Silicon Quantum Dots Grown by Ion Implantation and Annealing

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INTRODUCTION

Since the 1960’s quantum-size effects have been observed in three dimensional semiconductor nanocrystals. These effects have limited the motion of electrons and holes in semiconductor nanocrystals from one to three spatial directions. Nanocrystals that confine the motion of electrons/holes in one spatial direction and allow for free propagation in the other two spatial directions are called quantum wells. Quantum wires are nanocrystals that confine the motion of electrons/holes in two directions and if a nanocrystal confines the electron/holes in three directions it is called a quantum dot. These quantum size effects can be due to electrostatic potentials, the presence of an interface between different semiconductor materials, the presence of the semiconductor surface or due to a combination of these. In the case of a semiconductor nanocrystal, the quantum size effects are due to the crystalline properties of the semiconductor surface. Semiconductor nanocrystals that confine the electron/holes in three directions and are smaller then 10nm are referred to as a quantum dots. These structures are of particular interest because their optical and electrical properties can be readily modified. For example, the peak emission frequency of a quantum dot is extremely sensitive to the quantum dot’s radius and composition. This fascinating property gives rise to numerous fabrication techniques.

EARLY FABRICATION METHODS

One of the first fabrication methods (that is still being used today) is called colloidal synthesis. This approach stemmed from Louis Brus’s work at Bell Labs in the late 1970’s. Due to his work, semiconductor quantum dots were grown in the early 1980’s and have since been fabricated into metal and insulator quantum dots. This fabrication method is of great benefit because it is a relatively cheap and simple method; it only requires a reaction flask, a thermometer, two anion precursors and a long-chain solvent. In the case of fabricating semiconductor quantum dots, two common anion precursors are cadmium and selenium. These two precursors can form CdSe quantum dots of varying size that absorb from 410 to 670 nm wavelengths, depending on reaction conditions.

An early lithographic method for creating quantum dots on or near the surface of a semiconductor crystal was used to create a two dimensional structure. This structure was then etched down to a zero-dimensional structure; however, the size of the quantum dot was limited by the resolution of the lithographic steps. The thickness of the semiconductor layer was on the order of nanometers while the other dimensions were as large as a micron. This method was replaced by growing “self-assembled” quantum dots known as the Stranski-Krastanov growth method. This method deposits a semiconductor material with a larger lattice constant (e.g. Germanium) onto a semiconductor material with a smaller lattice constant (e.g. Silicon) causing strained epitaxial growth. This fabrication method has been used to create quantum dot lasers, a device capable of generating single photons and a single photon detector.

High dose ion implantation is another method used to fabricate quantum dots. This method is used to create high density encapsulated quantum dots in a host material. These quantum dots (QDs) and host materials range from Si QDs in SiO$_2$ to GaN QDs in Al$_2$O$_3$. Ion implantation produces a supersaturation of an impurity that leads to the formation of QDs encapsulated in the host material after a high temperature annealing process. The electrical and optical properties of the QDs formed by ion implantation depend on the beam current, implant
time, energy, annealing time and temperature. For an example, a simple change in the annealing temperature can either increase or decrease the photoluminescent intensity.\[6\]

Silicon has been used for decades as an electric material and has only been recently used as an optical material due to its indirect band-gap of 1.12 eV, which is not desirable for an efficient light-emitting device. Due to the numerous fabrication methods of QDs and the well understood fabrication methods used in creating silicon-based microelectronics, a silicon-based integrated optoelectronic circuit was proposed in 1993.\[7\] This was several years after the first reported visible photo-luminescence in 1990 from silicon QDs by H. Takagi.\[8\] This proposal has lead to the fabrication of silicon QDs using different methods to produce different optical properties. Some of these fabrication methods include microwave plasma decomposition of SiH$_4$, laser breakdown of SiH$_4$, plasma-enhanced chemical vapor deposition, high frequency discharge, and high dose ion implantation.\[5,9,10\] In this paper, the formation of silicon QDs by ion implantation will be discussed and compared to that of other fabrication methods resulting in similar optical properties.

**FORMATION OF SILICON QUANTUM DOTS BY ION IMPLANTATION**

High dose ion implantation is used to create high densities of encapsulated QDs in a wide range of host materials. This method allows the surface layers of the host material to be doped with an impurity above the solubility limit.\[5\] However, if the concentration of the impurity exceeds a critical level, precipitation occurs resulting in a reduction of the concentration of the impurity to the solubility limit. As a result, precipitates with a specific size distribution are formed. If the concentration of the impurity does not reach the critical level, the implanted sample is annealed. During this process, a phenomena known as Oswald ripening occurs, causing “coarsening” of the nanoclusters. This action is driven by the minimization of the interfacial energy.\[11\] According to Gibbs-Thomson's relation, the formation of larger clusters are favored over smaller clusters causing a size distribution throughout the host material. A schematic of the physical processes involved with ion implantation is shown in Figure 1.\[11\] A high resolution TEM image of Si QDs in SiO$_2$ is shown in Image 1.\[12\]
EFFECTS OF ION IMPLANTATION METHODS ON PHOTOLUMINESCENCE INTENSITY

