Solid-state reaction silicon nanocrystals in sol-gel tetraethylorthosilicate thin films

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**Solid-State Reaction Silicon Nanocrystals
in Sol-Gel Tetraethylorthosilicate Thin Films**

Lau Hon Wu

School of Electrical & Electronic Engineering

A thesis submitted to the Nanyang Technological University
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Table of Contents

Acknowledgments	i
Table of Content	ii
Summary	iv
List of Figures	vii
List of Tables	xiii
1. Introduction	
1.1 Motivation.....	1
1.2 Objectives.....	3
1.3 Major Contributions of the Thesis	6
1.4 Organization of the Thesis	8
2. Literature Review	
2.1 Introduction	10
2.2 Synthesis of Si Nanocrystals	13
2.3 Dispersion of Nanoparticles in Colloidal Suspension	18
2.4 Stability Characterization of Nanoparticles in Colloidal Suspension	23
2.5 Luminescence and Electrical Mechanisms of Nanocrystals	25
2.6 Applications of Silicon Nanocrystals	37
3. Synthesis, Characterization and Oxidation Effects of Solid-State Reaction Si nanocrystals	
3.1 Introduction	45
3.2 Synthesis of Solid-State Reaction Si nanocrystals	46
3.3 X-Ray Diffractometry and Transmission Electron Microscopy	47
3.4 Physical and Structural Characterization	54
3.5 Applied Stress, Residual Stress and TEM Analysis of Relaxed Lattice of Solid-State Reaction Si nanocrystals	57
3.6 Influence of Oxidizing Ambient to Solid-State Reaction Si Nanocrystals ..	74
3.7 Summary	82
4. Dispersion and Embedding of Solid-State Reaction Si nanocrystal in Tetraethylorthosilicate Thin Film	
4.1 Importance of Dispersion of Solid-State Reaction Si Nanocrystals in Ethanol	84
4.2 Process Flow to Disperse Solid-State Reaction Si Nanocrystals in Ethanol and Subsequent Formation of Dispersed Si Nanocrystals in TEOS Thin Film	85
4.3 Characterization of Dispersion of Solid-State Reaction Si Nanocrystals in	

Ethanol	87
4.4 Surface Chemistry and Bonding	108
4.5 Sol-Gel Process of Solid State Reaction Si Nanocrystals in TEOS Thin Film Layer	110
4.6 Summary	114
5. Photoluminescence Study of Solid-State Reaction Si nanocrystal and Solid-State Reaction Si nanocrystal Embedded in TEOS Films	
5.1 Introduction	116
5.2 Fabrication of Solid-State Reaction Si Nanocrystals in TEOS Film	117
5.3 Investigation of Luminescence Mechanism of Solid-State Reaction Si Nanocrystals in TEOS Thin Film	118
5.4 Summary	125
6. Electrical Studies of Solid-State Reaction Si Nanocrystal Embedded in TEOS Films	
6.1 Introduction to Electrical and Electronic Applications of Si Nanocrystals..	127
6.2 Fabrication of Solid-State Reaction Si nc Capacitors	130
6.3 Capacitance-Voltage (CV) and Memory Characterization of Si nanocrystal MOS Capacitor	133
6.4 Carrier Transport and Conduction Mechanism of Solid-State Reaction Si Nanocrystals.....	157
6.5 Summary	164
7. Conclusion and Recommendations	
7.1 Conclusion	166
7.2 Recommendations for Future Research	169

Author's Publications

Bibliography

Appendix

Summary

Silicon nanocrystals (Si nc) have exhibited its potential in light emission and memory effects for the past decade. Due to its compatibility with Si technology and materials, this form of nanostructure is highly valued by many research groups. Many methods have been proposed to fabricate Si nc which includes ion-implantation, chemical vapour deposition (CVD), laser ablation and co-sputtering. However, these methods are often expensive and require a matrix, such as SiO_2 or Si_3N_4 , to embed the Si nc. The presence of such a matrix creates complications for the study of the Si nc intrinsic characteristics. In seeking a method to eliminate these two constraints, solid state reaction (SSR) – a dry chemical or physical process without adding any solvent - (also known as mechanical milling in this case) is employed to fabricate Si nc in this project.

Si powder (with grain size of $\sim 1\text{-}20\ \mu\text{m}$) has been used as the starting material. Upon 20 hours of milling, Si nc with grain size as small as 10 nm has been successfully synthesized. In addition, different milling hours result in a variety of sizes ranges from 10 nm to 71 nm. This allows the study of size effects on various properties of Si nc. Extensive diffractometry, microscopy, spectroscopy, electrical and thermal characterizations have been employed to investigate these SSR Si nc. Structural investigations using transmission electron microscopy (TEM) reveals the size and lattice characteristics of the SSR Si nc. Multiple twins, dislocations and conglomerations have been observed in the SSR Si nc. Concurrently, it is found out that the kinetics in ordered twinning of the Si nc have a positive co-relationship with post milling lattice relaxation. As such, a model is developed to explain this phenomenon. To further reduce the size of

the Si nc, oxidation has been employed successfully with 40% size reduction. A model utilizing sintering and self-limited oxidation has been developed to explain the full oxidation cycle of these Si nc.

Other than structural investigations, luminescence characterizations have also been performed. Infrared photoluminescence that peaks at ~ 1.4 eV has been exhibited. The mechanism of the luminescence is found to be independent of hydrides, siloxane and even quantum confinement. Photoluminescence excitation reveals the possible existence of non-bridging oxide hole centers as the luminescence centers.

As a potential candidate for memory devices, an embedding matrix has to be used to contain the Si nc. However, on top of this, conglomeration which can result in lateral spreading of charges must be minimized. This conglomeration problem has taunted many fabrication methods such as ion-implantation, CVD and co-sputtering. Texanol-based organic vehicle has been used to embody the SSR Si nc. This creates a steric barrier between grain and grain. Most importantly, this organic vehicle can be eliminated at temperature of $< 300^{\circ}\text{C}$. Zeta potential, particle sizing and TEM results have verified the dispersion effects using this organic vehicle. Small conglomerate size ranges of eventual dispersed Si nc at 12 nm (~ 2 -3 grains) have been achieved. Furthermore, numerous dispersed single grains have also been observed.

Metal-oxide-semiconductor (MOS) capacitors have been synthesized with dispersed SSR Si nc embedded in the spin coated tetraethylorthosilicate thin film. A flat-band voltage (V_{FB}) shift of $\sim 0.35\text{V}$ with long retention time, which exhibits less than 1% loss in charges for 6000 sec, can be observed at room temperature. This suggests the possibility of realizing nano-memory devices. Studies on the carrier transport via highly

concentrated Si nc films have been conducted. A rectifying current-voltage (IV) trend with an ideality factor as high as 13.1 has been observed. The space-charge limited current charge transport model has been used to explain the phenomena observed in the current conduction characteristics. On simulation, the number of traps per Si nc grain is determined to be ~ 100 . This explains the reason for the high retention time and V_{FB} shift observed which is desirable for memory devices.

List of Figures

Chapter 2

Fig. 2.1 Development flow of the SSR Si nc devices.....	13
Fig. 2.2 Schematic view of motion of the ball and powder mixture.....	16
Fig. 2.3 Interaction between two sterically stabilized particles. (a) Separated particles with their adsorbed polymer chains interacting with the solvent. (b) Interpenetration of the polymer chains reduces the amount of polymer/solvent interactions and forces more polymer/polymer contacts, which increases the Gibbs free energy [95].....	21
Fig. 2.4 Formation of a micelle.....	23
Fig. 2.5 (a) Quantum confinement of Si nc where both photoexcitation and photoemission occur in Si nc. (b) Presence of luminescence centers where photoexcitation occur in Si nc and photoemission occurs in embedding material. (c) Special luminescence materials embedding the Si nc where both photoexcitation and photoemission occur in the embedding material.....	26
Fig. 2.6 (a) Basic bandgap of bulk silicon (b) Enlargement of bandgap due to quantum effect.	27
Fig. 2.7. Coulomb staircases in current-voltage characteristics. [150].....	36
Fig. 2.8 Functional applications of Silicon nanocrystals.....	37
Fig. 2.9 (a) Schottky type of Si nc LED (b) Vertical PIN Type of Si nc LED.....	39
Fig 2.10 (a) A schematic cross section and band diagram during (b) injection, (c) storage, and (d) removal of an electron from a nanocrystal	42

Chapter 3

Fig. 3.1 a) Illustration of lattice planes and b) schematics for obtaining the Bragg's Law.....	49
Fig. 3.2 Shimadzu XRD-600 x-ray diffractometer in School of Materials Science and Engineering.....	50
Fig 3.3 Powder XRD scan for a Si sample as a plot of scattering intensity vs. the	

scattering angle 2θ	50
Fig 3.4 Concept of finding t using eqn. (4).....	52
Fig. 3.5 JEM-2010 TEM in School of Materials Science and Engineering.....	53
Fig. 3.6 Mapping of a real image into its diffraction patterns.....	54
Figure 3.7a) XRD spectra of Si nc with milling hours from 2 to 100 hours and b) the average grain size for different milling hours derived from Scherrer's equation.....	54
Fig. 3.8 TEM image of the Si nc generated by 20 hours of milling.....	56
Fig. 3.9 Grain diameter distribution of 35 grains taken from HRTEM images.....	56
Fig. 3.10 DTA spectra for the different milling hours.....	57
Fig. 3.11 HRTEM image of Si single crystal synthesized by SSR method with 20 hrs of milling and left at room temperature for 2 months.....	63
Fig. 3.12 HRTEM of a typical multiple deformation twins formation in a (~ 30 nm) Si crystal after SSR with 20 hrs of milling and left at room temperature for 2 months. The inset reveals the FFT image of the Si nc.....	63
Fig. 3.13 Arrangement of atoms in a twin related structure where x-y is the trace of the twin compositional plane.....	64
Fig. 3.14 (a) HRTEM of a typical $\Sigma=3$ twin and (b) enlargement of Fig. 2(a) along the [011] direction for sample at milling condition of 20 hours and left at room temperature for 2 months.....	64
Fig. 3.15 HRTEM of two typical $\Sigma=3$ Si nc and their different grain boundaries with milling condition of 20 hours and left at room temperature for 2 months. The inset reveals the SAED of the Si nc on the right with a zone axis of [011] while the Si nc on the left has a zone axis of [111]	65
Fig. 3.16 Multiple {111} facets coalescence without the formation of a twin. The inset reveals the FFT image of the Si nc	66
Fig. 3.17 (a) The XRD spectra of unmilled Si particles and 20 hours milled Si nc after being left for 1.5 hrs, 5 hrs, 11 days (264 hrs), 48 days (1152 hrs) and 59 days (1416 hrs) and (b) the strain values with respect to the left hours for {111} and {110} planes respectively.....	67
Fig. 3.18 Schematics of the 4 stages of twin formation kinematics of Si nc,	

namely stage 1) Application of shear stress to a parent crystals, 2) tearing of parent crystal into smaller crystals, 3) contact of two smaller crystal and stress relaxation and 4) twinning process.....	73
Fig. 3.19 (a) TEM image of clusters of Si nc in TEOS thin film, (b) HRTEM of the grains necking in the cluster as shown in (a) after a soft bake of 150 °C and (c) DLS agglomerate size distribution.....	77
Fig. 3.20 Arrhenius plots of sintering for estimation of (a) activation energy E_A and (b) constant D for Si nc.....	77
Fig. 3.21 Experimental data of the grain size with respect to oxidation time and the curve fitting of the sintering and oxidation regions. Inset: Transitional schematic of the regions I, II and III.....	81

