1 + \frac{t + \tau}{A^2/4B}} - 1
\]  

(1-35)

For short oxidation times this gives:

\[
x_0 = \frac{B}{A}(t + \tau)
\]

(1-36)

For long oxidation times one obtains:

\[
x_0^2 \approx B(t + \tau)
\]

(1-37)

\( B \) is the parabolic rate constant. The values of \( B/A \) and \( B \) can be calculated from known constants such as the activation energies for oxidation. Hence the film’s thickness can be calculated for ‘wet’ (H\(_2\)O) and ‘dry’ (O\(_2\)) oxidation for a given oxidation temperature.

The reason that ‘wet’ oxidation was used to produce the samples in this work is because it can grow the required oxide thickness in much less time than ‘dry’ oxidation.

### 1.10. Rapid Thermal Annealing

Annealing is the term used when a material undergoes thermal processing. In this work thermal annealing serves two purposes:

- Removal of the implantation induced damage
- Formation and growth of Si-NCs by phase separation of excess silicon and silicon dioxide

Rapid Thermal Annealing is a process where the samples are rapidly heated to a high temperature. This heating lasts for short times. The annealing was performed using a commercial Jipelec Jetfirst 100 rapid lamp heating system. This was done in McMaster University in Canada. More details about how this rapid thermal annealing system works can be found in [21].
2. Chapter 2: Diffusion dynamics in Si-NC ensembles: Simulations using a Molecular Dynamics Model

2.1. Molecular Dynamics (MD) Model and sample preparation

2.1.1. Model description

The model used throughout this work is essentially that of Strobel et al.[29]. It is a simple model that uses a MC method in order to model the diffusion dynamics in Si-NC ensembles. This model has the advantage of both the simplicity and the high speed on a normal computer. Also, it allows building super-cells with the extraction of various parameters from it. A super-cell is in our case a simple cubic cell with very big dimensions. The first important thing to notice in this model is that it has a FCC (face centre cubic) lattice orientation. The host matrix is a simple cubic cell which in our case is SiO$_2$. The model allows a fraction excess of Si atoms to be distributed randomly on lattice sites. The Si atoms are contained in the host matrix which forms a background. The model contains equations which govern the energetics of the atoms. When the atoms are allowed to diffuse, the equations give the probability of a jump of an atom from one lattice site to a random neighbouring site. For each lattice site there are 12 nearest neighbours. If the atom position is $n_i$ then its nearest neighbours will be at $n_i + v_j$ where $v_j$ is the nearest neighbour vector. The nearest neighbour vector is a vector from a set of 12 vectors. Each nearest neighbour vector is a vector with unit steps in x-, y- and z- coordinates so that when the absolute number of unit steps is added for each vector they sum to 2. More specifically, $v_j$ is a vector out of a set of vectors which is: $([1,1,0], [1,-1,0], [-1,1,0], [-1,-1,0], [0,1,1], [0,-1,1], [0,1,-1], [0,-1,-1], [1,0,1], [-1,0,-1], [-1,0,1])$. This means that $j$ takes the values from 1 to 12 and for example $v_1 = [1,1,0]$.

Hence, the atoms are purely connected by nearest neighbour forces and an atom jumping can be essentially thought of an atom diffusing in SiO$_2$. The probability of an atom diffusionally jumping from one lattice site to another site is given by:

$$\frac{1}{\tau_0} \exp \left( - \frac{E_A}{k_BT} \right), \quad n_f \geq n_i$$

(2-1)
In equation 2-1, $\frac{1}{\tau_0}$ is the attempt frequency of jumps, $n_f$ is the number of nearest neighbours of the final site and $n_i$ is the number of nearest neighbours of the initial site. Hence equation 2-1 is only valid if $n_f \geq n_i$. When $n_f < n_i$ equation 2-2 is valid:

$$\frac{1}{\tau_0} \exp \left\{ - \left[ \frac{E_A + (n_i - n_f)E_B}{k_B T} \right] \right\}, \quad n_f < n_i$$

In equation 2-2 $E_B$ is the binding energy of silicon to itself. In order to normalize the time scale the MC step is defined to be:

$$\tau = \tau_0 \exp \left( \frac{E_A}{k_B T} \right)$$

As we will see in the results section, this model is capable of reproducing well the observed processes of nucleation, growth and further increases of size of Si-NCs by Ostwald ripening. When the simulation is finished running a recursive routine is used to count the cluster sizes. This routine counts all neighbour clusters and when there are no neighbours it starts over again. All the cluster sizes are then appended in a list which is analyzed in Mathematica in order to determine the Si-NC size. In order to calculate the size (i.e. diameter) of a Si-NC we assume that 1nm represents 50 Si atoms. We need to find how many nm represent 2 Atoms hence the equation for the volume becomes:

$$V = \frac{50}{2} \left( \frac{4\pi}{3} r^3 \right)$$

In equation 2-4 $V$ is the number of atoms forming half a Si-NC and $r$ is its radius. Solving for $r$ gives the size $d$ in the following equation:

$$d = 2 \left( \frac{6V}{100\pi} \right)^{1/3}$$

### 2.1.2. Phosphorus Model description

The next part was to investigate the effect of phosphorus on the nucleation and growth dynamics of the clusters using the molecular dynamics simulation. The program was modified so that any random site that is not occupied by a silicon atom and belongs to the face centre cubic orientation can have a phosphorus atom. In order for the model to be representative of the real situation the diffusion rates of the two atoms in silicon dioxide must be compared. The diffusion rates at 1100°C are
3*10^{-13} \text{cm}^2\text{s}^{-1}, 1.5*10^{-15} \text{cm}^2\text{s}^{-1} \text{ and } 1.1*10^{-16} \text{cm}^2\text{s}^{-1} \text{ for phosphorus in silicon, }
phosphorus in silicon dioxide and silicon in SRO respectively. Although the
diffusion rate of SRO is not equal to the diffusion rate of Si in SiO}_2, we assume that
it is a good approximation to the later. Phosphorus (P) is then introduced and the
equations of diffusion when a silicon atom is facing SiO}_2 (host matrix) or a P atom is
then the following:

\[ \frac{1}{7F\tau_o} \exp \left( -\frac{E_A}{k_BT} \right), \quad n_f \geq n_i \quad (2-6) \]

Equation 2-6 is the same as equation 2-1 but now the probability is divided by 7 and
is also divided by a constant \(F\). The division by 7 is because silicon diffuses 7 times
slower than phosphorus in oxide and the constant \(F\) determines how much faster
phosphorus diffuses in silicon than phosphorus in oxide. When \(n_f < n_i\) equation 2-7
is valid:

\[ \frac{1}{7F\tau_o} \exp \left\{ -\left[ \frac{E_A + (n_i - n_f)E_B}{k_BT} \right] \right\}, \quad n_f < n_i \quad (2-7) \]

In this study \(F\) is varied between 1 and 100. Now, when a phosphorus atom is facing
a silicon atom the probabilities of diffusion will be:

\[ \frac{F_2}{\tau_o} \exp \left\{ -\left[ \frac{E_A + (n_i - n_f)E_B}{k_BT} \right] \right\}, \quad n_f > n_i \quad (2-8) \]

\[ \frac{F_2}{\tau_o} \exp \left( -\frac{E_A}{k_BT} \right), \quad n_f \leq n_i \quad (2-9) \]

The variable \(F_2\) will depend on the environment of the initial position and will scale
from \(1/F\) to 1. Hence it will be given by:

\[ F_2 = \frac{1}{F} + \left( 1 - \frac{1}{F} \right) \frac{n_i}{12} \quad (2-10) \]

Also, one notices that the energy term of \((n_f - n_i)E_B\) is included since phosphorus
is facing a silicon atom. When the phosphorus atom is facing the host matrix (SiO}_2)
then the probability of diffusion becomes:

\[ \frac{F_2}{\tau_o} \exp \left( -\frac{E_A}{k_BT} \right) \quad (2-11) \]

Equation 2-11 is valid for \(n_f \geq n_i\) and \(n_f < n_i\).
2.1.3. Sample preparation