Silicon QDs that are fabricated with ion-implantation have very different optical properties based on the conditions they were formed. The position and shape of PL spectra depend on the QD’s size and size distribution. The position of PL peaks can be determined by solving the Schrödinger equation for a zero-dimensional quantum structure:

$$\Delta E = \frac{\hbar^2 i^2}{8mr^2}$$ (1)

Where the electron state energy above the band gap is $\Delta E = h\nu - E_g$ with recombination energy $h\nu$, Si band gap $E_g = 1.12$ eV, effective mass $m=0.155*m_0$, free electron mass $m_0$, QD size $r$, Planck constant $\hbar$, and quantum number $i$. Assuming a Gaussian distribution for the QD size $r$, the shape of PL spectra can be calculated by using the relation:

$$P(\Delta E) \propto \frac{nC^2}{2\sigma^2(2\pi\Delta E)^3} \exp \left\{ -\frac{1}{2} \left( \frac{r_0}{\sigma} \right)^2 \left( \frac{\Delta E_0}{\Delta E} \right)^{1/2} \right\} \left( \frac{\Delta E_0}{\Delta E} \right)^{1/2}$$

With the number of QDs $n$, mean QD radius $r_0$, coefficient $C = h^2i^2/8m$, and $\Delta E_0=C/r_0^2$. Thus, Eq. (2) establishes a correlation between the shape of PL spectra and the size $r$ with size distribution $\sigma$ of QDs.

For an example, photo-luminescence (PL) occurred from a sample of Si implanted in SiO$_2$ with a dose of $3\times 10^{16}$/cm$^2$ (compared to a dose of $6\times 10^{17}$/cm$^2$ at 400 keV) followed by a 1
hour high temperature anneal at 1100°C with Ar and 4% H\textsubscript{2} that was performed by Dr. C.W. White. These experimental conditions resulted in a peak wavelength shift from \( \sim 690 \) nm to \( \sim 760 \) nm (Fig. 2).\[5\] A weak optical transmission was also observed in the Si QDs implanted in SiO\textsubscript{2} after annealing, graphically shown in Figure 3. The absorption edge shifted to a lower energy as the dose and particle size increased. These results are in agreement if the resulting radiation was raised from quantum confined excitations, however interfaces could be partially responsible for the emission. Due to the significantly different energies of optical absorption and PL emissions, it was assumed that the radiation could not have been band-edge emission.\[5\]

![Figure 2. PL arising from Si (400eV) implanted SiO\textsubscript{2} after annealing at 1100°C for 1 hour with Ar and 4% H\textsubscript{2}.][5]

![Figure 3. Optical transmission measured through fused silica samples implanted by Si (400 keV) and annealed at 1100°C for 1 hour with Ar and H\textsubscript{2}. Results from the implanted samples were compared with those from un-implanted fused silica.][5]

Hydrogen passivation at different annealing temperatures also affects the PL intensity, the measured luminescence life time, and the number of luminescent QDs. Professor Robert Elliman performed ion implantation on 1.25 \( \mu \)m of thermally grown silicon dioxide layers with 400 keV Si\textsuperscript{+} ions to a fluence of \( 2 \times 10^{17} \) cm\textsuperscript{-2}. The annealing was done at 1000°C in Ar for 1 hour. Passivation was then achieved by annealing in forming gas (5% H\textsubscript{2} in N\textsubscript{2}) at different temperatures (100-800°C) (see Figure 4). As the passivation annealing temperature increased, the PL intensity also increased until a maximum intensity was reached at 500°C.\[6\] This increase in PL intensity was due to the forming gas passivation of the dangling bonds at the QD/SiO\textsubscript{2} interface and the defects in the matrix.\[12\] This caused a reduction in the number of non-radiative recombination centers. This intensity maximum can be seen in Figure 5a (defined by the shaded data points). The clear data points in Figure 5a represent the subsequent annealing in an ambient gas, such as nitrogen gas. Professor Elliman also showed that for low excitation levels:\[6\]

\[ \sigma \phi \ll \tau^{-1} \]

the PL intensity is given by the following equation:\[6\]

\[ I = \sigma \phi \frac{\tau}{\tau_R} n^* \] (3)
Where I is the measured PL intensity, \( \sigma \) is the absorption cross-section of the QDs, \( \tau \) is the measured luminescence lifetime, \( \tau_R \) is the radiative lifetime of the QDs and \( n^* \) is the number of luminescent QDs.\(^6\) Elliman was able to determine an optimum passivation temperature around 500-600ºC by using detailed modeling of the passivation and desorption processes.