Chapter 4

Fig. 4.1 Process flow of the fabrication.....	86
Fig. 4.2 Zeta potentials of Si nc with no organic vehicles, 20 wt% organic vehicles and 40 wt% organic vehicles respectively.....	88
Fig. 4.3 Total solid present in the bottom over the top of the solution with different pH level of the solution with and without organic vehicles	89
Fig. 4.4 the suspension containing (a) Si nc coated with organic vehicles and (b) Si nc without organic vehicle after centrifugation and filtration and c) solution of ethanol with organic vehicles only	92
Fig. 4.5 Concentration curve based on UV-VIS absorption spectrum	93
Fig. 4.6 Particle size distribution of Si nc in ethanol without and with 20 wt% organic vehicles	95
Fig. 4.7 Lognormal particle size distribution of the suspension without the Si nc coated without organic vehicles, with organic vehicles and with organic vehicles followed by 0.1 μm filter.....	96
Fig. 4.8 Lognormal particle size distribution of the suspension without organic vehicle and with organic vehicles going through the 0.1 μm filtration.....	97
Fig. 4.9 Particle size distribution of Si nc using filtration, centrifugation, filtration	

followed by centrifugation with and without organic vehicles.....	98
Fig. 4.10 Particle size distribution of Si nc using different weight percentage of organic vehicles and milling hours for the homogenization of the Si powder and organic vehicles	100
Fig. 4.11 Comparison of simulated resultant energy barriers over different sizes of Si nc in ethanol from Eqn 4.1	101
Fig. 4.12 Microscopic images using 100 times magnification for Si nc (a) with organic vehicles without centrifugation and filtration, (b) without organic vehicles without centrifugation and filtration, (c) with organic vehicles after centrifugation and filtration and (d) without organic vehicles using filtration followed by centrifugation and filtration.....	104
Fig. 4.13 AFM images for (a) pure TEOS thin film and Si nc (b) with organic vehicles using filtration followed by centrifugation and (c) without organic vehicles using filtration followed by centrifugation.....	105
Fig. 4.14 TEM images of (a) Si nc without organic vehicles before refinement, (b) Si nc with organic vehicles before refinement, (c) Si nc with organic vehicles after refinement and (d) Si nc after refinement with burnt out of organic vehicles.....	107
Fig. 4.15 Selected area electron diffraction patterns of (a) Si nc without organic vehicles and (b) Si nc with organic vehicles before refinement.....	107
Fig. 4.16 (a) Thermogravimetric analysis spectra of Si nc with organic vehicles from 27 °C to 600 °C and (b) Infrared absorption (FTIR) spectra of the organic vehicles, milled Si nc without and with organic vehicles at varying annealing temperatures in N ₂ ambient.....	108
Fig. 4.17 Reaction of the organic vehicles on the Si nc surface.....	110
Fig 4.18 SNT layer thickness variation using different mole ratio of ethanol to TEOS and spin speed.....	112

Chapter 5

Fig. 5.1 TEM image of SSR Si nc in TEOS thin film	118
Fig. 5.2 (a) PL spectra and (b) PL peak wavelength of SSR Si nc with average	

diameters of 10, 14, 19 and 25 nm respectively	119
Fig. 5.3 FTIR of SSR Si nc in TEOS thin film, TEOS thin film and 10 nm SSR Si nc	120
Fig. 5.4 PL emission energy with respect to Si nc size utilizing C. Delerue's equation, G. Ledoux and experimental data using SSR Si nc.....	121
Fig. 5.5 FTIR of SSR Si nc in TEOS thin film, TEOS thin film and 10 nm SSR Si nc	121
Fig. 5.6 PLE spectra of SSR Si nc at the size of 10 nm and SSR Si nc in TEOS dried at room temperature and annealed at 900 °C in O ₂ ambient for i) 15 mins and ii) 1 hr using an excitation energy of 2.54 eV	122

Chapter 6

Fig. 6.1 Fabrication schematics of these SNT and TSN structures.....	131
Fig. 6.2 CV characteristics of SNT structure annealed (a) in air at 500°C for 5 min, (b) in N ₂ ambient only at 900 °C for 15 min, (c) in O ₂ ambient only at 900 °C for 15 min and (d) in O ₂ ambient followed by N ₂ ambient at 900°C for 15 min respectively.	135
Fig. 6.3 Schematic cross section of metal-Si nc/SiO ₂ -Si substrate capacitor using spin coating.....	138
Fig. 6.4 C-V characteristics of (a) the pure TEOS thin film and (b) Si nc with organic vehicle in TEOS thin films annealed in O ₂ ambient at 900 °C for 1 hr with a CV double sweep from -8 V to 8 V then back to 8 V	139
Fig. 6.5 C-V characteristics of Si nc with organic vehicles in TEOS thin film annealed in O ₂ ambient at 900°C for (a) 1 hr and (b) 2 hr.....	141
Fig. 6.6 shows a) the SNT capacitor structure, b) the TEM image of Si nc in the SNT layer and c) the cross-sectional TEM of the SNT structure.....	141
Fig 6.7 C-V characteristics when the SNT capacitor is biased for 1 sec with a) positive 13 V and b) negative 25 V respectively.....	143
Fig. 6.8 V _{FB} shift, due to varying bias voltages for 1 sec, of a) TEOS thin film only and b) SNT layer.	143

Fig. 6.9 Retention time characteristics of the SNT capacitor biased at 16 V for 1 sec.	144
Fig. 6.10 Structure of SNT with TEOS control oxide capacitor.....	146
Fig. 6.11 Flat-band voltage shift due to (a) positive and (b) negative gate bias.	146
Fig. 6.12 Hysteresis due to (a) positive and (b) negative gate bias.....	147
Fig. 6.13 C-V characteristics of the SNT with TEOS control oxide capacitor at stressed at a voltage of 15V.....	148
Fig. 6.14 Retention time characteristics of pure TEOS thin film, Si nc in TEOS layer only and Si nc thin film with TEOS control oxide.	149
Fig. 6.15 Variation of V_{FB} shift at different stress time.....	150
Fig. 6.16 Schematics of tunneling kinetics in the case of Si nc in TEOS thin film with control oxide.	151
Fig. 6.17 (a) Current - voltage characteristics of Si nc in TEOS thin film with control oxide and TEOS thin film only, (b) Current density - E-field characteristics of Si nc in TEOS thin film with control oxide and TEOS thin film only.....	152
Fig 6.18 Structure of SNT with PECVD control oxide capacitor.....	153
Fig. 6.19 V_{FB} shift with respect to stress voltage for SNT with PECVD control oxide capacitor.....	154
Fig. 6.20 Comparison of retention times of SNT without control oxide capacitor stressed at 20 V and SNT with PECVD control oxide capacitor stressed at -16 V...	156
Fig. 6.21 TEM image indicating SSR Si nc in the film	158
Fig. 6.22(a) IV characteristics of a 150 μm diameter diode from 305 K to 400 K on a log-log plot. Inset: IV characteristics of the device from -10 to 1.5 V (linear scale) at 305 K. 6.23(b) Curve fitting of IV characteristic at 305 K based on Eqn 6.5.	159
Fig. 6.23(a) SCLC power law fits to the data in Fig 6.23(a) from 305 K to 400 K and (b) variation of exponent factor m with respect to inverse temperature.....	161
Fig. 6.24 High resolution TEM images revealing (a) dislocations and (b) grain boundaries in the SSR Si nc.	162

List of Tables

Chapter 2

Table 2.1 Various compounds of nanocrystals synthesized by different groups.....	11
Table 2.2 Discoveries made regarding Si nc.....	12

Chapter 3

Table 3.1 Different XRD peaks and strain values after 20 hours of milling left for 1.5, 5, 264 (11 days), 1152 (48 days) and 1416 (59 days) hours as compared to the unmilled one.....	70
Table 3.2 Grain size for (111) miller planes after 0 hr, 0.2 hr, 0.5 hr, 0.8 hr, 1 hr, 2 hr, 3 hr, 4 hr, 5 hr, 6 hr and 8 hr oxidation at 900°C.....	75

Chapter 4

Table 4.1 Peak size concentration of Si nc using filtration, centrifugation, filtration followed by centrifugation with and without organic vehicles.....	99
Table 4.2 Peak particle size distribution of Si nc using different weight percentage of organic vehicles and milling hours for the homogenization of the Si powder and organic vehicles.....	100
Table 4.3 Thickness (nm) responding to the data as featured in Fig 4.18.....	113

Chapter 5

Table 5.1 PLE intensity at about 1.88 eV of SSR Si nc in TEOS dried at room temperature and annealed at 900 °C in O ₂ ambient for i) 15 mins and ii) 1 hr.	124
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Chapter 1: Introduction

1.1 Motivation

Si nanocrystals (Si nc) have recently attracted much attention because of their light-emitting ability [1-3] that makes them suitable for Si-based optoelectronic ICs. In addition, there is renewed interest in their possible applications in nano-memory devices or other single electron devices [4-6].