The samples used in this study were already described in previous publications of Crowe et al.[47, 48]. In brief 500nm SiO₂ films were grown by ‘wet’ thermal oxidation from either single crystal (100) Si (TEM) or sputtered Si on Al₂O₃ (Raman). The oxide films were then implanted with Si⁺ at 80keV to an areal density of 8x10¹⁶cm⁻², which yields a 100nm wide band of excess Si atoms, centred ~100nm below the surface as verified by TEM. This distribution yields a Si peak concentration of ~8 at.% excess. Annealing of the Si supersaturated oxide films to obtain Si-nanocrystals and remove implantation damage was executed using a commercial Jipelec Jetfirst 100 rapid thermal processor in a nitrogen (N₂) ambient for isochronal anneal temperatures in the range 1050 to 1200°C and isothermal anneal times in the range 1 to 300s. Cross-sectional transmission electron microscopy (X-TEM) was then used to image and count nanocrystals in the diameter range 1-6nm to obtain size distributions described in references [21]. Table 1 summarizes the main preparation conditions for these samples.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Silicon implant dose (atcm²)</th>
<th>Silicon (at. % excess)</th>
<th>Annealing temperature in N₂, Tₐ (°C)</th>
<th>Annealing time in N₂, tₐ (s)</th>
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</thead>
<tbody>
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<td>8*10¹⁶</td>
<td>8</td>
<td>1050</td>
<td>3</td>
</tr>
<tr>
<td>I2</td>
<td>8*10¹⁶</td>
<td>8</td>
<td>1050</td>
<td>10</td>
</tr>
<tr>
<td>I3</td>
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<td>8</td>
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Table 1: Preparation for the samples discussed in chapter 2
2.2. Results

2.2.1. Nucleation, growth and Ostwald ripening of Si-NCs using MD model

Essentially, after fixing the volume fraction of Si in the MD model, there are two parameters that can be varied; the number of MC steps (MCS) and the ratio $E_B/k_B T$. Running the model as described in Section 2.1.1, for $x=0.08$ where $x$ is the Si volume fraction and for a range of ratio $E_B/k_B T$ we notice that realistic accretion occurs in the range 10-1000 MCS. For values of this ratio <0.6 (corresponding to very high temperatures or low binding energy) it is found that the silicon atoms do not accrete into nanoclusters, in effect the solubility of silicon exceeds 8% in this case. For values >3 then the binding energy is so high that dimers and trimers form immediately and do not dissociate or diffuse. Therefore we expect the value of $E_B/k_B T$ ratio that represents the physical situation to be lying between 0.6 and 3. Figure 2-1 shows a slice through a cubic cell with side=150 (150x150x150) for $E_B/k_B T = 0.9$ and MCS=30.

![Figure 2-1: slice through a cubic cell with side=150 (150x150x150) for $E_B/k_B T=0.9$ and MCS=30.](image)

Figure 2-2 shows a slice through a cubic cell with side=150 (150x150x150) for $E_B/k_B T = 0.9$ and MCS=1000. Figure 2-3 shows a zoom of the slice shown in Figure 2-2.
Figure 2-2: Slice through a cubic cell with side=150 (150x150x150) for $E_B/k_B T=0.9$ and MCS=1000

Figure 2-3: Zoom of the slice shown in Figure 2-3

Figure 2-4 shows a slice through a cubic cell with side=150 (150x150x150) for $E_B/k_B T = 0.9$ and MCS=10000. Figure 2-5 shows a zoom of the slice shown in Figure 2-4.
Figure 2-4: Slice through a cubic cell with side=150 (150x150x150) for $E_B/k_B T=0.9$ and MCS=10000

Figure 2-5: Zoom of the slice shown in Figure 2-4

It is clear from the above Figures that Nanocluster formation is reproduced well by what is essentially a very simple model, in particular the use of a FCC lattice reproduces faceting of the nanoclusters along 110 planes and the background distribution of dissolved silicon atoms. The particle sizes were extracted numerically from the data and particles containing less than 5 Si atoms were excluded. Figure 2-6 shows the size distribution for $E_B/k_B T = 0.9$ and MCS=30. The solid line is a log-normal fit as predicted by diffusion limited growth.
Figure 2-6: Size distribution for $E_B/k_B T=0.9$ and MCS=30. The solid line is a log-normal fit.

Figure 2-7 shows the size distribution for $E_B/k_B T = 0.9$ and MCS=1000. The solid line is a log-normal fit as predicted by diffusion limited growth.

Figure 2-7: Size distribution for $E_B/k_B T=0.9$ and MCS=1000. The solid line is a log-normal fit.

Figure 2-8 shows the size distribution for $E_B/k_B T = 0.9$ and MCS=10000. The solid line is a log-normal fit as predicted by diffusion limited growth.
Figure 2-8: Size distribution for $E_B/k_B T=0.9$ and MCS=10000. The solid line is a log-normal fit

The first thing to notice from Figures 2-6 to 2-8 is that log-normal distribution is quite a good fit for all MCS. This confirms that the growth and Ostwald ripening of Si-NCs is diffusion limited.

Figure 2-9 shows the size versus MCS in the range of 10-30000MCS for three values of $E_B / k_B T$ (0.8, 0.9 and 1.0).
Figure 2-9: Size versus mc steps (MCS) for $E_B/k_BT=0.8$, $E_B/k_BT=0.9$ and $E_B/k_BT=1.0$

One can clearly see from Figure 2-9 that in the first 50 MCS the size is about the same for all three values of $E_B/k_BT$. This is the accretion of Si-NCs and essentially the $E_B/k_BT$ ratio has the effect to change the growth of Si-NCs after 50 MCS. Hence, from Figure 2-9 we can see two phases; the accretion and the growth which includes the Ostwald ripening. Hence changing $E_B/k_BT$ has the effect to change the second phase. The next step is to use these curves to fit to our experimental data and fix both the MC step time and the value of for $E_B/k_BT$ in the silicon in oxide system. Figure 2-10 shows the size versus the anneal time for three values of $E_B/k_BT$ and the experimental results for 1100°C anneal temperature for our samples.
Figure 2-10: Size versus anneal time for $E_B/k_B T=0.8$, $E_B/k_B T=0.9$ and $E_B/k_B T=1.0$ with MC step of 40ms. Circles are data of annealing at 1100°C.

One can clearly see from Figure 2-10 that the best fit is for $E_B/k_B T = 0.9$. The MC step time in this case is 40ms, i.e. 1MCS=40ms. Varying the temperature of the anneal in the model corresponds to changing the value of $E_B/k_B T$, however changing T will also have the effect of speeding up the diffusion rate exponentially as given by the MC step in equation 2-3. In practice this dominates the temperature dependence of the dynamics of the formation process, so that the temperature variation in the ratio $E_B/k_B T$ is only very small in the range over which the temperature can be realistically varied if the nanocluster formation is to occur on a realistic time scale. The next step is to try to fit the data for 1050°C and 1150°C annealing temperatures. To obtain these fits we assume the value of $E_B/k_B T = 0.9$ and adjust the value of the MCS time to fit the change in nanocluster growth rate that occurs at the end of the accretion phase (this essentially occurs after 60MCS).

Although the data for 1050°C annealing temperature are sparser good fit is obtained for $E_B/k_B T = 0.9$. The MC step time in Figure 2-11 is 120ms.
Figure 2-11: Size versus anneal time for $E_B/k_B T=0.8$, $E_B/k_B T=0.9$ and $E_B/k_B T=1.0$ with MC step of 120ms. Circles are data of annealing at 1050°C

Figure 2-12 shows the fitting of the data from 1150°C annealing temperature using the same values of the ratio $E_B/k_B T$ as in Figure 2-10.

Figure 2-12: Size versus anneal time for $E_B/k_B T=0.8$, $E_B/k_B T=0.9$ and $E_B/k_B T=1.0$ with MC step of 11ms. Circles are data of annealing at 1150°C
One can clearly see from Figure 2-12 that the best fit is $E_B/k_B T = 0.9$. The MC step time is 11ms. Hence, the MD model can fit quite well all our data. The next step is to check whether the growth exponent for the fit of $E_B/k_B T = 0.9$ is $1/3$ as expected by LSW theory. Ostwald ripening is a process that occurs in this model after 300MCS. Figure 2-13 shows the size versus MCS for $E_B/k_B T = 0.9$. The solid line is a power law fit.

From Figure 2-13, one can see that the power law fit is a very good fit to the model for $E_B/k_B T = 0.9$. The growth exponent is 0.33 which agrees with LSW theory of Ostwald ripening. This also confirms that after 300MCS the Si-NCs are in the Ostwald ripening regime.