Figure 4. (Left) Typical QDs PL spectra of the reference sample (unpassivated) after annealing for 1 hour in 5% \( \text{H}_2 \) in \( \text{N}_2 \) at different temperatures. The annealing temperatures are indicated on the figure.\(^6\)

Figure 5. (Right) Plots of relative intensity (a), lifetime (b) and emitting QDs from equation 3 versus annealing temperature for 1 hour anneals. Data is from time-resolved PL measurements. The lines are provided as a guide to the eye only. Filled symbols—passivation (5% \( \text{H}_2 \)); open symbols—desorption (\( \text{N}_2 \)). The reference is an unpassivated sample.\(^6\)

Dr. Min of the California Institute of Technology\(^{12}\) prepared Si QDs 1 to 3 nm in diameter using similar methods described above. Min then obtained information regarding the formation of the QDs using XPS. The XPS spectra (Figure 6) shows the Si 2p core-level spectra of \( \text{SiO}_2 \) films implanted with \( 5 \times 10^{16} \text{ cm}^{-2} \) Si and annealed at temperatures between 400 and 1100ºC for 10 minutes. The gradual shift of the suboxide peak towards the \( \text{SiO}_2 \) binding energy with a distinct bulk Si peak appearing for samples annealed at temperatures above 600ºC (Figure 6) is characteristic of a phase separation of the sub-oxide into Si and \( \text{SiO}_2 \).\(^{12}\) Given the data from the XPS spectra, Dr. Min was able to determine that after high temperature annealing, there would still be optically active defects in the damaged matrix. This conclusion was based on the Si 2p core level of the matrix approaching the value for \( \text{SiO}_2 \) at an annealing temperature of 1100ºC in the XPS spectra.\(^{12}\)

A PL spectra of \( \text{SiO}_2 \) implanted with 50 keV Si\(^+\) (Figure 7b) resulted in a PL band around 790 nm and a defect-related PL band around 600 nm upon annealing at 1100ºC in a vacuum for 10 minutes. Figure 7b also shows the effect of different deuterium passivations ranging from \( 9.0 \times 10^{14} \) to \( 3.3 \times 10^{16} \text{ cm}^{-2} \). It is noted that a deuterium passivation of \( 3.3 \times 10^{16} \text{ cm}^{-2} \) resulted in the suppression of the defect PL band at 600 nm; however the PL band at 790 nm was never completely suppressed.\(^{12}\) This evidence suggests that the “red” PL band was due to the radiative recombination of quantum-confined excitons and that the 600 nm band was due to ion-irradiation-induced defects.\(^{12,13}\) Dr. Min determined that the “red” PL band shifts as a function
of annealing temperature. This is illustrated in Figure 7c for a dose of $5 \times 10^{16}/\text{cm}^2$ of Si$^+$ implanted samples annealed at different temperatures ranging from 800 to 1200°C. All of the samples were passivated with $3.3 \times 10^{15}/\text{cm}^2$ of deuterium. A clear shift in the “red” PL band was observed from 710 nm to 840 nm between samples annealed at 800 and 1200°C.\textsuperscript{[12]}

Dr. Iwayama\textsuperscript{[19]} investigated rapid thermal annealing as a way to enhance the PL intensity of Si QDs encapsulated in SiO$_2$ in the year 2006. Silicon dioxide samples were implanted with $5.0 \times 10^{16}$ or $2.0 \times 10^{17}$ ions/cm$^2$ with acceleration energies of 180 keV. These samples were rapid thermal annealed at 1050°C or 1100°C in a flowing nitrogen gas atmosphere for 5 minutes with temperature rise rates of 10 to 50°C per second. This was done prior to/after a furnace anneal at 1050°C for 1 hour in N$_2$.\textsuperscript{[19]} The PL spectra of the samples implanted with a dose of $5.0 \times 10^{16}$ ions/cm$^2$ were rapidly annealed before or after a furnace anneal are shown in Figure 8a and 8b.\textsuperscript{[19]} From Figure 8a, it is clear that the PL intensity is enhanced by a rapid thermal anneal, and both the temperature rise rate and the temperature at which the anneal occurs facilitate in the increased PL intensity. It was also demonstrated that longer hold times increase the intensity. This process of annealing helped with the crystallization of Si QDs and annihilated interfacial
non-radiative centers and imperfections in the QDs. However, samples that were rapidly annealed after a furnace anneal at 1050°C exhibited a decrease in PL intensity as the anneal temperature increased (Fig. 8b). Luminescence efficiency is known to be affected by both crystallinity of Si QDs and the interface states between the QDs and the silicon dioxide. Defects at the interface between the QDs and SiO$_2$ are generated due to the different thermal expansion coefficients of the two materials. These defects could cause the luminescent QD to become non-radiative while others may only decrease the photoluminescence.

Iwayama tested the effects of rapid thermal annealing on samples with a higher implanted dose of Si ions before a furnace anneal. This experiment resulted in a less effective increase in the PL intensity (Fig. 9). These results are also depicted in Figure 10 (Appendix). For samples implanted with a dose of 5.0x10$^{16}$ ions/cm$^2$, the effects of the furnace anneal time on PL intensity was tested. Some samples were rapidly annealed for 5 minutes at either 1050 or 1100°C at a temperature rise rate of 30°C per second. This was done before a 1050°C furnace anneal in durations of 1, 3 and 5 hours. Other samples were not rapidly annealed before the
furnace anneal following the same parameter given above (Fig. 11). From both figure 9 and 11 it is clear that the PL intensity increases with increasing furnace annealing time. It was demonstrated that the peak energies are independent of anneal times up to 10 hours, and that PL intensity increases along with the annealing time. However, the PL peak energies shift to a higher energy after a 15 hour anneal with a saturation of the luminescence intensity (Fig. 12). A schematic illustration of the enhancement and the peak shift of the PL band with rapid thermal annealing and prolonged anneal times are shown in Figures 13 and 14.