Although quantum effects have been known for many decades, they only found practical applications in the late 1980's, especially Si nc luminescence [7]. Photoluminescence (PL) with an intense and wide spectral emission peaking between 1.4 and 1.8 eV has been reported for Si nanocrystals embedded in SiO₂ thin films [8-11]. Room temperature electroluminescence (EL) emission of nc-Si/SiO₂ thin films has also been recently reported [12]. Si nc luminescence has opened up a new avenue of optoelectronic components based on silicon such as LEDs [12, 13] and lasers [3]. The charge trapping capability of Si nc has also opened up new generations of memory devices [14, 15]. It has recently been proposed that nanocrystals be used as charge storage elements embedded in the gate dielectric of a field transistor and located in close proximity (2-3 nm) to the transistor channel. The conditions for single electron memory device application, such as a large amount of charging energy for room temperature operation and an opaque tunneling barrier for suppressing co-tunneling or charge number fluctuation in the charge island, can be met in the nc-Si/SiO₂ system. Despite the random

distribution and size dispersion problems, nano-memory devices with a gate oxide containing nanocrystals have been reported operating at room temperature [4]. Electronic devices based on the application of single electron tunneling effects in nc-Si have the advantages of low-power consumption and high device density. For practical applications of single electron devices, Si-based processes are required for the device fabrication. In this project, spin coating of tetraethylorthosilicate (TEOS) thin film containing solid-state reaction (ball milled) Si nc as the additives was adopted. The Si ncs are first synthesized separately before being mixed with TEOS solution for spin coating. This approach has been unique as compared to other methods like co-sputtering of Si and SiO₂ plasma decomposition of silane gas and subsequent oxidation or Si ion implantation into SiO₂ that require growth of Si nc from chemical reactions. These methods will be described in greater details in Chapter 2.

Although the ball milling technique had been used in industry for decades [16], it has seldom been used for milling silicon into nanometric sized particlescale. Lam et al reported that Si nc of 5 nm with a 1 nm oxide coating had been ball milled [17]. This opened up a new avenue for the making of Si ncs. As compared to other methods, ball milling is a very well established process and potentially much cheaper than Chemical Vapour Deposition (CVD) or Implantation. This has made the ball milling method an attractive way to synthesize Si nc. Besides cost reduction and the well established process, mass production can also be easily attained using this method. Conventional high energy ball milling has been used to manufacture huge quantities of mechanically alloyed materials at one go. Compared to other methods, ball milling is a promising

method to synthesize Si nc in large quantities to fulfill the needs of commercial exploitation.

However, just producing the Si nc in powder form is not sufficient. It requires an adhesive film to embed these Si nc into the SiO₂ system in order for the further processing into optoelectronic and electronic devices. Conventional oxidation and CVD will not be feasible techniques for the embedding matrix as the nanocrystals are already grown externally. A better alternative is to use a sol-gel technique to form Si nc in an SiO₂ matrix which can be spin coated into a thin film. Spin coating is another well-established technique in microelectronics processing, commonly used to form a thin film of resist. This offers great advantages in both machinery and research costs. At the same time the control of the thin film is relatively easy, it is simple to control over the viscosity and spin speed [18]. Based on the advantages of high energy ball milling and sol-gel techniques, this project aims to combine these two techniques to create a new generation of Si nc, films and devices.

1.2 Objectives

In this work, Si nanocrystals (Si nc) is synthesized by using high energy planetary ball milling. These Si nc are further dispersed in ethanol and homogenized in TEOS solution. Upon homogenization, this suspension is being spin-coated onto Si wafer. Structural properties of these Si nc are being investigated. Studies related to optical and electrical applications are also being carried out. The objectives are as follows:

1. To produce and characterize Si nano-sized powders from commercially available Si powders ($\sim 1\text{-}20\ \mu\text{m}$) at room temperature using the ball milling technique.

Ball milling technique has been widely employed to produce nanometric powder [16]. Si nano-sized powders, ranging from 5 nm to 25 nm, can be generated by this method. As reported [16], reduction in size can lead to an increase in energy band gap due to the quantum confinement effect. The physical and structural changes in the Si nc at different stages of the synthesis process will be investigated using tools including the X-ray diffractometry (XRD), Fourier transform infrared spectroscopy (FTIR), Transmission electron microscopy (TEM) and Raman scattering.

2. To further reduce the size of Si nc obtained by ball milling using novel oxidation processes.

As quantum confinement effect is more prominent in crystals smaller than 5 nm, the oxidation of the milled Si nc will be investigated to further reduce the size of the nanocrystal. XRD and TEM will be employed to determine the size of the oxidized Si nc. The kinetic during the oxidation process will also be studied in order to understand its effects on the final size of the Si nc.

3. To disperse the milled Si nc in sol solution

Si nc in TEOS solution can be viewed as a form of colloidal suspension. The dispersion of Si ncs in the solution medium is essential for prevention of conglomeration and flocculation of the Si ncs. At the same time, constant dispersion is also necessary to give a constant Si nc density across the whole TEOS film upon spin coating. Characterization such as surface or zeta potentials measurements, settling test and TEM will be carried out to detail the dispersion stability effects of the Si nc in TEOS solution.

4. To fabricate Si nc in TEOS films and investigate their optical properties.

Sol-gel spin coating is a cheap and industrially available technique. A modified sol-gel process will be developed by incorporating the spin-coating of Si nc consisting TEOS film. This signifies an inexpensive and readily available method to study the Si nc-TEOS system. It provides a great potential not only in research, but also in industrial application of optoelectronic devices. The optical properties including photoluminescence (PL) and photoluminescence-excitation (PLE) will be characterized for the developed Si nc-TEOS system.

5. To fabricate capacitor devices using the spin-coated Si nc-TEOS films and investigate their electrical properties.

Charge trapping effects in Si nc have been successfully demonstrated [19] using ion implantation and CVD methods. The aim here is to fabricate capacitors using solid-state reaction (SSR) Si nc-TEOS and compare their charge trapping effects with others. Detailed investigation will be carried out on their electrical properties, including the study of defects using C-V measurements and current transport (I-V) of this system.

1.3 Major Contributions of the Thesis

The major contributions of the thesis are as follows:

A range of SSR nanometric Si nanocrystals (Si nc) from about 10 to 25 nm has been successfully synthesized by an inexpensive ball milling method. Microstructural properties of these SSR Si ncs have been extensively studied by high resolution transmission electron microscopy (HRTEM). These Si ncs were found to be highly strained and upon relaxation of lattice after milling, the ordered lattice plane fracturing and nano-twinning processes were observed. A model has been determined and a model has been developed to explain the fracturing and nanotwinning kinetics during the lattice relaxation.

A thermal oxidation was further implemented to reduce the size of these SSR Si ncs, to approximately 7.7 nm, successfully. Using x-ray diffractometry (XRD) and TEM study, it is discovered that the sintering process that leads to an increase in crystalline size

dominates during the early stage of the oxidation process. This was then followed by the oxidation process that decreases the crystalline size in the later stage. An oxidation kinetics model, involving these competing forces of sintering and oxidation, has been developed. This model is built on the basis of the classical sintering and modified Deal-Grove oxidation equations. The sintering activation energy and compressed lattice induced mechanical stress of SSR Si ncs upon oxidation can be determined using this model.

Uniform dispersion of the SSR Si nc from agglomerates and clustering is being achieved by the addition of Texanol-based organic vehicle. Despite the usual Van der Waals and electrostatic forces involved in colloidal suspensions, the steric forces of the Texanol-based organic vehicle coated Si ncs have been determined to be the dominating factor in this dispersion. Small agglomerates and single crystals (about 8 to 12 nm) have been successfully extracted using this method. At the same time, due to its non-ionic nature and low boiling point at about 250 °C, further applications of these dispersed Si nc in memory devices without ionic impurities have been made possible.

Infrared emission from SSR Si ncs has been observed. Various possible luminescence mechanisms, such as quantum confinement, siloxene, etc have been discussed and non-bridging oxide hole centers (NBOHCs) have been identified as dominating luminescence centers for the SSR Si nc.

A novel MOS capacitor has been demonstrated using SSR Si_{nc} s embedded in tetraethylorthosilicate (TEOS) thin film as the dielectric for the first time. The memory effect based on charge trapping in the TEOS capacitor with long retention time ($< 1\%$ loss in charge for 6000 sec) has been observed. Space-charge limited current model has been demonstrated to explain the carrier transport in the TEOS system. From this model, the influences of Si_{nc} s population and temperature on the carrier transport were determined.

1.4 Organization of the Thesis

In **Chapter 1**, a brief introduction to the applications of nc-Si is presented. The motivation behind this study is also discussed in this chapter. The objectives and major contributions in this thesis are also summarised.

In the following chapter, **Chapter 2**, a literature review is presented; the different methods for synthesizing nanocrystals are described; the physical properties of such nanocrystals characterized using various techniques including XRD, TEM, etc, are discussed; the theory of colloidal dispersion of Si_{nc} and the applications of Si_{nc} -TEOS film structures based on their optical and electrical properties are introduced. In **Chapter 3**, the structural properties of SSR, un-oxidized and oxidized Si_{nc} are studied in detail. The oxidation effects on the sizes of Si_{nc} are also discussed in detail. Following after that, in **Chapter 4**, the technique and understanding of creating a well-dispersed Si_{nc} in ethanol are discussed. Further results of embedding these dispersed Si_{nc} in TEOS thin film are also presented. The optical studies are described in **Chapter 5**, where PL and

PLE measurements are presented. The mechanisms of the light emission in the SSR Si nc are also discussed. Detailed electrical studies on the nc-Si/SiO₂ system including charge trapping and carrier transport are presented in **Chapter 6**. These studies lead to the discovery of a new type of memory effect. A summary of the work carried out in this thesis as well as conclusions and recommendations for future research are presented in **Chapter 7**.

Chapter 2: Literature Review

2.1 Introduction

Nanocrystal has been an important research area for the past decades. Tracing back to the early 1980s, A. I. Ekimov and A. A. Onushchenko [20, 21] and L. Brus with co-workers [22, 23] have already published pioneering articles on size-dependent absorption spectra of semiconductor nanocrystals. At the same time, S. V. Gaponenko et al. also reported on the inhomogeneous broadening of the optical absorption spectra of glasses doped with semiconductor crystals [24]. Ever since these reports were published, the optical properties of nanocrystals have been extensively studied by many other research groups. Many different kinds of nanocrystals have been synthesized to study their optical characteristics. Different kinds of nanocrystals synthesized by different groups over the years are summarized in Table 2.1.