### 2.2.2. Arrhenius Plot

The next step is to plot the Arrhenius relationship for the three fits of 1050°C, 1100°C and 1150°C. Diffusion activation energy is the barrier needed for an atom to overcome to diffuse to a nearest neighbour. This is given by $E_A$ in equation 2-1. From equation 2-3 when we take natural logarithms on both sides we see a linear relationship between the natural logarithm of the MC step and the activation energy,

![Figure 2-13: Size versus MCS for $E_B/k_B T = 0.9$ after 300MCS](image)
which is \( \ln \tau = \ln \tau_0 + \left( \frac{E_A}{k_B T} \right) \). The activation energy will be the gradient of this equation and Figure 2-14 shows the Arrhenius plot and a linear fit.

![Figure 2-14: Arrhenius plot of natural logarithm of MC step time and inverse of temperature. The solid line is a linear fit to the data.](image)

From the gradient of the Arrhenius plot and equation 2-3 we find the activation energy \( E_A = 3.87 eV \) and \( \tau_0 = 157 fs \). By extrapolation of the fit of the Arrhenius data we find that the accretion (approximately 50 MCS) will take 1.8s at 1100°C, 0.11s at 1230°C and 34 minutes at 857°C. Thus confirming that the formation of nanocrystals by diffusion limited growth is only feasible in the range 950-1250°C and that this gives one only limited control over the value of \( E_B/k_B T \) which can be used to control the process in ways other than the rate of growth in time.

### 2.2.3. Solubility of Si in SiO₂

Figure 2-15 shows the fraction of unbonded silicon in the matrix as a function of anneal time (in MCs) for three values of the ratio \( E_B/k_B T \). This was derived from the data by simply counting the atoms with no silicon nearest neighbours. Clearly when we look at the silicon nanocrystal situation we are seeing a solubility which is a function of the complex structure of the nanocrystals. However, this is still a useful
parameter to study as it is of relevance to oxide in the presence of nanometer scale silicon structure and thus of interest to modern CMOS device fabrication.

![Figure 2-15: Fraction of isolated silicon for $E_B/k_B T=0.8$ (squares), $E_B/k_B T=0.9$ (circles), and $E_B/k_B T=1.0$ (triangles). The solid lines are exponential fits to the last four data points of each set of data respectively.](image)

One can see from Figure 2-15 that in the first 10 MCS the fraction of isolated silicon falls very fast. As can be seen from figure and is to be expected from thermodynamics, the predicted solubility of silicon in the oxide matrix is strongly temperature dependent (through the ratio $E_B/k_B T$). The fraction of isolated silicon was fitted by exponential fits for each ratio of $E_B/k_B T$ so that the fits are asymptotes. It is found that the value of free silicon is the asymptotic value for each fit. The values of free silicon are 6.43%, 4.41% and 2.35% for $E_B/k_B T = 0.8$, $E_B/k_B T = 0.9$ and $E_B/k_B T = 1.0$ respectively. If we take $E_B/k_B T = 0.9$ as being appropriate for $T=1100^\circ C$ (our best fit), we can interpret the values of 0.8, 0.9 and 1.0 as corresponding to sample temperatures of 964$^\circ C$, 1100$^\circ C$ and 1272$^\circ C$ respectively. As has already been discussed, with such a phenomenological model it is difficult to interpret calculated parameters in terms of real measurables. However if we continue with our interpretation on each unit in the SiO$_2$ matrix as being an SiO$_2$
molecule than we can interpret the measured number of isolated atoms ($N_{Si}$) as solubilities per SiO$_2$ molecule as given by:

$$[Si] = [SiO_2] \frac{N_{Si}}{(1-x)N+N_{Si}}$$

(2-20)

In the above equation $[SiO_2] = 2.3 \times 10^{22}/cm^3$, $N$ is the total lattice sites in the model equal to 1687500, $x = 0.08$ is the volume fraction of silicon and $N_{Si} = 135000 \times \varphi$, i.e. the total Si atoms times the free silicon fraction. For 964°C, 1100°C and 1272°C the values above then correspond to solubilities per cm$^3$, $[Si]$, of $1.27 \times 10^{20}$, $8.10 \times 10^{19}$ and $4.69 \times 10^{19}$ respectively. The solubility of Silicon in thermal oxide is poorly known, Agarwal et al [49] estimated experimentally the solubility of Si in SiO$_2$ to be $\sim 4 \times 10^{20}/cm^3$ at 1100°C. This is 5 times larger than our figure above but can be considered to be reasonably close. More recently Sarikov et al [50] reported from free energy consideration an Arrhenius type dependence with solubility values in the range $10^{19}$-10$^{21}$/cm$^3$ for temperatures 600-1200°C. If we assume as similar dependence:

$$\Delta C_{[Si]} = \Delta C_{[Si]}^0 exp \left( \frac{-E_{sol}}{kT} \right)$$

(2-21)

and plot the three values above (Figure 2-16) we obtain values for $\Delta C_{[Si]}^0 = 7.21 \times 10^{21}/cm^3$ and the activation energy of solution of 0.534eV. In equation 2-21 $\Delta C_{[Si]}$ is the solubility of silicon.
Figure 2-16: Arrhenius relationship of concentration of solubility of silicon and inverse of temperature. The solid line is a linear fit to the data. The gradient is the activation energy of solution $E_{sol}$.

The value of $\Delta C_0^{[Si]}$ is sensitive to the exact value of $E_p/k_B T$ chosen, however we expect the value of $E_{sol}$ relatively insensitive to this ratio as it represents a binding energy which governs the rate of increase of the solubility, our value 0.534eV is close to the 0.36 reported in ref[50]. The discrepancy can be related to inaccuracy in the model of simulating the isolated clusters at these temperatures.

2.2.4. Adding phosphorus in the model

The next part was to add phosphorus to the model as explained in section 2.1.2. In this model a bit representation is used where 1 represents Silicon, 2 represents Phosphorus and 0 represents the host matrix, i.e. SiO$_2$. A Mathematica routine is used to count the NNs of each phosphorus atom. Unfortunately, this aspect of the model has not been fixed yet meaning that phosphorus does not dope the Si-NCs but stay outside them in almost all cases. Of course, this is an indication that phosphorus may diffuse very fast in Si-NCs and hence not easily found inside Si-NCs as it will end up slowly moving outside them.
The first thing that was tried was to use a Binding energy ratio \( (E_B / k_B T) \) or simple BE) of 0.9 as this is the one for our best fit. Also the value of \( F \) is 10 (see section 2.1.2) in this case so that the probability of diffusion of silicon is

\[
\frac{1}{7 \times 10^5 \tau_0} \exp \left( -\frac{E_A}{k_B T} \right)
\]

This is the same as the original model (without phosphorus, i.e. \( \frac{1}{\tau_0} \exp \left( -\frac{E_A}{k_B T} \right) \)) but now multiplied by \( \approx 0.14 \times 0.1 \).

Figure 2-17: Size versus MCS for \( E_B / k_B T = 0.9 \) and \( F = 10 \). The concentration of phosphorus varies at 0, 0.006 (0.6%), 0.012 (1.2%), 0.015 (1.5%), 0.025 (2.5%) and 0.03 (3%).

Figure 2-17 shows the size versus the MCS for concentrations of P of 0, 0.006, 0.012, 0.025 and 0.03. One can clearly see that the size increases for increased concentration of phosphorus. This result agrees with the results of Hao et al[51], who reported an increased size in the presence of phosphorus. For 50000MCS which correspond to 700MCS of the original model the size increase is about 0.17nm. For P=0.015 the fraction of isolated phosphorus atoms was plotted versus MCS. This is shown in Figure 2-18.
One can clearly see from Figure 2-18 that the fraction of isolated phosphorus atoms increases with increasing MCS. This is because Ostwald Ripening is happening at these MCS which has the effect to decrease the number of Si-NCs by growing of the larger ones and shrinking of the smaller ones. Hence the surface area is decreasing and the volume is increasing. This leads to more phosphorus atoms being isolated.

The next thing attempted is to increase $F$ to 100, so that now the probability of diffusion of silicon will be the equation 2-1 (i.e. $\frac{1}{\tau_0} \exp \left( -\frac{E_A}{k_B T} \right)$) multiplied by $0.01*0.14$. The phosphorus concentration was varied at 0, 0.015 and 0.03. Figure 2-19 shows the size versus the MCS for these three concentrations of P.