Professor Iwayama believed that annealing at high temperatures induces diffusion and nucleation of excess Si atom and that prolonged annealing induces growth of the Si QDs. This growth forms clusters of small QDs that interact with each other through a thin intervening oxide layer. Due to the decrease in excess Si following a prolonged exposure, clusters of smaller Si QDs formed into larger QDs in a process known as Ostwald ripening. Ostwald ripening causes the average distance between QDs to increase, which, consequently, causes a much weaker interaction between QDs. This weak interaction can thus be neglected, leaving quantum confinement to explain the photoluminescence of Si QDs.

Figure 11. (left) Photoluminescence spectra of samples implanted to a dose of $5.0 \times 10^{16}$ ions/cm$^2$ and rapidly thermally annealed for 5 min at (A) 1050°C or (B) 1100°C with temperature rise of 30°C/s prior to a furnace anneal at 1050°C for 1, 3 and 5 h. Dashed lines show the spectra of the samples annealed at 1050°C for 1, 3 and 5 h without rapid thermal anneals. Inset shows the expanded results for the as-implanted samples and the samples only after rapid thermal anneal for 5 min.

Figure 12. (above) Photoluminescence spectra of samples implanted to a dose of $5.0 \times 10^{16}$ ions/cm$^2$ and annealed at 1050°C up to 20 h (1, 3, 5, 10, 15 and 20 h), without rapid thermal anneals.
As revealed in the XPS spectra obtained by Dr. Min, the luminescence intensity scales coupled with the volume density of Si-Si bonds are associated with the QD density. Increasing the dose, annealing temperature, annealing time, or any combination of these processing parameters will result in an increase in the Si 2p core-level signal in XPS, suggesting an increase in the volume density of Si-Si bonds (or QD density). It has been shown by Dr. White that a simple increase in the dose of silicon implanted into the SiO$_2$ matrix results in an increase in the PL intensity and a shift in the PL band.

Professor Elliman showed that an increase in PL intensity can result from hydrogen passivation at different temperatures reaching a maximum intensity around 500-600ºC. He was also able to determine that the PL intensity of low excitation levels are a function of the
absorption cross-section of the QDs, the photon flux of the excitation source, the measured luminescence lifetime, the radiative lifetime of the QDs, and the number of luminescent QDs.

**SILICON QUANTUM DOT DISTRIBUTION WITHIN SILICON DIOXIDE**

From the diagrams, it can be seen that the bands in the PL spectra are broad. This broadening effect is due to the presence of different size QDs within the matrix, which is in agreement with the quantum-confinement theories that predict an increase of the band gap as a function of decreasing size.\[^{14,15}\] It is known that if Si\(^{+}\) ion implantation is performed using a single-ion energy, a Gaussian concentration depth profile of excess Si will result. It is also known that the nucleation and growth rates of Si QDs are strongly dependent on the local degree of supersaturation. It is then expected that the average QD size to be depth dependent\[^{13}\] Professor Brongersma implanted 35 keV Si ions at a fluence of 6x10\(^{16}\)/cm\(^2\) into a 110 nm thick SiO\(_2\) film. The sample was then annealed at 1100ºC for 10 minutes in a vacuum to induce nucleation and growth of Si QDs. To determine the silicon concentration at different depths throughout the matrix, Brongersma etched off the oxide in a series of subsequent etch steps of 10 seconds each using a buffered hydrofluoric acid at room temperature. Rutherford backscattering spectrometry (RBS) was then used to determine the Si concentration depth profiles after each etch step.\[^{13}\] The silicon concentration depth profiles obtained by professor Brongersma are shown in Figure 15. It is important to note that the Si concentration depth profiles were derived from the RBS spectra taking into account the depth-dependent electronic energy loss calculated from the relative Si/SiO\(_2\) concentrations using Bragg’s rule, assuming the volume averaged density of Si is 2.32 g/cm\(^3\) and SiO\(_2\) is 2.29 g/cm\(^3\).\[^{13}\] The concentration of silicon before etching, indicated in Fig. 15 by 0, has a peak concentration of 48% at a depth of 45 nm below the sample surface. Near the surface the concentration is about 33%, this corresponds to that of stoichiometric SiO\(_2\).\[^{13}\] It can be seen that the Si concentration depth profile in the matrix is not Gaussian shaped, as predicted by a Monte Carlo calculation using TRIM ‘97 and that an asymmetrical curve is actually seen (Fig. 16).