Element Group	Year	Nanocrystal Compound	Researchers
II-VI	1990	CdTe	Potter and Simmons [25]
	1995	CdTe	Murray et al. [26]
	1991	PbS	Wang and Herron [27]
	1994	PbS	Borrelli and Smith [28]
	1994	GaAs	Salata et al. [29]
	1996	InP	Micic et al. [30]

III-V	1995	GaSb	Hatami et al. [31]
	1991	GaP	Ekimov [32]
	1995	GaP	Micic et al. [33]
IV	1990	Si	Canham [34]
	1992	Si	Prokes et al.[35]
	1994	Si	Brus [36]
	1995	Si	Schruppler et al. [37]
	1995	Ge	Maeda [38]

Table 2.1 Various compounds of nanocrystals synthesized by different groups.

The most critical discovery of the visible red luminescence of porous silicon at room temperature is by L. T. Canham in 1990 [34]. This discovery leads to the possible integration of a silicon light source into the existing integrated chips (ICs) without the compatibility problem. It provides for the potential for both commercial and industrial applications. Therefore, in this thesis, the emphasis will be on the silicon nanocrystals (Si nc). The historical events involving Si nc can be summarized in Table 2.2.

Year	Events on Silicon Nanocrystals	People/Group
1982	Size-dependent absorption spectra of semiconductor nanocrystals	Ekimov et al [20]
1983	Room temperature Photoluminescence (PL) from a-Si:H	Wolford et al [39]

1990	First room temperature visible red PL of P-Si/ Quantum confinement mechanism	Canham [7]
1991	First Electroluminescence (EL) of P-Si	Richter et al [40]
1991	Synthesis of Si nc by gas evaporation	Okada et al [41]
1992	Siloxene mechanism	Brandt et al [42]
1992	Hydride (SiH _x) mechanism	Tsai et al [43]
1992	Synthesis of Si nc by co-sputtering	Maeda et al
1993	Non-Bridging Oxide Hole Center (NBOHC) mechanism	Prokes [44]
1994	Synthesis of Si nc by ion implantation	S. Iwayama [45]
1995	Quantum confinement luminescence centers mechanism	Qin et al [46]
1996	Single charge Si nc memories	Tiwari et al [4]
1997	Synthesis of Si nc by ball milling	Shen et al [47]
2000	Optical gain in Si nc	Pavesi et al [3]
2000	Dispersed etch porous Si	Nayfeh et al [48]
2001	Chemical synthesis of Si nc	Holmes et al [49]
2003	World's first 4 Mbit memory device based on Si nc	Motorola Inc
2005	Field-effect EL in Si nc	Walters et al [50]
2006	World's first 24 Mbit memory device based on Si nc	Freescale Co.

Table 2.2. Discoveries made regarding Si nc.

In the following sections, the flow of the content will follow the fabrication and development of the SSR Si nc devices as feature in Fig. 2.1.

Fig. 2.1 Development flow of the SSR Si nc devices

2.2 Synthesis of Si Nanocrystals

Si nc can be synthesized by various techniques. They can be classified into two approaches, namely the top-down approach or the bottom-up approach. The top-down approach involves reducing the size of Si wafer or particles into nanocrystals. This approach can be achieved via three methods namely the electrochemical etching, oxidation and milling processes. Conversely, the bottom-up approach employs the nucleation of Si ions or species to form the nanocrystals. This approach can be achieved via methods including CVD, ion implantation, and laser ablation. From the bottom-up approach, it is observable that the Si nc is fabricated in a host matrix. The most commonly host matrix are SiO₂ [51-54]. SiO₂ has proven to be a robust matrix that provides good chemical and electrical passivation of nanocrystals. In addition, the

fabrication is fully compatible with mainstream CMOS processes, and thus allows the integration of optoelectronic devices into Si circuits.

2.2.1 Top-down approach

Etching of Si wafer to obtain porous Si (PS) [11, 34, 42, 55-59] can be done by performing electropolishing experiments on Si wafers using hydrofluoric acid (HF)-containing electrolyte. Utilizing an increasing current over a specific threshold, a partial dissolution of the Si wafer will start to occur. PS formation is then obtained by electrochemical dissolution of Si wafers in aqueous or ethanoic HF solutions. With the use of Si wafer as the anode, a platinum spiral or grid as the cathode and high-purity HF in 40% aqueous solution diluted in ethanol at different concentrations as the electrolyte, electrochemical etch can take place. Often, dilution of the solution is necessary to increase the wettability of the Si wafer surface. The etching process can be controlled by varying the current or the potential.

The Deal-Grove's oxidation equation [18] describe aptly the consumption of Si wafer by oxidants. Hence it is possible to create Si nc using the oxidation process. Liu *et al.* has reported the oxidation of Si nanowires [60]. He has demonstrated the reduction of size of the Si nanowire via oxidation. Other groups [61-64] have also reported on the oxidation of Si quantum dots. However, the size reduction is a self-limiting process as oxidation hours prevail. This is attributed to the stress and strain occurring at the surfaces of the oxidized Si structures.

Mechanical milling has been widely used to prepare nanocrystalline metallic materials and alloys [65-74]. It had been reported that mechanical milling is able to create crystalline-to-nanocrystalline Si [17, 75, 76]. The synthesis of SSR Si nc is performed with mechanical attrition of Si powder using balls and vials. Extraction of milled powders at different hours can yield nanometric powder of different sizes [9]. Mechanical alloying is a form of ball milling process where a powder mixture placed in the ball mill is subjected to high energy collision from the balls [16]. This technique has created a new avenue to produce materials other than the traditional high temperature synthesis route. It has attracted much attention and inspired many research interests due to its promising results, wide possible applications and potential scientific values. At the same time, it is an economical method where huge amount of materials can be synthesized creating even more interest in this field. Mechanical alloying has now been recognized as a unique technique. It has been utilized in different areas of material processing and applied to many different material systems. These material systems include composites, amorphous [76], nanocrystalline alloys [73, 76], intermetallic compounds [69], etc. They are made possible and successful by mechanical alloying which otherwise cannot be synthesized using conventional methods.

There are a few types of ball mill systems employed in mechanical alloying. They are namely the planetary ball mill, conventional horizontal ball mill and the attritor. Though there are a few systems available, the principles of their operations are the same. During ball milling, the particles are subject to constant cold welding and fracturing [16].

Therefore, the critical condition is to strike a balance between these two competing forces in order to alloy successfully. Of these three ball mill systems, the most commonly used system in laboratories is the planetary ball mill due to its compactness and only small quantities of samples are required. The ball mill consists of one turn disc (sometimes called turn table) and two or four bowls. The turn disc rotates in one direction while the bowls rotate in the opposite direction. The centrifugal forces created by the rotation of the bowl around its own axis together with the rotation of the turn disc are applied to the powder mixture and milling balls in the bowl. As a result, the powder mixture is fractured and cold welded under high energy impact.

Fig. 2.2 Schematic view of motion of the ball and powder mixture [16]

Fig. 2.2 shows the motions of the ball and the powder. Since the directions of rotation of the bowl and the turn disc is opposing, the centrifugal forces are alternatively synchronized. During this process, friction is generated when the milling balls and powder mixture are alternately rolling on the inner wall of the bowl. Impact results when they are lifted and thrown across the bowl to strike at the opposite wall. The impact

energy is intensified when the balls strike one another. The impact energy of the milling balls in the normal direction attains a value up to 40 times higher than that due to gravitational acceleration. Using this high impact attrition, nanometric sized grains can be attained [9, 17, 72, 73]

2.2.2 Bottom-up approach

Nanocrystals embedded in SiO_2 films can be prepared by co-sputtering from two electrodes, one with a semiconductor (Si Ge, etc.) target and the other with a quartz target [38, 77-83]. This method enables the production of alloyed materials with a controlled composition. An entire series of mixed compositions with different microstructures can be obtained by varying the RF power applied to the targets.

Si nanocrystal in SiO_2 films can also be fabricated via plasma-enhanced chemical vapor deposition (PECVD) [84]. A Si-rich SiO_2 film can be formed using very high frequency (VHF) PECVD from an $\text{N}_2\text{O}:\text{SiH}_4$ mixture. Attaining a VHF and right pressure can cause the gas to form plasma, which will then allow the Si ions to be doped in situ with SiO_x film formation [85].

Low-pressure chemical vapor deposition (LPCVD) can be used to deposit a thin Si layer onto the SiO_2 , which is thermally grown on a Si wafer [54, 86]. Such a deposition is normally carried out in a very high vacuum reactor at $\sim 500^\circ\text{C}$ with pure SiH_4 . Then, SiO_x films can be formed by oxidation at $\sim 900^\circ\text{C}$ for various durations.

One of the most commonly employed bottom-up techniques to create Si nc in SiO₂ is through the implantation of Si ions into SiO₂. SiO₂ films are first thermally grown on Si substrates. The Si ions are then implanted at the selected energy level (1-200 keV) with a dose ranging from 10¹⁶ to 10¹⁷ cm⁻² [45, 51, 53, 87-92]. Subsequent annealing in N₂ ambient at temperature ranging from 900 °C to 1100 °C for 1 hr has been commonly used for the nucleation of the Si nc in the SiO₂ film.

Recent formation of Si nc can be attained by laser ablation [93-101]. The Si target can be ablated by a laser beam using laser pulses in an inert gas ambient. The ablated species will then accumulate on the substrate. Subsequent annealing in oxygen gas will lead to the formation of Si nc embedded SiO₂ films.

In addition, Si nc embedded SiO₂ films can be deposited by thermal evaporation of SiO powders onto rotating substrates [102]. It is further reported by co-evaporating Si and Al₂O₃ onto Si wafers that Si nanocrystals can be embedded in Al₂O₃ matrix [103].

2.3 Dispersion of Nanoparticles in Colloidal Suspension

2.3.1 Introduction to Dispersion of Colloidal Suspension

Colloids are traditionally divided into two groups called lyophilic (“solvent-loving”) and lyophobic (“solvent-hating”) [104] respectively, depending on how easy the system

can be re-dispersed in solution again from its dried form. A lyophilic colloid can be dispersed easily by adding a suitable solvent to the dry form. This dry particle will first swell as it takes up the liquid and will finally form a homogeneous colloidal solution. As for lyophobic colloid, it can only be dispersed by vigorous mechanical agitation (or by the application of some other external source of energy).