One can clearly see that there is clearly an increase in size for increased phosphorus concentration. However the difference in size between phosphorus concentrations of 0.015 and 0.03 is almost inexistent. This is because at this BE the clusters break and bigger clusters cannot be formed. This is an error of the model that is fixed when the BE is increased to 1.5 (as it can be seen in the next few pages).
The fraction of isolated phosphorus atoms is also plotted in Figure 2-20 for the same probability and $P=0.015$.

One can see from Figure 2-20 that the fraction of isolated phosphorus atoms increases with monotonically with MCS in agreement to Figure 2-18.

Now, the BE is increased to 1.0 to investigate the effect of a reduced temperature and decreased solubility. In this case much less clusters break and the effect of adding phosphorus to the model can be better observed. Figure 2-21 shows the size versus MCS when $F$ is 10 for $E_B/k_B T = 1.0$. 

Figure 2-19: Size versus MCS for $E_B/k_B T=0.9$ and $F=100$. The concentration of phosphorus varies at 0, 0.015 and 0.03.

Figure 2-20: Fraction of isolated P atoms for $E_B/k_B T=0.9$, $F=100$ and P level is at 0.015
Figure 2-21: Size versus MCS for $E_B/k_B T=1.0$ and $F=10$. The concentration of phosphorus varies at 0, 0.015 and 0.03.

In Figure 2-21 the dashed line represents concentration of $P=0.015$, the dotted line represents concentration of $P=0.03$ and the solid line is for $P=0$. It is clear from Figure 20 that the size increases with increased phosphorus concentration.

Following this, the effect of increasing the binding energy even more is investigated. BE energy is now increased to 1.5, i.e. $E_B/k_B T = 1.5$. $F$ is now 10 so that the factor that equation 2-1 is multiplied by is $0.14 \times 0.1$. Figure 2-22 shows the size versus MCS for $E_B/k_B T = 1.5$ and $F=10$. Again the solid line is for $P=0$, the dashed line is for $P=0.015$ and the dotted line is for $P=0.03$. 
Figure 2-22: Size versus MCS for $E_b/k_B T=1.5$ and $F=10$. The concentration of phosphorus varies at 0, 0.015 and 0.03.

The next part is to increase $F$ to 100 and run the model for different MCS and various phosphorus concentrations. Figure 23 shows the results of size versus MCS for this case. Again the solid line is for $P=0$, the dashed-dotted line is for $P=0.006$, the dashed line is for $P=0.015$ and the dotted line is for $P=0.03$.

Figure 2-23: Size versus MCS for $E_b/k_B T=1.5$ and $F=100$. The concentration of phosphorus varies at 0, 0.015 and 0.03.

One can see from Figure 2-23 that the size of Si-NCs increases with increasing phosphorus concentration, in agreement with all previous results.
2.3. Discussion and conclusions

The results presented in Chapter 3 of this report show that a simple diffusion model which runs on current top performance workstations can reproduce the experimental results quite well. By running the model one can see three stages of the evolution of clusters:

- **Accretion:** This is the stage at the first 50 MCS of the model and is the same irrespective of the binding energy. The accretion stage is however dependable on the amount of silicon in the host matrix.
- **Growth:** The clusters grow by diffusion of atoms. This process lasts from 50MCS to 300MCS but some clusters may experience growth even for later than 300MCS.
- **Ostwald Ripening:** This is the stage where the biggest clusters grow and the smaller shrink by transfer of their atoms to bigger clusters. This stage can start as early as 300MCS for some clusters but is definitely the only process happening after 1000MCS.

A value of \( \frac{E_B}{k_B T} = 0.9 \) was found to be the best fit for all data of size for different annealing temperatures. Essentially the ratio \( \frac{E_B}{k_B T} \) alters the growth rate of the clusters but the accretion rate is constant. When the ratio \( \frac{E_B}{k_B T} = 0.9 \) is chosen the MC step time can be varied in order to fit the data for different annealing temperatures.

The fraction of isolated silicon atoms is found to increase with increasing binding energy modified through the ratio \( \frac{E_B}{k_B T} \). This is found from calculating the amount of free silicon for three different ratios of \( \frac{E_B}{k_B T} \), namely 0.8, 0.9 and 1.0. It is found that these data describe an Arrhenius relationship and the gradient of this relationship gives the energy of solution. The pre-exponential factor is related to the solubility of Silicon in \( \text{SiO}_2 \).

When phosphorus was added to the model it was found that the size increases in the presence of phosphorus. This happens for all values of the ratio \( \frac{E_B}{k_B T} \) investigated and it the size increase depends on the P concentration level. The larger is the P concentration level the bigger is the size increase. The effect is clearer for bigger values of the ratio \( \frac{E_B}{k_B T} \), for e.g. \( \frac{E_B}{k_B T} = 1.5 \), since for these ratios the clusters
in the simulation do not break (they stay together). When the probability of diffusion of silicon in oxide is made 1000 times slower than phosphorus diffusion in silicon then clusters were not formed. Finally, the fraction of isolated phosphorus atoms was calculated and it is increasing with increasing MCS, perhaps due to Ostwald Ripening that reduces the surface area and increases the volume of the clusters formed.
3. Chapter 3: Experimental studies of phosphorus doped Si-NCs

3.1. Introduction

In this Chapter I will present some experimental results on P doped Si-NCs. The experimental study involves Photoluminescence spectroscopy and Time Resolved Photoluminescence Spectroscopy. The purpose of this study is to investigate the effect of phosphorus ion implant doping on the luminescence associated with silicon nanocrystals as a function of the annealing environment. These experiments demonstrate that by keeping the silicon and phosphorus excess constant and changing the isothermal anneal time a quenching or enhancement of the luminescence intensity can be observed. These results will be explained based on the interaction of phosphorus dopants with silicon nanocrystals. The results and work presented in this Chapter were published in [30].

3.2. Phosphorus doped Si-NCs

The interaction of shallow dopant impurities with Si-NCs has been the subject of lot of the research during the past 15 years [52-56]. More specifically, it is of particular interest the interaction of donor, i.e. phosphorus (P) and acceptor, i.e. boron (B) impurities with Si-NCs. Recently this research found application on all silicon tandem solar cells [51, 57]. If devices are going to be realized from e.g. P doped Si-NCs, a good understanding of the structural properties is needed and how they are correlated with optical and electronic properties of P doped Si-NCs.

P doping of Si-NCs was achieved in previous research using various methods such as Si excess doping of phosphosilicate glasses (PSG)[56, 58], ion implantation of phosphorus and silicon excess is SiO₂ [59], phosphine gas doping of free-standing Si-NCs produced from the gas phase [60] and deposition of SiO/SiO₂ multilayer structures with introducing a P doped SiO₂ layer close to the SiO film and subsequent thermal treatment to form Si-NCs and doped them with P[61]. It has been reported [62] that below a certain size limit, impurity levels generated by P may not be shallow and consequently additional carriers may not be generated. In other words, as Chan et al. reported, below a specific size limit found about 2nm, P atoms...
are energetically expelled towards the surface. In general, it has been a difficult task so far to dope Si-NCs with P [61] due to their small size and large surface to volume ratios. This means that extremely large concentrations of phosphorus dopants are needed in order to dope Si-NCs.

Previous work has shown that doping Si-NCs with P can have both the effects of quenching [54, 63] and enhancing the Si-NC photoluminescence (PL) [53, 54, 64]. An important discovery was made by Mimura et al [54] who reported an infrared (IR) absorption band for heavily P doped Si-NCs. This IR absorption increased with P concentration and it was attributed to intravalley transitions of electrons which were supplied by P doping. This was directly related to the PL quenching that was observed, in the (PSG) prepared in this study, for heavy P doping. More specifically, the free electrons result in quenching in the exciton luminescence by opening a non-radiative de-excitation path via Auger recombination.

More recently the Manchester group published a paper [30] that shows that, dependent on the specific annealing time of P doped Si-NCs, there can be a quenching or an enhancement of the photoluminescence.