**Figure 15 (above).** Si concentration as a function of depth in a SiO\(_2\) film that was implanted with 35 keV Si at a fluence of 6x10\(^{16}\)/cm\(^2\), and annealed a 1100ºC for 10 min to nucleate QDs. Depth profiles after etching in buffered HF for times ranging from 0 to 120s are also shown. Their depth scales are all shifted such that the SiO\(_2\)/Si interface is located at a depth of 112 nm.\[^{13}\]

**Figure 16 (left).** (a) Room-temperature PL spectra obtained from a SiO\(_2\) film containing Si QDs, after etching in buffered HF for times ranging from 0 to 120s. (b) Difference spectra obtained by subtracting the PL spectra for subsequent etch steps in (a), and corrected in such a way that the spectral intensity at a fixed wavelength is proportional to the average concentration of QDs emitting at that wavelength. The inset shows the pump intensity profile as a function of depth in the SiO\(_2\) film, resulting from internal reflections of the pump light at the SiO\(_2\)/Si interface and SiO\(_2\)/air interface.\[^{13}\]
Professor Brongersma also obtained PL spectra of the sample before and after etching (Fig. 16). Before etching the sample the PL spectrum ranged from 500 nm to well beyond 900 nm. This data corresponds to emissions from ≥2 nm diameter QDs. A peak in PL intensity is observed at 790 nm, corresponding to an average QD size of ~3-4 nm in diameter. As etch time increases, a decrease in PL intensity and a shift in peak PL intensity is observed. It should noted that after etching for 10-40 seconds, small QDs contributing to the PL spectra in the 500-800 nm range have been removed, causing an apparent “red” shift of the peak position. After etching for 120 seconds small luminescent remains. Brongersma contributed this luminescence to QDs left on the substrate after the oxide layer was completely etched off. Using atomic-force microscopy the presence of QDs on the substrate was verified.

Given the RBS spectra and PL intensity spectra along with knowledge of the classical particle coarsening theory, it was determined that small QDs would only be found in areas of low supersaturation, i.e. near the surface. However the theory did not describe the high density of small QDs near the SiO$_2$/Si interface observed, as the supersaturation in that region was still high (~8%). Brongersma determined that the surface of the SiO$_2$ and the SiO$_2$/Si interface both act as a sink for diffusing Si, therefore altering the local nucleation and growth kinetics to form a high density of small QDs. This phenomenon has also been observed in Germanium QDs encapsulated in SiO$_2$. Using this knowledge, one may use surfaces and interfaces to fit size distributions of Si QDs in SiO$_2$ in the future.

**MECHANISM FOR THE PHOTOEMISSION IN SILICON QUANTUM DOTS**

Quantum dots emit light when excitations from electron-hole pairs recombine radiatively. Several possible mechanisms have been suggested in which radiative recombination can occur (Fig. 17). In a perfect, defect free world the energy of the emitted photon ($h\nu$) is equal to the band gap energy ($E_g$). However, since nothing is defect free recombination/generation occurs via interface states or defects. These interface states and defects cause the energy of the emitted photon to not equal the energy of the band gap.

In the case of silicon QDs there is no universally accepted mechanism to explain the photoluminescence. Some scientists speculate that the photoluminescence of Si QDs is due to quantum confinement effects while the peak shift is due to the size of the QDs. Others believe that the absorption of photons leads to the generation of electron-hole pairs within the Si QDs, thus causing the emission of photons from surface states found at the interface between the Si, QDs, and SiO$_2$. Both of these proposed models can not explain certain experimental data. For example, the first model can not explain why the photoluminescence intensity grows during annealing without changing the peak energy. Likewise, the second can not explain the dose dependent PL peak energy shift. In 1998, professor Iwayama proposed the “reactive nanocluster model” to better explain the dose dependent PL peak shift (Fig. 18).

This model takes into account Si QD size, band-gap widening, and the local concentration of Si QDs. Iwayama has proposed that the band-gap widening due to the quantum confinement effect is key in the photoabsorption process found in Region 1, and that the interface energy between the Si QDs and SiO$_2$ plays an essential role in the luminescence process in Region 2 of Figure 18. It is believed that the interface energy state is affected by dot-to-dot interactions in a thin Si/SiO$_2$ interface. With an increase in the implanted Si dose, the local concentration of Si atoms increases before annealing, causing an increase in the local concentration and size of Si QDs as observed by others. An increase in the size and number
of Si QDs (i.e. a dense population of Si QDs) causes an increase in the interactions between Si QDs and a decrease in the interfacial energy state. However, once nucleation of aggregates occurs, a point would be reached where the formed Si QDs would no longer diffuse into the SiO$_2$, causing the number of QDs to remain constant with prolonged annealing.\cite{22}

Figure 18. Schematic illustration of a reactive nanoclusters model of PL in which the nanoclusters react via a thin oxide interface.\cite{21}

Based on these assumptions, Iwayama was able to explain the dose dependent PL peak shift for Si quantum dots. Since the luminescence intensity of Si QDs is determined by the number of properly-sized Si QDs and/or their luminescence efficiency, an increase in the dose of Si ions and growth of Si QDs causes the total QD concentration to increase, causing the PL intensity to increase as well. This has been experimentally observed by Iwayama and other scientists.\cite{5,12,13,21} However, Iwayama observed that above a dose of 1.5x10$^{17}$ ions/cm$^2$ the PL intensity decreases as the dose increases.\cite{21} He concluded several reasons for this reduction in PL intensity. First, he proposed that with the growth of Si QDs, the band-to-band transition energy of the confined Si QD system should be smaller than the emission energy. He also proposed that the interaction between the QDs affects the PL efficiency. Second, as the QD size increases, the interface-to-volume ratio decreases and the probability of the energy transfer to the interface will decrease (especially if there are defects in the QDs).\cite{21} In all of these cases, the Si QDs are not properly distributed in SiO$_2$, causing more defects and a decrease in PL intensity to occur. To observe the highest PL intensity, the Si QDs must be properly distributed in SiO$_2$ at an appropriate size.\cite{21,22}