A colloid is considered stable if the particles remain separated from one another for a long periods of time without agglomerations and flocculations [104]. For lyophilic colloids, stability results from the fact that the solution is thermodynamically stable as the solution has a lower Gibbs free energy than the separated suspended components. Such a colloid is considered indefinitely stable. However, in the case of a lyophobic colloid, there is always an attractive (van der Waals) force between the suspended particles. When they get close enough to one another, this force dominates and the particles become aggregated together. The system may look to be stable for some time only if there are other external forces, such as attrition and vibration, present to separate the particles in the course of Brownian motion. They are, however, considered thermodynamically unstable, and the barrier to coagulation is merely a kinetic one. Given enough time the suspended particles will ultimately form aggregates. Although the solvent does have a role to play, the fact that the colloid does not disperse spontaneously suggests that salvation effects are not sufficient to produce a stable colloid. If repulsive forces are not strong enough, the particles will be attracted together to form what are called flocs or floccules which are said to be unstable in the colloid sense.

Although lyophobic colloids are unstable, there is a method to make it “stable” by the addition of organic materials around the suspended particles. This method involves the coating of a sufficiently thick layer of polymer or organic solvent to mask the attracting effect of the underlying particles. Two forms of stabilizers can be used to induce the stability of lyophobic colloids, namely the steric stabilizers and surfactants.

2.3.2 Steric Stabilization

Dispersion of solids in liquids can be stabilized by steric [105-108] or physical barriers, and can in the absence or presence of electrical barriers. This form of physical barriers can be produced when portions (lyophilic chains) of the adsorbed molecules layer onto the surfaces of the solid particles extend into the liquid phase and interact with each other. These interactions [109] will typically produce two main effects, namely (1) a mixing effect and (2) an entropic effect. For the case of mixing effect, it is due to solvent-chain interactions and the high concentration of chains in the region of overlap. When the adjacent particles come close to one another to within or less than twice the thickness of the adsorbed layer on the particles, mixing effect becomes significant. This effect is largely dependent on the relative strengths of the solvent-chain and chain-chain interactions. When solvent-chain interaction is stronger than the chain-chain interaction, the free energy of the system is being increased when the regions consisting of the extended portions of the adsorbed molecules overlap, and an energy barrier is induced within close proximity. On the other hand when the chain-chain interaction is greater than the solvent-chain interaction, the free energy will decrease when the regions overlap. As

a result, attraction, rather than repulsion occurs. The entropic effect is due to restriction of the motion of the chains extending into the liquid phase when adjacent particles come into close proximity with one another. When the separation between particle surfaces become less than the thickness of the adsorbed layer, this effect becomes particularly important. Fig. 2.3 illustrates the repulsive effect of steric stabilization of colloids. When two such particles approach, the interaction between the adsorbed chains causes a repulsion that can be sufficient to induce stability. Its magnitude can be calculated by estimating the effect of the particle separation on the free energy of the adsorbed molecules. As they are in close contact, the number of the chain-chain contacts is increased at the expense of chain-solvent interactions; and for a lyophilic (solvent-loving) polymer, it leads to an increase in the free energy, and results in a repulsive force between two particles.

Fig. 2.3 Interaction between two sterically stabilized particles. (a) Separated particles with their adsorbed polymer chains interacting with the solvent. (b) Inter-penetration of the polymer chains reduces the amount of polymer/solvent interactions and forces more polymer/polymer contacts, which increases the Gibbs free energy [104].

The free energy of mixing of the adsorbed molecular chains, as the particles come close together, can be broken into an enthalpic and an entropic part [104, 109]:

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}} \quad (2.1)$$

A positive value of ΔG_{mix} (repulsion) can arise either from a positive value of ΔH_{mix} (enthalpic stabilization) or negative value of ΔS_{mix} (entropic stabilization) or both. It is to note that this form of stabilization apply particularly to systems in which the absorbed polymer is anchored to the surface of the particles and cannot be desorbed or moved out of the way as the particles approach one another.

2.3.3 Surfactants

Surfactant [104] is a contraction of the name surface active agent. The molecules of surfactant consist of two different regions of extreme opposite characteristics: one part is polar (either a dipole or a charged group) and the other is a non-polar (usually a hydrocarbon or halocarbon chain). As the molecules of surfactants aggregate together, due to the attractive nature of the hydrocarbon chains and the repulsive nature of the charge group, the micelles are often formed. When a particle is present, the hydrocarbons will be absorbed to the surface forming a micelle with the charge groups dangling outside as observed in Fig 2.4. These charged groups can results in electrostatic repulsion when 2 micelles approach each other. Similarly, when the surface of the particle is oppositely charged with the charged group of the surfactant, reverse micelles can be formed resulting in attraction between micelles.

Fig. 2.4 Formation of a micelle

2.4 Stability Characterization of Nanoparticles in Colloidal Suspension

The stability of a colloidal suspension is commonly defined as the amount of time the particles can be suspended in the solvent. There are two common characterization techniques for this stability, namely, the zeta potential and particle sizing, and the settling test.

(a) Zeta Potential and Particle Sizing

The zeta potential [110, 111] is the measurement of the double layer potential of the particles with respect to the potential of the vast solvent. This measurement is normally preformed by passing an electric field through the colloidal suspension and recording the mobility of the particles flowing in accordance of the electric field. From the collected data, the zeta potential can be calculated. As materials are getting smaller into the nanometric scale, the detection of its mobility poses a great difficulty. However, with the incorporation of the dynamic light scattering theory [112] into the mobility measurement,

this difficulty can be overcome. Dynamic light scattering [112], also known as Quasi Elastic Light Scattering and Photon Correlation Spectroscopy, is particularly suited to determining small changes in mean diameter such as those due to the adsorbed layers on the particle surface or slight variations in manufacturing processes. A beam of laser is allowed to pass through a colloidal dispersion which results in the particles scattering some of the laser in all directions. If the particles are very small as compared with the wavelength of the light, the intensity of the scattered light is uniform in all directions (Rayleigh scattering); for larger particles (above approximately 250 nm diameter), the intensity is angle dependent (Mie scattering). The observed time-dependent fluctuations in the scattered intensity can be detected using a photomultiplier capable of operating in photon counting mode. The fluctuations often occur as a result of Brownian motion and the distance between them is therefore constantly varying. Constructive and destructive interference of light scattered by neighbouring particles within the illuminated zone gives rise to the intensity fluctuation at the detector plane which, as it arises from particle motion, contains information about this motion. Analysis of the time dependence of the intensity fluctuation can therefore yield the diffusion coefficient of the particles where the mobility can be derived. Further expansion of this result using Stokes Einstein equation and the viscosity of the medium, the hydrodynamic radius or diameter of the particles can be then calculated.

(b) Settling Test [113]

This characterization works on the basis of the gravitational effects [110] on the settlements of the particles. Particles with greater electrostatic repulsions tend to have a

longer dispersion time. The dispersion time is also dependent on the pH of the colloid, as such, a range of pH levels has been used in the settling test. Extractions of the colloid suspension from the top and bottom volumes of the test tube were collected and heated at 160 °C to observe their ratio of the mass of total solid that remained.

2.5 Luminescence and Electrical Mechanisms of Nanocrystals

2.5.1 Luminescence Mechanisms

Bulk Silicon has an indirect bandgap characteristic. This trait has disabled its ability to emit visible light even in argon atmosphere. Ever since Canham reported on the red luminescence of porous Si quantum wire [34] and attributed the mechanism to quantum confinement effects of the nanostructure, various researches groups have reported many verifications [37, 38, 114-116], as well as challenges to this claim [35, 59, 117-120]. Although many groups have reported on the PL by Si nc [120-125], up to today, there is still no single conclusive mechanism of Si nc PL that all researchers conclude. However, after many works of characterizing the Si nc, there are some well-established mechanisms posed by the researchers. They are namely, 1) Quantum confinement of Si nc, 2) Presence of luminescence centers, 3) Special luminescence materials embedding the Si nc.

Basically, these 3 mechanisms can be summarized in Fig. 2.5. The first mechanism is attributed to the intrinsic effect of the Si nc. This theory believes that both

photoexcitation and photoemission occur inside the Si nc, and the passivation plays no part in the luminescence effects. The second mechanism explains the PL as a combinational effect of both the Si nc and the embedding material. In this theory, photoexcitation occurs in the Si nc, but the excited electrons and holes can tunnel through the Si nc interface and recombine in the embedding materials. The third mechanism believes that the Si nc has no part to play in the luminescence. Both the photoexcitation and photoemission occur in the embedding material.

Fig. 2.5 (a) Quantum confinement of Si nc where both photoexcitation and photoemission occur in Si nc. (b) Presence of luminescence centers where photoexcitation occurs in Si nc and photoemission occurs in embedding material. (c) Special luminescence materials embedding the Si nc where both photoexcitation and photoemission occur in the embedding material.

(a) Quantum Confinement of Si nc

In 1990, Canham first presented the visible PL property of porous Si at room temperature. Visible luminescence ranging from green to red in colour was soon reported

In the weak confinement limit, the crystal radius, a , is small, but a few times larger than the Bohr radius, a_B . Coulombic attractions and repulsions between electrons and holes are taken into considerations, other than the usual kinetic energy. Size reduction has a direct impact on the effective exciton binding energy, R_y^{eff} , as [36]

$$R_y^{\text{eff}} = R_y \left[1 + \left(1 - \frac{\mu}{M} \right) \left(\frac{a_B}{a} \right)^2 \right] \quad (2.2)$$

where R_y is the Ryberg energy, μ is the reduced mass and M is the combined effective mass of electron and hole. From Eqn 2.2, it can be determined that crystal size reduction causes the electrons and holes to be more confined. As a result, the effective exciton binding energy becomes greater. In this way, it will require greater absorption of photons' energy to emit luminescence. From many papers [37, 114, 127], it is widely shown that this luminescence experiences a blue shift from the infra-red to the visible red spectrum with increasing confinement.

In the case of strong confinement limit, the crystal radius, a , is small, and is a few times smaller than the Bohr radius, a_B . In this case, this crystal can be considered as a quantum dot due to the strong confinement. Coulombic attractions and repulsions between electrons and holes are no longer being taken into considerations as there are no correlated motion between electrons and holes as a result of the confinement. However, it is important to note that an electron and a hole are confined in space comparable with the

by Canham *et al.* and attributed the mechanism of this PL to the quantum confinement in the form of quantum wire when width ~ 3 nm [34]. The quantum confinement effect is, perhaps, the most established theory to explain the PL effect in Si nc [34, 37, 114, 126-133]. The fundamental idea of this form of mechanism revolved in the changes of energy band gap as a result of the size reduction of silicon particle [132]. Upon excitation and relaxation, radiative and non-radiative emissions are possible processes. A variation in bandgaps represents different emission energy. Fig. 2.6 illustrates this fundamental idea. With decreasing size, bandgap energy increases from E_g to $E_g 2$, illustrating the basic concept of quantum confinement.