The PL decay rate for a Si-NC is given by:

$$w_{PL} = w_{NR} + w_R$$  \hspace{1cm} (3-1)

In equation 3-1, $w_{PL}$ is the PL decay rate, $w_{NR}$ is the non-radiative decay rate and $w_R$ is the radiative decay rate. Also, the PL intensity $I_{PL}$ is directly proportional with the PL decay rate, i.e. $I_{PL} \propto w_{PL}$. We rejected the hypothesis that the PL enhancement comes from an increase in the radiative decay rate, since we measured the PL decay rate and it was found smaller for P doped Si-NCs than intrinsic Si-NCs. It was rather proposed that the decrease in the PL decay rate is due to a decrease in the non-radiative decay rate which is consequently due to a decrease in the defect density in P doped Si-NCs compared to intrinsic doped Si-NCs. In previous studies by Fujii et al. it was found that the formation of Si-NCs produce a high density of dangling bond defects ($P_b$ centres) that are probably non-radiative recombination centres when the thin films are photo-excited [65]. The enhancement of the PL intensity for short anneal times is attributed to a decrease in the density of $P_b$ centres by a charge compensation mechanism as reported in previous studies [56, 65]. This means that optically inactive Si-NCs will become optically active when a P atom
eliminates a $P_b$ centre on the surface of the Si-NC. Thus, the trap energy level formed by the dangling bond will be eliminated and photo-excited carriers will be allowed to luminesce. On the other hand, when Si-NCs become bigger P atoms are more likely to dope substitutionally the Si-NCs. When these donors are ionized the free electron generation is increased which leads to a quenching of luminescence found in [30]. An increase in the free electron generation means that an efficient de-excitation path, via Auger recombination, of electron-electron-hole ($eeh$ Auger process) will be opened that is non-radiative. The study of [30] has further findings which are potentially important in the work reported here:

Increasing the annealing time results in bigger Si-NCs due to growth and Ostwald ripening. The emission energy of PL intensity is a rough approximate of the Si-NC bandgap. For P doped Si-NCs we note a shift in emission energy which is approximately 3 times larger than intrinsic Si-NCs. This implied an accelerated growth in the presence of P and perhaps an accelerated regime of Ostwald ripening. Previous reports have shown that P doping of Si-NCs results in an accelerated phase segregation[66] due to lowered melting temperature[67] and increased thermal expansion coefficient compared to pure silica which results in an enhanced ion diffusion length[68]. However, it would be very interesting to see if a simple diffusion model such as the one used in this work is enough to account for the accelerated growth in the presence of phosphorus and in which extent. The increased size in P doped Si-NCs compared to intrinsic Si-NCs prepared by ion implantation was confirmed by Hao et al [51].

This chapter presents a combined study of the PL and lifetime of phosphorus doped Si-NCs samples can be found which was published in [30]. The purpose of this study is to investigate the changes in the PL Intensity and lifetime between phosphorus doped Si-NCs and intrinsic Si-NCs (i.e. Si-NCs with no other species or dopants) of samples annealed at the same temperature and for a range of anneal times.
3.3. Experimental techniques

3.3.1. Photoluminescence spectroscopy

Photoluminescence is the emission of photons of certain wavelength (energy) from an exciton after they have been excited using a laser or other source of a certain wavelength (energy). The excitation occurs from the ground state of the quantum confined system, $E_0$, to an excited state $E_n$, via absorption of photons of energy $E = h\nu \geq E_n$. Photoluminescence is a very important method to characterize the electronic structure of a luminescent material since it gives valuable information about the energy level transitions and how bright each transition is relative to another.

Jablonski energy diagrams are used to describe absorption and emission of light. A typical Jablonski diagram is shown in Figure 3-1. Light is absorbed via the excitation source and the molecules or quantum dots are excited from the ground state, $E_0$, to a higher vibrational state. After relaxation to the first excited state, $E_1$, there is a possibility of recombination and emission of a photon with energy $\Delta E = E_1 - E_0$. This process is often named as fluorescence and it is experienced in many light-emitting systems; namely molecules and quantum dots.

In ensembles of Si-NCs the photoluminescence observed is a superposition of many mechanisms. It is now arguable that the reason of light emission from LD-Si is the
recombination of quantum confined excitons (electron-hole recombination), that emit light at different energies and therefore wavelengths in the VIS-NIR range. However, luminescence from Si-NCs ensembles is oftend broadened by the existence of a distribution of sizes of Si-NCs and other mechanisms such as spectral diffusion and the presence of phonon replicas in Si-NCs. In order to study the effect of photoluminescence in silicon rich silica films the set-up shown in Figure 3-2 was used which comprises an epi-fluorescence type of confocal microscope. The samples were excited using the 405nm line of an InGaN or solid state diode laser filtered by a bandpass filter before hitting the 90:10 beam splitter. The laser line was focused using a microscope objective lens (x60) on the sample. The PL was passed through a 450nm long pass filter (LPF) then collected with an ocular and dispersed using an optical fibre to the Bayspec detector which detects signal in the range of 400-1070nm. The spectra were analysed by means of PC software that can be used to change different settings of the detector, such as the integration time and the average number of spectra used to obtain one.

Figure 3-2: Epi-fluorescence set-up used to obtain the PL spectra for our samples
3.3.2. **Time resolved Photoluminescence spectroscopy**

Time resolved Photoluminescence Spectroscopy was performed in collaboration with Dr Kenyon’s group at University College London (UCL). The samples were excited using a Diode Pumped Solid State (DPSS) laser emitting at 473nm. A prism and a diaphragm were used to steer the laser beam and remove unwanted wavelengths respectively. The laser beam was modulated using a Pockels cell at frequency of 2.5kHz. A Near Infrared (NIR) sensitive Hamamatsu photomultiplier tube (R5507-72) was used to detect the PL transients and they were recorded using a digital storage oscilloscope.

3.3.3. **TEM Microscopy**

The maximum resolution that one can obtain with a light microscope, d, is limited by the wavelength of the light, \( \lambda \), and the numerical aperture of the system, NA. This is shown in Equation 3-2:

\[
d = \frac{\lambda}{2\text{nsina}} \approx \frac{\lambda}{2NA}
\]  

(3-2)

In equation 3-2, \( a \) is the lens collecting semi-angle, \( n \) is the refractive index of the medium which the lens is immersed.

The revolution came when Louis Victor-De Broglie discovered that electrons has both wave and particle properties. This means that a wave of electrons can be thought to behave as a beam of electromagnetic radiation. The de Broglie relation gives the wavelength of the electrons, as:

\[
\lambda_e = \frac{h}{p} = \frac{h}{m_0v}
\]  

(3-3)

For equation 3-3, \( \lambda_e \) is the wavelength of the electrons, \( h \) is Planck’s constant, \( p \) is the momentum of the electrons, \( m_0 \) is the mass of the electrons and \( v \) is the speed of the electrons. In the TEM the electrons have momentum and are accelerated by a high potential which results in an increase in their kinetic energy given in equation 46:

\[
eV = \frac{1}{2} m_0v^2
\]  

(3-4)

In equation 3-4, \( V \) is the potential that electrons are experiencing. The electron wavelength is then given by equation 3-5:
In equation 3-5, $E$ is the energy of the accelerated electron and $c$ is the speed of light. Electrons are generated using a process known as thermionic emission from a filament which is usually made of tungsten. This process is similar as the one in a light bulb. Alternatively they can be generated by field electron emission. The electrons are then accelerated by an electric potential. Subsequently they are focused on the sample by electrostatic and electromagnetic lenses. The transmitted beam contains a lot of information, such as the electron density, phase and periodicity. The beam is used to form an image where the interior of a material can be viewed. A schematic of the TEM is shown in Fig 3-3.

\[
\lambda_e \approx \frac{h}{\sqrt{2meE(1 + \frac{E}{m_0c^2})}}
\]  

(3-5)

Figure 3-3: Schematic of the TEM[69]

The TEM at its top has an emission source which can be a tungsten filament. When this filament is connected to a high voltage source and given enough current the gun will emit electrons either by thermionic or field electron emission in the vacuum. Electromagnets are used to move the electron beam according to a magnetic field. Thus, the electron beam can be manipulated. In addition, electrostatic fields can cause the electron beam to be deflected at a constant angle. The optical configuration
of the TEM can be easily modified by enabling, having their strengths changed and disabling completely the lenses. This is in contrast with the optical microscope. The angle of convergence is an important parameter in the operation of the TEM which can be changed through the use of lenses. The magnification can be changed by modifying the current passing through the lenses. There are three stages of lensing; condenser lens, objective lens and projector lens. The purpose of the condenser lens is to form the primary beam. The objective lens focuses the beam that comes through the sample. The projector lens is used to expand the beam onto the phosphor screen or any other imaging device. The magnification of the TEM is a result of the ratio of the distances between the objective lens’ image plane and the specimen. The size of the objective aperture limits the scattering angle of the electrons reaching the screen. This enables the image to form in bright or dark field contrast mode. In bright field mode the image formed is due to the absorption of electrons to the various parts of the sample, being brighter where the sample is thinner or where the atomic number of atoms is low. Dark field mode is due to diffraction of electrons from crystal planes.