**DEFECTS CAUSED BY ION IMPLANTATION**

During Si ion implantation, each individual Si ion produces many-point defects in the SiO$_2$ matrix on impact, such as oxygen deficient centers (vacancies) and excess Si (interstitials). To study these defects Professor Nicklaw of Vanderbilt University performed ab initio calculations using density function theory (DFT).\cite{18} Traditional methods in quantum theory, in particular Hartree-Fock theory, are used to calculate the ground state energy are based on the complicated many-electron wavefunction. The many-electron wavefunction is dependent on the
number of electrons \(N\) and the number of spatial variables, in this case 3, resulting in \(3*N\) variables. To simplify this non-linear calculation, DFT replaces the many-body electronic wavefunction with the electronic density. The electronic density is only a function of three variables, versus \(3*N\), and is a simpler quantity to deal with both conceptually and practically. In other words, by using DFT instead of a traditional quantum theory the Schrödinger equation for a many-electron system, the calculation simplifies to a set of independent, single electron Schrödinger equations. The details of the DFT approach can be found in reference 18, C.J. Nicklaw et al.

To begin, Nicklaw determined the base structure for amorphous silicon dioxide (Fig. 19) to a 72 atom unit cell, with a volume of 1122.79Å\(^3\) and a density of 2.13g/cm\(^3\).\(^{[18]}\) This structure was compared to the results of M. Boero et al.\(^{[27]}\) and found to be a valid representation. Four structures were then generated to examine possible defects in silicon implanted a-SiO\(_2\). Each structure includes an excess silicon atom within the structure with or without an oxygen vacancy. The first defect structure, D1, represents an implanted Si atom interacting with an oxygen vacancy. The second and third, D2 and D3, represent the result of a collision of a Si atom with oxygen in the amorphous silicon dioxide during ion implantation.\(^{[18]}\) In structure D2, the oxygen atom was displaced more then 3Å from its base position in amorphous silicon dioxide, while in D3 the oxygen atom was displaced less then 2Å away. These displacement lengths are expected in implanted samples as a result of the transfer of kinetic energy from the implanted Si atoms to the oxygen atoms.\(^{[18]}\) The forth defect structure, D4, is the result of a silicon atom coming to rest or diffusing into a region with no pre-existing defects. Using the base structure and DFT the band-gap was determined to be 5.74 eV.\(^{[18]}\) This is approximately 3.04 eV lower then the expected value of ~8.7 eV. Professor Nicklaw attributed this difference to the crude approximation involved in using DFT. Due to the difference between the expected and theoretically calculated band-gap, the calculated energy states of the defect structures only give a “relative picture of the positions of their energy states.”\(^{[18]}\) Using DFT, Nicklaw determined the
theoretical band-gaps, ground state energies, and the first excited state energies for the four defect structures.

This resulted in four significantly different ground state defect structures (Figs. 20-23) with four very different first excited state energies. The ground state structure of D1 (Fig. 20) is a double oxygen vacancy:

\[ \equiv Si - Si - Si \equiv \]

The ground state structure of D2 (Fig. 21) is a double defect oxygen vacancy and a double defect structure of:

\[ \equiv Si - O - O - Si \equiv \]

Figure 22 depicts the double defect structure of the ground state of D3:

\[ \equiv Si - O - Si - Si \equiv \]

The last defect structure examined by Nicklaw was that of a silicon atom diffusing into a-SiO$_2$ with no defects, which produced a “Y-center”[18] (Fig. 23):

\[ OSi_2 \equiv Si \]
The calculated ground and first excited energy states of the various defects are depicted in Fig. 24 in the theoretical silicon dioxide band-gap. Upon examining the collected data, all of the defect structures have ground and first order excited states within the theoretical band-gap of a-SiO$_2$. However, the double oxygen vacancy structure was determined to be the most stable defect in its excited state and that the structure is very reactive due to its location within the calculated bad-gap. It can be seen that the other defect structures have ground states within the band-gap, but their respective excited states are very close to the conduction band edge $\sim 0.50$ eV, making D3 and D4 shallow states. These defects could explain charge compensation and electron trapping.\cite{18}

![Figure 24. The calculated energy of states of the various defects in the theoretical SiO$_2$ bandgap.\cite{18}](image)

**OTHER FABRICATION TECHNIQUES**

Ion implantation has several disadvantages including a large nanocrystal size distribution, (20-40%), damage to the surface of the QDs, silicon oxide defects, and poor nanocrystal depth and shape control. Several fabrication techniques have been used to create photoluminescence Si QDs instead of ion implantation. Some of these fabrication methods include microwave plasma decomposition of SiH$_4$, laser breakdown of SiH$_4$, plasma-enhanced chemical vapor deposition, high frequency discharge, and colloidal.\cite{9,10,23} Each of these fabrication methods will be discussed to examine possible benefits over ion implantation.