Fig 2.6 (a) Basic bandgap of bulk silicon (b) Enlargement of bandgap due to quantum effect.

Quantum confinement theory evolves from quantum physics [134]. Using the Schrodinger equation with a Hamiltonian, theorists are capable of finding expression to relate the energy with the size of the crystal. This relationship is of much importance as this will show why Si nc is capable of emitting visible light in room temperature due the shift in energy which is correlated to the size of the nc. Theorists attempt to use the illustration of quantum dot to relate the quantum confinement effect. They subdivided the confinement into 2 limits: Weak confinement [125] and strong confinement [36].

extension of the exciton ground state in ideal infinite crystal. Therefore, independent treatment of electron and hole is not justifiable. In other words, considerations of the kinetic energy, coulomb potential and the confinement potential [22, 23] are critical. Hence, the elementary excitation in this quantum dot can be classified as an exciton with a notation “exciton in a quantum dot” [135, 136]. By using a two-particle Hamiltonian Schrodinger equation reduces the energy of the exciton to the form,

$$E_{\text{exciton}} = E_g + \left(\frac{a_b}{a}\right)^2 R_y \left[A_1 + \left(\frac{a}{a_b}\right) A_2 + \left(\frac{a}{a_b}\right)^2 A_3 + \dots \right] \quad (2.3)$$

This equation makes use of the effective mass approximation, as there is a correlation between the radius and the mass. Again, similar to the weak confinement limit, an increase in confinement results in an increase of exciton energy. However, the increment in intensity will be even greater than that in the weak confinement limit due to the contribution of the latter components in the equation.

Another common explanation of quantum confinement effects is through the surface to volume (S/V) ratio [37, 137]. Schuppler *et al.* [37] had shown that the size has a direct impact on the S/V ratio, which results in very different PL peaks [24]. Nonetheless, Sun *et al.* had also modeled the correlation between the S/V ratio with the change in energy band gap of the nanocrystalline silicon particles [137]:

$$\frac{\Delta E_g}{E_g} = \gamma_1 (C_1^{-m} - 1) + \gamma_2 (C_2^{-m} - 1) + \delta \quad (2.4)$$

where γ_i is the S/V ratio, C_i is the bond contraction, m is 1 for ionic crystal and 2 for semiconductor and, $\delta = [nV(R)]/[N^2v(d)]$ where n is the number of cluster, $V(R)$ is the valence energy band as a function of cluster radius, N^2 is the number of atoms in 1 cluster and $v(d)$ is the crystal field as a function of atomic radius.

In either methods of the explanation via quantum confinement effects, both show that as the size of the particles get smaller, the energy band gap will be widen. In this way, this mechanism will allow luminescence of nanocrystalline Si at room temperature although it is an indirect band gap material.

(b) Presence of Luminescence Centers

G. G. Qin and Y. Q. Jia proposed that the mechanism responsible for the luminescence of Si nc is a combination of photo-reactions of both the Si nc and the luminescence centers (LC) present in the embedding material [138]. These LCs are actually defects or impurities or both. They [138] proposed that the photoexcitation takes place in the Si nc and the excited electrons and holes gain sufficient energy to tunnel through the Si nc interfaces and recombines radiatively in the LCs [11, 46, 138-141]. Therefore, the wavelength of the photoemission will be the bandgap energy of the LCs [11, 46, 138-141].

They have also modeled the case of nanocrystals (nc) embedded in another material, stating that the rate of carriers captured in the LC ($1/\tau_{cp}$) as:

$$\frac{1}{\tau_{cp}} = 2 * N_{LC} \int_{R_{LC}}^{\infty} J_1 * \sigma_{cp} * L^2 dw \quad (2.5)$$

where N_{LC} is the concentration of LCs, R_{LC} is the radius of the LCs, J_1 is the tunneling current density from nc to LC, σ_{cp} is the cross section for capture of carriers by an LC and L is the diameter of the nc. From Eqn 2.5, the critical concentration amount of LCs providing the luminescence, $N_{LC(CRIT)}$, can be derived as:

$$\frac{1}{\tau_{cp}} = \frac{1}{\tau_{IN}} \quad (2.6)$$

where $1/\tau_{IN}$ is the rate of excited carriers in generated in Si nc.

From Eqn 2.6, the quantitative explanations of the different mechanisms for the PL can be given. When $N_{LC} > N_{LC(CRIT)}$ and $N_{nc} > N_{nc(CRIT)}$, the presence of LCs are the major mechanism. When $N_{LC} > N_{LC(CRIT)}$ and $N_{nc} < N_{nc(CRIT)}$, the PL is most probably due to the embedding material. When $N_{LC} < N_{LC(CRIT)}$ and $N_{nc} > N_{nc(CRIT)}$, quantum confinement in Si nc dominates.

There are many instances to show that LCs can be a PL emission mechanism instead of the quantum confinement effects. In the quantum confinement model, it is mainly the size dependency effect of Si nc on energy bandgap. It is predicted that when the size goes below 2 nm, the bandgap will increase exponentially [142, 143]. However, Schuppler *et al.* [37] has reported that the increment is much smaller than those proposed by quantum

confinement models [142, 143]. At the same time, Zacharias and Fauchet reported that GeO_2 and Ge ncs with radii varying over a wide range of 1.5 to 25 nm, the PL peak wavelength remained almost the same [144]. It is well known that oxidation of silicon will consume the silicon to develop SiO_2 . This will makes the remaining silicon smaller. If this applied to Si nc, it is expected to make the Si nc smaller. By quantum confinement model (See Eqns 2.4 and 2.5), the PL should exhibit a blue-shift. However, Mizuno *et al.* reported that when porous silicon was allowed to oxidized in room ambient, the PL has a red-shift instead [145]. Mizuno has also reported that the lifetime of porous silicon kept in vaccum with PL peak energy at ~ 2.7 eV was $0.3 \mu\text{s}$ [145]. However, reports [55, 146] of oxidized Si ncs with PL peak energy ~ 2.7 eV showed that the lifetime of this form is 1-10 μs , which presents a great difference with porous silicon in vaccum. This further suggests that radiative recombination may not be occurring in the Si ncs.

(c) Special Luminescence Materials Embedding Si nc

The third kind of mechanism tries to relate the luminescence to the materials or impurities embedding the Si ncs. The materials and impurities surrounding the Si ncs possess a bandgap themselves, they are also capable of the processes of photoexcitation and photoemission. Radiative recombination can also occur in these materials [39, 42, 43, 58, 147]. Therefore, many researchers raise the doubt on whether the Si nc is actually causing the luminescence. Many other luminescence centers revolving the embedding the Si nc are proposed such as 1) siloxene [42], 2) hydrogenated amorphous silicon (a-Si:H) [39] or hydride species (SiH_x) or polysilanes [43, 117], and 3) Non-Bridging Oxide Hole Centers (NBOHC) [58].

Siloxene luminescence mechanism is first proposed by Brandt *et al.* [42] for the PL in Porous Silicon (P-Si) involving luminescence from Si-O-H complexes that comprise siloxene ($\text{Si}_6\text{O}_3\text{H}_6$). These materials are believed to consist structures of linear chains or sixfold rings of Si interconnected by oxygen or Si layers with alternating OH or H terminations. These siloxene should exhibit visible PL in a similar range to P-Si [147, 148]. In the siloxene model [42, 145], the isolated Si_6 rings were suggested as the source of the PL in P-Si. Calculations have been reported in support of this PL model [147, 148]. Despite the many similarities [42, 149], there are some significant drawbacks. Hydrogen in siloxene will desorb below 500 °C, therefore high temperature oxidation will result in SiO_x type of structure, and not siloxene compound. Hence, siloxene luminescence mechanism is insufficient to explain PL in P-Si.

Hydride species (SiH_x), polysilanes and hydrogenated amorphous silicon are possible structures arising from P-Si. Wolford *et al.* [39] reported room temperature PL resulting from a-Si:H. They reported a 5 K luminescence in the range of 1.3–2.05 eV. Blue shifting in the PL is exhibited as hydrogen content increases. PL of 1.8–2.0 eV is reported with the highest content of hydrogen. It is suggested that the hydrogen complexes [SiH , SiH_2 , SiH_3 , or $(\text{SiH}_2)_n$] were the sources for the room temperature luminescence. Monohydrides [150] and polysilane [151] have both been demonstrated to possess a wider bandgap as in Si. They are capable of emitting visible luminescence. Some similarities can be observed between P-Si and hydrogen complexes: 1) P-Si [20] exhibits the same 1.7 eV emission range as a-Si:H [39], 2) P-Si [31] and hydrides [39] experience a red-shift when there is a reduction in hydrogen, and 3) Other similarities like recombination lifetimes, E-field

quenching, and excitation dependence are also reported [57]. However, the drawbacks are also similar to siloxene. Hydrides/polysilane and a-Si:H faced the most serious problem of oxidation above 700°C as this temperature is high enough to desorb the hydrides and crystallize the a-Si:H [152]. Therefore, hydrides/polysilane and a-Si:H mechanisms are also insufficient to explain the luminescence after oxidation at high temperature.

Another suggestion for the mechanism of PL is Non-Bridging Oxide Hole Centers (NBOHC). It is simply an additional hole present in the oxide. Munekuni *et. al.* has summarized that there are 3 kinds of NBOHCs [153]. The first NBOHC is the Si-O, which exhibits a lower energy PL (between infrared to red) with low quantum efficiency. This NBOHC causes little shift in PL with heat treatment. The second NBOHC is the Si-O ... H-O. This form of NBOHC is stabilized with a hydrogen bond and is commonly seen in silica containing a high concentration of hydroxyls or hydrides. However, this NBOHC can only exist at a temperature lesser than 350 °C as higher temperature will vaporize the H-O bonds. It was shown that this form of NBOHC with increasing OH content will result in a blueshift accompanied with an increase in quantum efficiency [153-155]. Similarly, for the reverse, it is also true. With a decrease in H-O bonds, redshift will be exhibited and there will also be a drop in quantum efficiency [43]. The third NBOHC is likely caused by the strain of bonding at interfaces due to different material configuration and density [9, 155]. The third NBOHC is stable at high temperature (as high as 800 °C). It does not exhibit any PL shift or shape change during high temperature, as compared to PL at room temperature. Emission model [153] based on NBOHC has been proposed to explain red PL in freshly made and oxidized P-Si. It is proposed that this type of center

exists at or near the Si/SiO_x interface in a not fully relaxed continuous random oxide network. Both the interfacial strain and chemistry need to be considered for the emission energy [154]. It is also pointed out the presence of Si nc in the system is important since the creation of NBOHC may occur in the presence of interfacial strain, which is expected to increase with decreasing size.