Structural characterization of the samples was performed by X-TEM using a Philips CM-12 operated at 120 kV. This was performed by collaborators in McMaster University in Canada. Dark-field examinations were carried out with two beam diffraction condition (g=220) relative to the silicon substrate (rather than using the polycrystalline ring from the nanocrystals) in order to compare the size (and depth) distribution for all analyzed samples. Whilst the random orientation of the nanocrystals naturally yields an underestimate for the absolute density using this technique, the relative density, size, and distribution of nanocrystals in the implanted layer as a function of annealing time can be determined in a highly repeatable manner. Our experimental observation showed that the amount of observable nanocrystals depends on the chosen segment of the poly-ring and varies from ~10% to 15% of the total population. For each sample, several high magnification (125 and 200k) images were also taken in sequence, accounting for the entire nanocrystal distribution, and from which the nanocrystal sizes could be more accurately measured.
3.3.4. Sample preparation

Wet thermal oxidation was used to grow 500nm SiO$_2$ films from single crystal (100) Si. These films were then implanted with Si$^+$ to an aerial density of 8x10$^{16}$atcm$^2$. This yields a distribution of excess silicon atoms in a ~100nm wide band, centered ~100nm below the surface as predicted by SRIM 2003 and verified by TEM.

The peak concentration of the implanted distribution is ~10 at. % excess silicon as verified by Rutherford backscattering spectroscopy. Half of the wafer was additionally implanted with P$^+$ at 80keV to 5x10$^{15}$atcm$^2$. This yields a similar profile as silicon but now the peak distribution of phosphorus is ~0.8 at. %. The samples were then annealed using a commercial Jipelec Jetfirst 100 rapid thermal processor in a nitrogen (N$_2$) ambient at 1050°C for times in the range 1-600s. All the samples were then annealed in forming gas N$_2$:H$_2$ (5%) at 500°C for a further 5 minutes to remove “dangling-bond” type interfacial defects (Pb-centres).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Silicon implant dose (atcm$^2$)</th>
<th>Silicon (at. % excess)</th>
<th>Phosphorus implant dose (atcm$^2$)</th>
<th>Phosphorus (at. %)</th>
<th>Annealing temperature in N$_2$, T$_A$ (°C)</th>
<th>Annealing time in N$_2$, t$_A$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>8*10$^{16}$</td>
<td>10</td>
<td>0</td>
<td>0</td>
<td>1050</td>
<td>1</td>
</tr>
<tr>
<td>B</td>
<td>8*10$^{16}$</td>
<td>10</td>
<td>0</td>
<td>0</td>
<td>1050</td>
<td>5</td>
</tr>
<tr>
<td>C</td>
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<td>10</td>
<td>0</td>
<td>0</td>
<td>1050</td>
<td>10</td>
</tr>
<tr>
<td>D</td>
<td>8*10$^{16}$</td>
<td>10</td>
<td>0</td>
<td>0</td>
<td>1050</td>
<td>50</td>
</tr>
<tr>
<td>E</td>
<td>8*10$^{16}$</td>
<td>10</td>
<td>0</td>
<td>0</td>
<td>1050</td>
<td>100</td>
</tr>
<tr>
<td>F</td>
<td>8*10$^{16}$</td>
<td>10</td>
<td>0</td>
<td>0</td>
<td>1050</td>
<td>600</td>
</tr>
<tr>
<td>G</td>
<td>8*10$^{16}$</td>
<td>10</td>
<td>5*10$^{15}$</td>
<td>0.8</td>
<td>1050</td>
<td>1</td>
</tr>
<tr>
<td>H</td>
<td>8*10$^{16}$</td>
<td>10</td>
<td>5*10$^{15}$</td>
<td>0.8</td>
<td>1050</td>
<td>5</td>
</tr>
<tr>
<td>I</td>
<td>8*10$^{16}$</td>
<td>10</td>
<td>5*10$^{15}$</td>
<td>0.8</td>
<td>1050</td>
<td>10</td>
</tr>
<tr>
<td>J</td>
<td>8*10$^{16}$</td>
<td>10</td>
<td>5*10$^{15}$</td>
<td>0.8</td>
<td>1050</td>
<td>50</td>
</tr>
<tr>
<td>K</td>
<td>8*10$^{16}$</td>
<td>10</td>
<td>5*10$^{15}$</td>
<td>0.8</td>
<td>1050</td>
<td>100</td>
</tr>
<tr>
<td>L</td>
<td>8*10$^{16}$</td>
<td>10</td>
<td>5*10$^{15}$</td>
<td>0.8</td>
<td>1050</td>
<td>600</td>
</tr>
</tbody>
</table>

Table 2: Preparation conditions for samples discussed in Chapter 3
3.3.5. **SRIM (Stopping Range of Ions in Matter)**

Stopping Range of Ions in Matter (SRIM) is a process which allows one to predict with a good accuracy (~5%)[70] the statistical distribution of implanted ions in a matrix (e.g. Si⁺ in SiO₂). SRIM is a stochastic process that employs Monte Carlo[70, 71] simulations in order to calculate the ion range distributions. During the course of this work we used the freeware simulation SRIM 2008[72] developed by Ziegler et al. [70] to obtain predicted statistical distribution for ion ranges vs. depth and atomic concentration vs. depth for Silicon (Si⁺) and Phosphorus (P⁺) implanted into SiO₂.

Figure 3-4 shows the simulation in process for implanting silicon in 200nm SiO₂ target, ion distribution analysis, ionization and energy to recoils graphs. The implantation energy is 80keV.

![SRIM simulation windows](image)

**Figure 3-4:** SRIM simulation windows: top left is the simulation run of the implantation of silicon into SiO₂ target. The top right window shows the statistical ion range distribution, which can be well fitted by a Gaussian distribution.

Figure 3-5 shows the at.% versus depth in nm for the implantation of Si ions in SiO₂ target.
Figure 3-5: SRIM implant calculations for 4 different implantation energies, at.% vs Depth (nm)

For the samples used in this study the at. % excess of silicon and at. % of phosphorus versus the depth is shown in Figure 3-6.

Figure 3-6: SRIM profile showing si at. % excess and p at. % versus depth
3.4. Results and discussion

3.4.1. TEM results

Figure 3-7 shows the evolution of the (intrinsic) silicon nanocrystal size distribution with isothermal annealing time.

As the annealing time increases, the rapid formation of clusters is followed by an increase in their mean size and a corresponding reduction in their relative density. This phenomenon is characteristic of Ostwald ripening after the phase segregation of a meta-stable alloy[22, 73]. For a fixed concentration and annealing temperature, the homogeneous growth of the clusters is primarily limited by ion diffusion in the host matrix [74, 75]. However, it is well known that the formation energy can be lowered significantly, and the rate of cluster growth enhanced at pre-existing defect, or impurity sites, via heterogeneous growth[22].
3.4.2. PL Spectra

The PL spectra for the samples containing no phosphorus (P=0) are shown in Fig 7-1. $T_A$ is the annealing temperature which is kept constant at 1050°C. The legend on the right shows the annealing time of each sample studied.

![Image of PL spectra](image)

**Figure 3-8: PL spectra of samples with P=0 for different annealing times**

From the above figure one can see that the PL Intensity increases monotonically with annealing time when there is no phosphorus. The samples prepared for this study exhibit PL spectra typical of silicon nanocrystals[76, 77], with a broad peak centred close to 1.5 eV (800 nm). The peak of the emission band is monotonously redshifted with increasing anneal time, indicative of a reduction in the recombination energy as the mean size of the nanocrystals increases, in accordance with a quantum confinement model.

Figure 3-9 shows the normalised PL Spectra for the same samples. In the following explanation of the results, the term intrinsic nanocrystals will be used for the samples prepared with silicon excess and annealed to form silicon nanocrystals and the rest of the samples will be termed as phosphorus doped.
From Figure 3-9 one can clearly see that with increasing annealing time the samples red-shift. The x-axis can be converted to energy and this gives Figure 3-10.