**MICROWAVE PLASMA DECOMPOSITION OF SILANE GAS**

Using microwave plasma decomposition of silane gas the first visible PL from Si QDs was observed at room temperature by Takagi in 1992.\cite{9,24} The experimental step up is shown in Figure 24. Takagi produced silicon QDs using 2.45 GHz microwave plasma decomposition of SiH$_4$ with Hz and/or Ar gas mixture in a resonant cavity with a microwave power of 150 W. Dissociated species of SiH$_4$ combined with each other and formed Si QDs or nanocrystals (depending on size). The size of the Si QDs/nanocrystals was varied from 2.5 to 20 nm (diameter) by altering the mixture ratio of gases and the power of microwave. The Si QDs, or nanocrystals, were forced out of the resonant cavity through a nozzle into a chamber which was evacuated to $10^{-6}$ Torr. The Si nanocrystals/QDs were then deposited on a quartz substrate at room temperature.\cite{9} Using this method causes a size distribution curve to be seen by TEM analysis (Fig. 25). For the data in Figure 25 the average diameter estimated by X-ray diffraction was 3.9 nm. Through TEM analysis it was observed that the Si QDs/nanocrystals had a spherical
shape with little to no defects. Takagi was able to determine that the Si QDs/nanocrystals were single crystals of the diamond structure. Following these tests the surface amorphous layer was oxidized in a humid atmosphere (60°C and 85% RH). It was observed that by varying oxidation times the diameters of the QDs/nanocrystals were also varied. After oxidation, the Si QDs/nanocrystals were covered by SiO$_2$. It is important to note that there was not a visible luminescence from the Si QDs/nanocrystals until after surface oxidation.

This method provides easy control over the size of the QDs/nanocrystals and thus the PL peak energy. It also provides a method to produce relatively defect free QDs, which leads to a higher luminescence efficiency. However, this method does not provide for easy integration into electronic devices today.

**LASER BREAKDOWN OF SILANE GAS**

Another fabrication technique that uses silane gas to form Si QDs is called “laser breakdown of silane gas.” To produce Si QDs pure SiH$_4$ gas was first introduced into a vacuum chamber with a background pressure of < 10$^{-6}$ Torr and a SiH$_4$ gas pressure of 10 Torr. The pressure of the silane gas was used to control the diameter of the Si QDs formed. Laser pulses of ~200 mJ per pulse at 1.06 urn with a 10 ns pulse duration were focused into the vacuum chamber and a spark was observed at the focal point. The Si QDs were deposited on quartz, or Germanium wafer substrates. Lastly, the samples were oxidized and exhibited strong visible PL at room temperature. TEM images were taken of the sample to provide proof of oxidized Si QDs (Fig. 26). Sharp rings in the electron diffraction pattern were observed indicating that the core was c-Si with the diamond structure. To determine the composition of this surface layer, the oxidized Si QDs were analyzed by X-ray photoemission spectroscopy (XPS) (Figure 26). The XPS data showed that an a-SiO$_x$ layer, (including a small amount of SiO), was formed on the surface of the Si sphere. Given the data obtained by the TEM and XPS the oxidized Si QDs consisted of a c-Si core and an 1.6-nm-thick a-SiO surface layer. The size distributions of oxidized Si QD samples are shown in Figure 27. It was determined that the distribution of the overall diameter of these QDs can be described by a log-normal function.
Where \( D \) is the diameter, \( \sigma \) and \( \mu \) are shape and scale parameters, respectively. The average diameter, \( D \), was calculated using Equation 3. The overall diameter, \( D_{\text{tot}} \), includes the diameter of the c-Si core \( D_c \) and the 1.6 nm thickness of the SiO\(_2\) surface layer: \( D_{\text{tot}} = D_c + 3.2 \text{ nm} \). The average diameter was found to be 3.8 nm. Once again there was no visible photoluminescence before surface oxidation. After the surface was oxidized, an efficient visible PL was observed in the red spectral region.\(^{[9]} \)

This fabrication technique allows for easy control over the average diameter of the Si QDs, however this process can not be easily integrated into current processes to form microelectronic devices.

\[
dF(D) = \frac{1}{D \sqrt{2\pi \sigma^2}} \exp\left[-\frac{(\ln D - \mu)^2}{2\sigma^2}\right]dD, \tag{4}
\]

**Figure 26 (left).** High-resolution TEM lattice image of oxidized Si QDs composed of a c-Si core and a \( \sim 1.6-\text{nm thick} \) a-SiO\(_x\) surface layer.\(^{[9]} \)

**Figure 27 (right).** The size distribution of oxidized Si QDs produced by laser breakdown of SiH\(_4\) gas. The solid curves are optimum log-normal functions. The size distribution of Si QD is asymmetric and includes the diameter of c-Si core and the thickness of SiO\(_2\) layer.\(^{[9]} \)