2.5.2 Charge Trapping Mechanisms

(a) Single Electron Tunneling

In a quantum sphere, when the electron mean-free-path exceeds the dimension of the device structure, quantum mechanisms will dominate the physical natures of the devices. At this scale, electron transport is governed by tunneling. The quantum confinement effects related to the electron wave nature lead to redefinitions of capacitance and electrical forming. Single electron tunneling [1] is perhaps the most established tunneling and charge trapping mechanism being proposed for nanocrystals so far. It is hypothesized that Si ncs are quantum dots which occur like discrete islands in the vast matrix. A quantum dot is believed to be a storage place for a single charge [14, 15, 156]. Single electron must gain sufficient energy in order to tunnel from the negative electrode to these islands or from the islands to the positive electrode. Charges can be stored inside these discrete islands. The energy, E , acquired by the tunneling electrons is the summation of coulomb (E_c) and thermal (E_t) energies which can be summaries as,

$$E = E_c + E_t \quad (2.7)$$

The thermal energy is proportional to the multiplication of Boltzman's constant and the absolute temperature regardless of electrons interaction. However, the coulombic forces involve single electron energy across the barriers. Likharev *et. al.* [157, 158] has done extensive and high precision studies on the coulomb energy of quantum dots at low temperature (>77 K). The low temperature is critical for this study as thermal energy can cause fluctuations in the current readings. Likharev reported that this coulomb energy is discrete over different applied voltages and give rise to coulomb staircase as a result of coulomb blockage. This energy can be expressed as

$$E_c = \frac{q^2}{2C} \quad (2.8)$$

As a result an increase in capacitance will be observed with a corresponding building of charges. Thus, if there is a sweep in the voltage, the build up of the induced charges will be compensated at periodic intervals by the tunneling of discrete charges onto the nanocrystals. This will result in a competition between a continuously induced charge and a discrete compensation which is known as Coulomb oscillation. This oscillation can be observed in a measurement of the current [6, 159-163]. One typical I-V characteristic showing the Coulombic staircases is presented in Fig. 2.7.

Fig. 2.7. Coulomb staircases in current-voltage characteristics. [162]

2.6 Applications of Silicon Nanocrystals

As a result of continual contribution by the researchers worldwide, Si nc applications have expanded extensively over its uses in optoelectronics which include different kind of Light Emitting Diodes (LEDs) and lasers. At the same time, another important application is evolving from Si nc, that is its ability as memory devices [5]. The charging and discharging characteristics of Si nc embedded in SiO₂ have been extensively studied by researchers [161, 164-166]. It has been shown that the single electron charging characteristics of Si nc give rise to superior switching speed as compared to electronic switching. In fact, researchers have also looked into the possibilities of blending Si nc optoelectronic properties into its memory devices – optoelectronic memory devices (in short photonics IC). Fig. 2.8 illustrates the functional applications of Si nc.

Fig. 2.8 Functional applications of Silicon nanocrystals

2.6.1 Optoelectronic Applications

Optoelectronic applications have risen in importance due to the high speed and low loss that they can offer. Coupled with the increased use of optical fibers in communications, it paves an indispensable path for optoelectronic devices. As optoelectronics revolve around the use of light, a light source is essential for these devices. The two most common types of light sources in the industry are LEDs and Lasers.

(a) LEDs

LEDs have been vastly employed in applications like automotive lightings, LEDs signs and signals, mobile digital electronics and photo sensors. Electroluminescence (EL) of Si nc has been reported [12, 13, 40, 167] following the reports of its room temperature photoluminescence [34]. This characteristic of Si nc provides another alternative type for LEDs. Like any other LEDs, the Si nc LEDs have similar structures. Basically, there are 2 main types of structure [56]: 1) Schottky type and 2) Vertical PIN type. Fig. 2.9 illustrates the structure of these 2 types. Of these 2 structures, the latter is a better preference as the highly doped regions provide for the sources of electrons and holes to facilitate higher quantum efficiency [23].

The first Si nc LED originated from porous silicon [40]. Though it is easy to construct, it poses many problems including: 1) Low external quantum efficiency ($\eta_{\text{ext}} \leq 10^{-4}$), 2) High threshold voltage ($V_{\text{th}} \geq 10$ V), and 3) High current density ($J_{\text{th}} \geq 10$ mA/cm²) for detectable level of electroluminescence (EL). However, the main problem of this type of LED is instability. The quantum efficiency of this LED drops drastically after 1 hour of use [22]. This can be traced to the breaking of Si-H bonds at the surface of the Si ncs due the heat generated by the applied current. Upon breakage, the dangling bond concentration increases and results in the quenching of the EL. This process is irreversible and moreover, further high temperature (~ 1000 °C) fabrication processes, like oxidation and activation annealing, makes this form of LED impossible to integrate into the standard microelectronic process.

Fig. 2.9 (a) Schottky type of Si nc LED (b) Vertical PIN Type of Si nc LED

To curb this problem, passivation of the Si ncs LEDs is introduced. Oxygen [8, 10] and nitrogen [10] are employed to rid the dangling bonds. L. Tsybeskov [10] has reported

that there is no degradation in the EL during 1 month of pulsed operation under oxygen terminated ("O" terminated) Si ncs. This stability of "O" terminated Si ncs formed the foundation for the future use of Si ncs and after this report, many works have been done on this basis [8, 10, 12, 13, 37].

(b) Lasers

Up to date, the nanocrystal-based lasers have not been greatly explored. The laser application in Si nc has been shelved due to the low quantum efficiency of Si nc EL [56]. However recently, breakthrough in the efficiency of Si laser [2, 3] has been reported and this has opened a new avenue for Si nc application. Other than Si laser, rare-Earth doped Si nc laser with high efficiency has been reported. The first rare-Earth doped Si nc laser was reported by T. Kimura *et al.* [168]. This opened an alternative avenue to Erbium-based optoelectronics as its Er^{3+} emission wavelength at $1.54\ \mu\text{m}$ is the most optimal wavelength for today semiconductor optics fibres. Coupled with absence of intermediate states between the $^4\text{I}_{13/2}$ and $^4\text{I}_{15/2}$ manifolds, this structure makes population inversion possible [169]. Therefore, Er doped Si ncs is very promising for a wide ranges of devices such as LEDs, optical amplifiers and even lasers.

Currently, most of the Er doped Si nc lasers are fabricated by 2 fundamental steps [169-172]: 1) formation of Si nc in SiO_2 matrix, followed by 2) implantation of Er ions. However, this method has caused much confusion over the mechanism of the luminescence at $1.54\ \mu\text{m}$ as researchers are unsure whether it is due the Er ions inside the Si nc or in the SiO_2 matrix which cause the luminescence. Dorofeev *et al* [172] has suggested using sol-gel to spin coat Er with silicate-based SOG. But, it is followed by an

additional step of implantation of Si ions to form the Si ncs. Therefore, the same problem is encountered. In this sense, improvement in the fabrication method has to be done.

Many theorists have provided different view points over the luminescence of Er doped SiO₂ matrix with Si ncs. Fujii *et al.* [173] has discovered that as the doping concentration of Er increases, the luminescence of Si nc wavelength suffers a quench in intensity whereas, the Er wavelength at 1.54 μm marks an increase in intensity. This has led to many explanations ever since. Qin *et al.* [138] has suggested that the mechanism of this luminescence is due to the excitons in the Si nc tunneling through the energy barrier to the luminescence centers in the Er ions embedded into the SiO₂ matrix. Chen *et al.* [174] has suggested that it is the radiative emission of the Si ncs which enables Er absorption and subsequent emission at 1.54 μm . Despite the many diverse proposals for the mechanisms over the luminescence of this structure, there has been no consensus reached among all the groups for the unified mechanism. However, it is often agreed by many groups [138, 170, 171, 173, 174] that the excitation occurs in Si ncs and there is a transfer of energy from the Si ncs to the Er in the SiO₂ matrix.

2.6.2 Electrical Applications

(a) Memory Devices

Since Tiwari *et al.* [4] first proposed the idea of integrating Si ncs into the memory devices, Si nc based memory devices have attracted much attention [5, 163, 175, 176]. It is a memory device that utilizes direct tunneling into three-dimensionally confined nanocrystal to produce the bistability in the conduction of a transistor channel [156, 176]. It is fast with quasi-non volatile characteristics and can operate at room temperature.

Furthermore, it can be fabricated with minimum perturbation of conventional Si technology. Motorola Inc. has demonstrated what it claims as the world first 4-Mbit memory device based on silicon nanocrystals on April 2003. Motorola has developed techniques designed to help simplify the manufacturing of these memories. Using traditional deposition equipment, researchers at Motorola DigitalDNA Laboratories, deposited silicon nanocrystals resembling 50-angstrom diameter spheres between two layers of oxide. The silicon spheres are engineered to hold and prevent lateral movement of charge to other isolated nanocrystals. This is expected to increase reliability and scalability because a single oxide defect does not lead to complete charge loss as in a conventional floating gate nonvolatile memory. Fig. 2.10 illustrates a basic unit of a transistor operating with nanocrystals embedded in the gate oxide. Operations such as Write, Store and Erase are carried out in the nanocrystals. In this way, this device can be seen as flash memory, just like an Electrically Erasable Programmable Read Only Memory (EEPROM). Controls of these operations are done mainly by the thickness of the control oxide, thickness of the tunnel oxide, number of nanocrystals and the applied voltage.

Fig 2.10 (a) A schematic cross section and band diagram during (b) injection, (c) storage, and (d) removal of an electron from a nanocrystal.

This form of memory has created many motivations for scientists and researchers to dwell into the tunneling mechanisms of electrons from the inversion regions into the Si ncs [5, 19, 161, 177]. These motivations are further supported by Joe Mogab, Vice President, Advanced Products Research and Development Lab, Motorola's Semiconductor Products Sector who has even mentioned that "Silicon nanocrystal-based memories have the potential to be an evolutionary replacement for conventional flash memory, which is widely used in automobiles, appliances, wireless devices and industrial controls."