The same plot as Figure 3-10 can be plot with different colors as in the Reference[30]. This gives Figure 3-11.
Figure 3-11: Second plot of Normalised PL spectra of samples with P=0 for different annealing times (energy axis)

The PL Spectra for the samples containing phosphorus are shown in Figure 3-12.

Figure 3-12: PL spectra of samples with P=0.8 at. % for different annealing times

P=0.8 at. %, T_a=1050°C
From Figure 3-12 one can see that initially, that is up to 5s annealing time, the PL Intensity increases and then it begins to decrease with increasing annealing time. The Normalized PL Intensity is shown in Figure 3-13.

Figure 3-13: Normalised PL Spectra of samples with P=0.8 at. % for different annealing times

One can see from Figure 7-5 that the PL Intensity redshifts with increasing annealing time. This red-shift if examined carefully is even bigger than the red-shift of the samples with P=0. The x-axis can be converted to energy and this gives Figure 3-14.
Figure 3-14: Normalised PL spectra of samples with P=0.8 at. % for different annealing times (energy axis)

The same plot as Figure 3-14 can be plotted with different colors as in the Reference [30]. This gives Figure 3-15.

Figure 3-15: Second plot of Normalised PL Spectra of samples with P=0.8 at. % for different annealing times (energy axis)

3.4.3. Analysis and discussion of PL data

The PL spectra were fitted with log-normal distributions. The PL spectra with the fit for the sample with P=0 annealed for 1s is shown in Figure 3-16.
Figure 3-16: Normalised PL Intensity for sample with $P=0$ and annealing time of 1s. The red line is a log-normal fit to the data.

After fitting all the PL Spectra for $P=0$ (intrinsic nanocrystals, one can obtain the fits as shown in Figure 3-17.

Figure 3-17: Log-normal fits for Normalised PL Spectra for all the samples with $P=0$ (intrinsic nanocrystals)

The same technique can be applied for the samples containing $P=0.8$ at. %. Then the following Figure is obtained.
From the above fits the wavelength at the maximum PL Intensity can be found. This can be converted to energy which is the peak energy. The peak energy for the samples with $P=0$ is shown in Figure 3-19.

The peak energy for the samples with $P=0.8$ at. % is shown in Figure 3-20.
One can clearly see that the red-shift in energy is greater in the presence of phosphorus. The next step is to plot the difference between the peak energy between the samples containing phosphorus and the samples with 0 phosphorus concentration. This is shown in Figure 3-21.

Comparing Figure 3-19 and 3-20 one notes that the shift in emission for this range of annealing time for the phosphorus doped samples is ≈3 times bigger than the intrinsic nanocrystal samples. This suggests that the growth is accelerated when
formation takes place in the presence of phosphorus. The accelerated growth can be attributed to the “softening” of the phosphorus doped glasses at much lower temperatures than un-doped SiO$_2$ matrices. This is due to the substitution of the Si-O-Si bond with hydroxyl radicals, for example Si-O-POH, which increases the open volume density[78]. Consequently, this lowers the melting temperature[67] and increases the thermal expansion coefficient relative to pure silica glass and can result in an increased ion diffusion length[68]. For the silicon rich oxide system this leads to an accelerated segregation of the Si and SiO$_2$ phases[66]. The re-crystallization of bulk silicon is also known to be accelerated following amorphization via high dose phosphorus ion irradiation[79]. Previous microscopy studies, in which the silicon nanocrystal size was observed to increase with phosphorus doping [51], further support this hypothesis. The Integrated PL Intensity for the samples with intrinsic nanocrystals and the phosphorus doped samples is shown in Figure 3-22. The Integrated PL Intensity is found from the area under the PL Intensity curve.

![Figure 3-22: Integrated PL Intensity for intrinsic nanocrystals (open squares) and phosphorus doped si-ncs (filled squares). The lines are a guide to the eye.](image)

The ratio of the integrating PL Intensities is shown in Figure 3-23. This ratio is the integrated PL intensity of phosphorus doped Si-NCs, $I_{PL}(P)$, over the integrated PL Intensity of intrinsic nanocrystals, $I_{PL}(0)$. 

75
For the smallest annealing time ($t_A=1\text{s}$) the size distribution exhibits the smallest mean diameter and largest density of relatively small nanocrystals. When $t_A=1\text{s}$ one can see from Figure 3-23 that formation in the presence of phosphorus results in a $\approx 50\%$ higher integrated luminescence intensity compared with intrinsic nanocrystals. Also from Figure 3-21 one can see that for $t_A=1\text{s}$ the formation in presence of phosphorus results to the emission peak being blueshifted by $\approx 20\text{meV}$ compared with the intrinsic nanocrystals. However, as the anneal time increases, the PL enhancement is rapidly quenched and the blue-shift disappears. At $t_A=600\text{s}$, the emission intensity of the phosphorus doped nanocrystals is a factor $\approx 5$ smaller and almost $40\text{meV}$ further to the “red” side compared with intrinsic nanocrystal peak. Similar results were reported by Tchebotareva et al.[63] when investigating the effect of increasing phosphorus concentration on silicon nanocrystal luminescence for films prepared by ion implantation.

**3.4.4. Lifetime results**

The total PL decay time is the time needed for an excited carrier to fall from the excited state to the ground state. The total PL decay rate is the inverse of the total PL decay time (or lifetime), i.e. $w_{PL} = \frac{1}{\tau_{PL}}$. The total PL decay rate comprises of two parts, the non-radiative, $w_{NR}$, and the radiative decay rate, $w_R$, i.e:
This can be converted to decay times which gives the lifetime of the sample. This is given by:

$$\frac{1}{\tau_{PL}} = \frac{1}{\tau_R} + \frac{1}{\tau_{NR}}$$

(3-7)

In equation 3-7, $\tau_{PL}$ is the total PL decay time, $\tau_R$ is the radiative decay (or transition) time and $\tau_{NR}$ is the non-radiative decay time. It is also important to remember that the PL Intensity is proportional to the radiative decay rate, i.e.

$$I_{PL} \propto w_{PL}$$

(3-8)

In equation 3-8, $I_{PL}$ is the PL Intensity. The total PL decay rate for all the samples and different wavelengths is shown in Figure 3-24.

---

**Figure 3-24:** Evolution of the spectrally resolved PL decay rates for the phosphorus doped (red squares) and intrinsic (grey squares) silicon nanocrystals as a function of isothermal (1050 °C) anneal time.

The total PL decay rate with some fits for the phosphorus doped Si-NCs sample annealed for 1s is shown in Figure 3-25.
Dangling bond (Pb-centre) type defects can be thought to be the main reason for non-radiative recombination centres for photoexcited carriers in these films. Previous studies[73, 80] have shown that initial formation of the nanocrystal interface necessarily produces a high density of these defects. The presence of phosphorus atoms in the matrix probably mediates this interface formation by acting as a “seed” centre, which encourages heterogeneous nucleation. It is expected that when the implant profiles of the two species (phosphorus and silicon) are overlapping, the nanocrystal formation sites will correlate with the position of phosphorus impurity centres. In this case the dangling bond formation can be suppressed via charge compensation, as previously evidenced by electron paramagnetic resonance studies[81]. This would reduce the density of non-radiative defects and give rise to an increase in the contribution to the luminescence [55, 56]. This effect is more pronounced for particularly smaller nanocrystals in the ensemble population because of their higher surface to volume ratio.

The hypothesis that the luminescence enhancement for the phosphorus doped nanocrystals comes from an increase in the radiative transition rate, $w_R = \frac{1}{\tau_R}$ as previously suggested [82], is rejected. This is because the total PL decay rate, $w_{PL}$, which is shown in Figure 3-24, is smaller for the phosphorus doped nanocrystals at short anneal times (where the PL enhancement is observed).
It is proposed that, as $w_{NR} \gg w_R$, a decrease in the measured decay rate (increase in the measured lifetime) for the phosphorus doped silicon nanocrystals most likely indicates a smaller contribution of $w_{NR}$ (lower defect density) to the total decay rate. Now for the larger nanocrystals their density and crystalline fraction both increase with anneal time. The probability for these nanocrystals that phosphorus atoms occupy substitutional lattice sites increases. Because of their smaller band-gap, ionization of these substitutional donors results in an increase in the free carrier concentration \cite{68, 81}. This results in the opening of an efficient, non-radiative de-excitation channel for photogenerated electrons via Auger recombination, which would dramatically reduce radiative efficiency. This is confirmed by these results because at long anneal times the PL Intensity of the phosphorus doped samples is quenched compared to the intrinsic nanocrystals. Similar observations to these were reported when varying the phosphorus concentration for a fixed nanocrystal size distribution\cite{76, 83}.