**PLASMA-ENHANCED CHEMICAL VAPOR DEPOSITION**

In plasma-enhanced chemical vapor deposition fabrication method of Si QDs, a silicon oxide layer (SiO\(_x\)) or silicon-rich nitride layer is deposited with a PECVD system onto a Si wafer. During the deposition of silicon oxide, the SiH\(_4\):N\(_2\):O:H\(_2\) flow rate ratio was held constant at 1:2:4 with a gas pressure of 160 Pa and a rf power density of 50mW/cm. The thickness of the film was 1.6 \( \mu m \) with a substrate temperature of 250 to 25\(^\circ\)C.\(^{[23]} \) At this point in the process, zero Si QDs had been formed and there was no photoluminescence seen. The sample was then annealed for 30 minutes in Ar/N\(_2\) ambient to change the film into a structure consisting of Si QDs in SiO\(_2\). Annealing and substrate temperatures have been shown to control PL intensity. PL intensity of a sample annealed at 1100\(^\circ\)C is a factor of 1.2 times higher then a sample annealed at 1000\(^\circ\)C.\(^{[24]} \) A drastic increase in PL intensity was observed with a decrease in substrate temperature from 250\(^\circ\)C to room temperature. The flow ratio of SiH\(_4\)/N\(_2\)O controls the PL peak energy. As the flow ratio decreased from 1:1.15 to 1:3.5, the PL peak energy and intensity increased.\(^{[23]} \) Decreasing the flow ratio means an increase in oxygen content or a decrease in Si volume content.
This method uses a low fabrication temperature and standard microelectronic manufacturing equipment. However, individual QDs fabricated using this method have size fluctuations. In terms of ease of integration into the present microelectronic devices, this method would be the easiest however a better understanding regarding nucleation dynamics is needed.

**HIGH FREQUENCY SPARK DISCHARGE**

In 1993, Hummel produced photoluminescent Si quantum dots by high frequency spark discharge.\[^9\] The experimental set up is shown in figure 28 (see Appendix). Each pulse used a unidirectional 15kV source with a single pulse length of 20 ns, repeated every 60 μs at room temperature. The spark discharge occurred between the tungsten tip (anode) and the specimen (cathode). The spark process generally created a circular pattern having a diameter of ~3-5 mm.\[^9\] Visible photo-luminescence from various QDs was observed under 325 nm laser excitation at room temperature.

This is a simple fabrication method with only a select few parameters however the circular pattern created is too large to incorporate into microelectronic devices today.

**COLLOIDAL**

Si QDs formed using the colloidal fabrication method are synthesized using tetramethylsilane (TMS) as a precursor which decomposes, in a temperature range of 660-720°C, into silicon. A common solvent used in this process is called trioctylamine (TOA).\[^26\] TOA is used as a source of N upon its decomposition in the same temperature range as TMS. The precursor mixture of TMS with TOA, (1:1 Molar ratio), was allowed to react under Argon in a gradually heated furnace at 680°C for 1 hour. Upon cooling to room temperature the final product, Si QDs, was cleaned and dried.\[^26\]

This method results in a large size distribution of Si QDs, unwanted byproducts, and different PL peak energies due to by products and/or surface composition.\[^26\] Due to the presence of by products there has been no correlation found between the PL peak energy and the size of the QDs. This method can not be used to create QDs to be used in silicon based microelectronic devices due to the large amount of observed impurities.

As mentioned above, Si QDs and related materials are currently fabricated by using many different methods. Many researchers clearly show that Si QDs have a strong visible photo-luminescence after high temperature annealing processes. It has also been shown that even though there are many different fabrication methods, only a select few can me integrated into silicon-based microelectronic device processes.
CONCLUSION

This paper has discussed different fabrication techniques of silicon quantum dots and some of their properties. The effects of fabricating Si quantum dots using ion implantation on photoluminescence intensity and peak energy, the silicon oxide defects, size distribution and the mechanism of photoluminescence of silicon quantum dots was discussed in detail. It has been demonstrated that the photoluminescence intensity is dependent on annealing time, temperature, ion dose, and process of annealing (furnace or rapid thermal anneal, or any combination therein). The photo-luminescence peak energy was shown to depend on the annealing temperature and ion dose. Ion implantation causes defects on the quantum dot surface, host material, the surface of the host causing lower luminescence intensity and a large size distribution. However this method shows promise to be integrated into silicon based microelectronics, due to the manufacturing equipment used to perform this method.
REFERENCES

Figure 10. Enhancement of photoluminescence intensity as a function of implanted Si ion dose, ranged from $5.0 \times 10^{16}$ to $2.0 \times 10^{17}$/cm$^2$. Rapidly thermal annealed for 5 min at 1100°C with temperature rise rate of 30°C/s prior to a furnace anneal at 1050°C for 1 hour.\[^{19}\]

Figure 17. Emitting light when excitations from electron-hole pairs recombine radiatively. If the QD is defect free the energy of the emitted photon ($h\nu$) is equal to the band gap energy ($E_g$). If the QD is not defect free recombination/generation occurs via interface states or defects the energy of the emitted photon to not equal the energy of the band gap.\[^{20}\]
Figures 28. Principal arrangement for spark processing under DC condition using a tungsten tip as the anode and the specimen as cathode. The spark process creates a circular pattern having a diameter of 3-5 mm.\cite{9}

Figure 29. Photoluminescence spectra of spark-processed materials under 325 nm laser excitation. Conditions of spark processing: 15kV, 0.02 \(\mu\)s repetition rate in air. Visible luminescence is observed in Si and Ge QDs.\cite{9}