### 3.4.5. Threshold size for dopant activation in silicon

Hence we observe a transition from defect passivation to free carrier generation. This implies that there exists a “threshold size” where this transition takes place. This transition can be thought as dopant activation. It is possible to obtain a rough estimate of this “threshold size” by combining the X-TEM data we have taken for the intrinsic nanocrystals and that of Hao et al\cite{51} in which the phosphorus induced size increase was measured for a range of annealing temperatures. The sample preparation in Ref. [51] is different to that described in the present study but similar concentrations of both phosphorus and silicon were used which is the most important factor in determining the structural and optoelectronic properties of the films. Therefore, these results can be used to find this “threshold size”. According to the data in Ref.[51], annealing phosphorus doped films for 1 h at 1000 °C yields nanocrystals that are ≈12.5% larger than the similar samples not containing phosphorus, i.e. intrinsic nanocrystals. At 1100 °C, this percentage increases to ≈90%, and, although no data are available for the annealing temperature of 1050°C used in these experiments, interpolation can be used. This reveals the percentage increase in our case to be ≈52%. Figure 3-26 illustrates how this would affect the evolution of intrinsic nanocrystals over the annealing time range we have employed.
Figure 3-26: (Left axis) Evolution of the measured intrinsic (black squares) nanocrystal mean diameter and that estimated (for a 52% size increase) for the phosphorus doped (grey squares) nanocrystals. (Right axis) Ratio of the integrated pl intensities, $I_{PL}(P)/I_{PL}(0)$ (red squares) as a function of the isothermal (1050 °C) anneal time. The blue arrows and circle indicate the nanocrystal size at which $I_{PL}(P)/I_{PL}(0)=1$ (and therefore provides an estimate of the “threshold size” ($d_{\text{threshold}} \approx 1.85 \text{ nm}$) above which the majority of nanocrystals contain free carriers after the ionization of substitutional phosphorus donors.

An estimate of the “threshold size” can be found from Figure 3-26 which gives $d_{\text{threshold}} \approx 1.85 \text{ nm}$. Above this size the majority of silicon nanocrystals contain free carriers. Below this estimate the majority of silicon nanocrystals have a phosphorus atom in the surface which each passivates a dangling bond defect. This estimate agrees closely with Chan et al. where they estimated that for phosphorus doped silicon nanocrystals where the size is less than 2 nm the donor will be energetically expelled towards the surface[62].
3.5. Conclusions

- Ion implantation of silicon in silicon dioxide (SiO$_2$) followed by rapid thermal annealing results in Si-NCs formed. For isothermal annealing, increasing the thermal budget by increasing the annealing time results in bigger mean size of Si-NCs. Si-NCs grow with a process known as Ostwald Ripening where larger nanocrystals grow in expense of smaller nanocrystals.
- Other species can be implanted in SiO$_2$ films and the position of the new species can be similar with the position of silicon ions (at excess).
- PL Spectra are redshifted with increasing annealing time due to increase in the mean size of Si-NCs in agreement with the quantum confinement theory.
- The presence of phosphorus in films with Si-NCs results in an accelerated growth of Si-NCs. This is due to the softening of phosphorus glasses for lower thermal budget which results in an increased ion diffusion length. It was found that for long anneal times the PL spectra are shifted by 40meV to the “red” for the phosphorus doped Si-NCs compared to the intrinsic Si-NCs.
- For short anneal times the PL Intensity of phosphorus doped Si-NCs is enhanced compared to intrinsic nanocrystals (undoped Si-NCs). This can be attributed to passivation of dangling bond defects at the surface of Si-NCs. These defects are thought to be the most likely reason for Si-NCs being optically inactive, i.e. not luminescing. The enhancement found in this study is 50%, however in other studies greater enhancements were found.
- For long anneal times the PL Intensity is quenched dramatically. As size increases the probability that a Si-NC contains a phosphorus atom inside is increased. This means that the fraction of phosphorus atoms that contains ionized substitutional donors increases for long anneal times. The PL Intensity quenching is due to the opening of an efficient, non-radiative, recombination path due to Auger recombination.
- The change in lifetime, or total PL decay time, in phosphorus doped Si-NCs is due to a change in the non-radiative decay rate. Phosphorus doped Si-NCs have a smaller total PL decay rate for short anneal times. This can be explained by a change in the non-radiative decay rate, which is decreased due to the passivation of Pb-centres from phosphorus donors.
The hypothesis that PL enhancement comes from an increase in the radiative decay (transition) rate is rejected. It was found that the total PL decay rate for short anneal times, where the PL enhancement is observed, is smaller for phosphorus doped Si-NCs compared to intrinsic Si-NCs. This is attributed to the decrease of the non-radiative decay rate for short anneal times in the presence of phosphorus.

The transition from defect passivation (dangling bonds or Pb centres) to free carrier generation allowed us to estimate a “threshold size” below which phosphorus contributes mainly to passivation of dangling bonds at the interface of Si-NCs and SiO₂. Above this “threshold size” phosphorus is ionized inside Si-NCs resulting in an increase of the free electron generation and efficient de-excitation via Auger recombination. The “threshold size” is estimated to be 1.85nm (in diameter).
4. **Chapter 4: Suggestions for future work**

Fujii et al. [66] have shown that co-doping silicon nanocrystals with boron and phosphorus can result in an enhancement in the PL intensity. The first reason for this enhancement is the shorter radiative lifetime of an exciton trapped at a donor-acceptor pair than a free exciton. The second reason is that the number of defect free, i.e. optically active Si-NCs increases by doping. However for heavy co-doping of phosphorus and boron there is a subsequent decrease in the PL intensity. The Si-NCs are growing in size by the increased doping due softening of glass matrices and resultant longer diffusion length of Si during annealing. This results in a fluctuation of the number of impurities in each nanocrystal and although the total number of impurities can be the same, there is a very low chance that a Si-NC will have the same number of phosphorus and boron impurities. Hence, the Si-NCs will not be perfectly compensated and will result in n- or p-type Si-NCs in which the PL Intensity is quenched due to effective non-radiative Auger recombination. In another study Fujii et al. [58] reported below bulk-band-gap photoluminescence from co-doped Si-NCs with boron and phosphorus. This was assigned to transitions between donor and acceptor states in Si-NCs.

A similar study can be performed for future work to the one presented in Chapter 3 but including boron as a dopant. The films containing Si-NCs can be co-doped with phosphorus and boron and an isothermal annealing can be performed for different annealing times. Photoluminescence and Time Resolved PL will be important in this future study. PL experiments will show whether boron enhances the PL Intensity and how this depends on the annealing time. Time resolved PL will indicate whether there is still a reduction of the PL lifetime and whether this is due to a reduction in the non-radiative decay rate. Another thing that can be done is trying doping some films containing Si-NCs with boron only and varying the isothermal annealing time. Again PL Intensity and time resolved PL experiments will indicate any possible enhancement or quenching and changes in the PL lifetime. Furthermore, the change of PL peak energy can be investigated for co-doped Si-NCs when the annealing time is varried.

Regarding Chapter 2, in future work there are various things that could be done. One of them is making phosphorus diffuse in silicon 1000 times faster than phosphorus in...
oxide. Another improvement is fixing phosphorus doping of Si-NCs in the model. This means that in an improved model some phosphorus atoms will dope some Si-NCs by having some phosphorus atoms inside some Si-NCs. A phosphorus atom inside a Si-NC will result in quenching of PL Intensity by Auger recombination. Although the existing model correctly predicts a size increase of Si-NCs in the presence of phosphorus, this feature will enable one to calculate the position of phosphorus with respect to the doped Si-NC. Also, one could calculate the ratio of phosphorus in oxide and the ratio of phosphorus in silicon. In this way one could predict how many Si-NCs will be doped and design the parameters so that there are not many Si-NCs with a phosphorus atom inside them. Another optimization is the number of phosphorus atoms on the surface of Si-NCs. An increased number of the latest will result in an enhancement of PL Intensity. In conclusion, optimizing the above parameters is important in the design of future opto-electronic devices.
References