According to Motorola, the fully functional 4-Mbit test chip represents a major milestone in the search for successors to floating gate-based flash memories, which many believe will not continue to scale to smaller geometries. These advances could lead to memories that are smaller, more reliable and more energy-efficient than floating gate-based flash memories. However, the charge trapping and conduction mechanisms are still in debate. Many attributed the charge trapping mechanism to single electron tunneling into the nanocrystals. Nonetheless, some attributed it to the deep traps at the interfaces of the Si nc and matrix. As for conduction mechanisms, they are even more vigorously argued.

2.6.3 Optoelectronic Memory Applications

Optoelectronic memory devices are evolutionary devices in attempt to replace present electrically-based integrated chips by light-based integrated chips [167, 178]. LNL Technologies Inc. says the goal is for these optoelectronic devices to replace bulky

telecommunications gear with size of a quarter that combine lasers, routers, receivers and other devices commonly used in fiber-optic networks. Simple optical chips already are on the market, but aren't nearly as sophisticated as the chips inside a personal computer, with processors that contain billions of transistors.

Chapter 3: Synthesis, Characterization and Oxidation Effects of Solid-State Reaction Si nanocrystals

3.1 Introduction

Silicon nanocrystals (Si nc) has exhibited its potential in electronic [4-6] and optical applications [2, 3, 7]. Many methods have been reported to generate Si nc in a SiO₂ matrix. They include ion-implantation [51-53], co-sputtering [4] and plasma deposition [5]. However, to study the characteristics of the Si nc, the amount of SiO₂ must be minimized. Mechanical milling has been widely used to prepare nanocrystalline metallic materials and alloys [6]. It had also been reported that mechanical milling is able to create crystalline-to-nanocrystalline Si [7]. This technique provides a medium to study nanocrystalline Si in its own form. It is different from the commonly employed ion implantation and plasma deposition methods where the nanocrystalline Si are embedded in a layer of oxide [3-4].

Although the mechanical milling method allows for independently produced Si nc, there are some associated problems and challenges. Firstly, the reduction of size by high energy ball milling requires random fracturing as discussed in Chapter 2. This often results in dislocations. The study of these dislocations will be covered in detail later in this chapter. Furthermore, current reported mechanical milling technique involves high energy milling in metallic vials which results in huge amount of metallic impurities and amorphous Si [7]. In this chapter, the author details the mechanical milling of Si powder

using agate (SiO_2 -based) vials to generate nanometric SSR Si particles. The structural and physical properties of these SSR Si particles will also be examined in details. Furthermore, the author also reports on the oxidation effect on these SSR Si nc which can reduce the size of the Si nc to less than 10 nm.

3.2 Synthesis of Solid-State Reaction Si Nanocrystals

Lu *et al.* [16] summarized the mechanical alloying (or SSR) process into four different stages. They are the initial, immediate, final and completion stages. At the initial stage, powders in the bowl are flattened as a result of the compressive force by the collisions of the balls. Micro-forging leads to deformation in the shapes of individual particle, or a cluster of particles impacted repeatedly with high kinetic energy. However, that there is no net change in the mass of this powder at this stage. At the intermediate stage, cold welding becomes significant. The intimate mixture of the powder constituents decreases the diffusion distance to nanometric range. Fracturing and cold welding become the two major processes at this stage. Although some dissolution occur, the chemical composition of the alloyed powder is still inhomogeneous. At the final stage, considerable refinement and reduction in particle size appear evident. The microstructure of the particle appears to be more homogeneous in microscopic scale than the two earlier stages. True alloys may have been formed at this stage. At the completion stage, the powder particles possess an extremely deformed metastable structure. The lamellae are no longer resolvable by optical microscopy. Further milling beyond this stage cannot physically improve the dispersoid distribution. Real alloy with composition close to the starting constituents is

therefore formed. In our research, planetary ball milling has been employed to produce nanometric Si powder.

Commercial crystalline Si powder purchased from Alfa Aesar with nominal purity of 99.9988% and average particle sizes between 1-20 μm was used as the starting material. Mechanical milling was performed in a Fritsch Pulverisette planetary mill at ambient temperature. Agate balls and vials were used in the mechanical milling. The weight ratio of the balls and Si powder is 20:1 with a milling speed of 200 rpm. Transfer of Si powder into the vials were carried out and sealed in N_2 box. Extraction of Si powder was also done in N_2 box. This is to minimize the complications arise from the interaction with surrounding oxygen and moisture. Different weight of Si powder was extracted at 2, 20, 40, 60, 80, 100 and 120 hrs of milling respectively. For every extraction, the weight ratio of the balls and Si powder was maintained at a ratio of 20:1. These SSR Si nc were characterized under Shimadzu XRD-600 x-ray diffractometer, JEM-2101F high resolution transmission electron microscopic (HRTEM), Raman spectroscopy measurement and Perkin-Elmer 7 differential thermal analysis (DTA). Oxidation of the SSR Si nc was carried out at 900°C from 15 mins to 8 hours in O_2 ambient. The furnace used was Lindberg Furnace.

3.3 X-Ray Diffractometry and Transmission Electron Microscopy

There are many methods used to characterize the microstructure of nano-materials. They include XRD, TEM, FTIR, Raman spectroscopy, etc. However, among these techniques,

the two most powerful ones are the X-ray diffractometry and transmission electron microscopy. These two methods allow for in-depth investigations into the lattice information which can later be translated into other structural results like d-spacing, grain size, lattice stress, dislocations and as well as defects present.

3.3.1 X-Ray Diffractometry (XRD)

X-ray diffraction is a versatile, non-destructive analytical technique for identification and quantitative determination of the various crystalline compounds, known as 'phases', present in solid materials and powders. Commonly, XRD method is applied to measure the size and d-spacing of a crystalline structure [179]. The widths of the peaks in a particular pattern provide an indication of the average crystallite size. Large crystallites give rise to sharp peaks, while the peak width increases as crystallite size reduces. Another piece of information that can be extracted is the micro-strain. Micro-strain can be indicated by a peak shift that occurs as a result of variations in d-spacing. However, the relationship between broadening and diffraction angle 2-theta is different from that of crystallite size effects, making it possible to differentiate between the two phenomena. To understand the concepts of XRD, the most fundamental and important law is the Bragg's Law. Subsequent equations involving the grain size and lattice strain are derived from this law.

3.3.1.1 Lattice Planes and Bragg's Law

X-rays primarily interact with electrons in atoms. If the wavelength of these scattered x-rays do not change (meaning that x-ray photons do not lose any energy), the process is

called elastic scattering (Thompson Scattering) in that only momentum has been transferred in the scattering process. These are the x-rays that are measured in diffraction experiments, since the scattered x-rays carry information about the electron distribution in materials. On the other hand, in the inelastic scattering process (Compton Scattering), x-rays transfer some of their energy to the electrons and the scattered x-rays will have different wavelength from the incident x-rays.

The peaks in a x-ray diffraction pattern are directly related to the atomic distances. In a bulk crystal, the atomic arrangement is capable of presenting different lattice planes as observed in Fig 1a). For a given set of lattice plane with an inter-plane distance of d , the condition for a diffraction (peak) to occur can be simply written as $2d\sin\theta = n\lambda$ which is known as the Bragg's law. In the equation, λ is the wavelength of the x-ray, θ is the scattering angle, and n is an integer representing the order of the diffraction peak. Fig. 3.1b) illustrates the schematics for obtaining the Bragg's Law. The Bragg's Law is one of most important laws used for interpreting x-ray diffraction data.

Fig. 3.1a) Illustration of lattice planes and b) schematics for obtaining the Bragg's Law.

The Shimadzu XRD-600 x-ray diffractometer as shown in Fig 3.2 in the School of Materials Science and Engineering is employed for the experiments. The Shimadzu XRD-6000 system was employed for the powder samples. The X-ray radiation source used was Cu K α , obtained at 30 kV, 20 mA with a scanning speed of 2 °/min at a step of 0.02°. The data measured are in reflection mode with solid powder samples.

Fig. 3.2 Shimadzu XRD-600 x-ray diffractometer in School of Materials Science and Engineering.

Fig 3.3 shows a powder XRD scan for a Si sample as a plot of scattering intensity vs. the scattering angle 2θ . The peak positions, intensities, widths and shapes all provide important information about the structure of the material.

Fig 3.3 Powder XRD scan for a Si sample as a plot of scattering intensity vs. the scattering angle 2θ .

3.3.1.2 Stress Measurement

Structural and stress properties in materials can be determined from precision lattice constant measurements. For polycrystalline samples high resolution powder diffraction measurements generally will provide adequate accuracy for stress evaluation. The interpretation of stress measurement data is complicated and model dependent. Normally, a shift in 2θ values signifies a change in stress or strain incurred on the lattice. It represents a change in d-spacing of a specific lattice plane. Using the differentiation of Bragg's law, the relationship between the change in d spacing and 2θ can be written as [179]:

$$\Delta 2\theta = \frac{-2\Delta d \tan \theta}{d} \quad (3.1)$$

From this equation, a shift to higher values of d symbolized more stress is induced on the structure.

3.3.1.3 Grain Size Measurement

The crystal size can be determined by the Scherrer formula [180]:

$$t = \frac{K\lambda}{\beta \cos(2\theta)} \quad (3.2)$$

where t is the thickness of crystal $\perp$ to diffraction plane, K is a constant (normally the value is 0.9) and β is the full width at half maximum (FWHM) of the diffraction peak.

From Eqn 3.2, it can be observed that t will be larger as β becomes smaller. However, for the instrument, there is always an upper limitation of FWHM. Therefore this instrument error is accounted as

$$\beta = \sqrt{\beta_{meas} - \beta_{inst}} \quad (3.3)$$

where β_{meas} is the measured FWHM and β_{inst} is the instrument upper limit FWHM. Other than the instrumental error, there is another source of error, that is the the X-ray induced lattice broadening. X-ray carries energy and can be imparted onto the lattices. This must also be accounted for in the calculation of the grain size. Using Eqn. 3.2, 3.3 and the X-ray broadening effect, the following expression can be obtained [16],

$$\sqrt{\beta_{meas} - \beta_{inst}} \cos \theta = C \sin \theta + \frac{K\lambda}{t} \quad (3.4)$$

where C is a constant. Using a straight line equation ($y = mx + c$) where $y = (\beta_{meas} - \beta_{inst})^{0.5} * \cos \theta$ and $x = \sin \theta$, it can derived t from the y-intersect. Fig 3.4 illustrated the concept of finding t using Eqn. 3.4.

Fig 3.4 Concept of finding t using eqn. (4).

3.3.2 Transmission Electron Microscopy (TEM)

In this kind of microscope [181], electrons are speeded up in a vacuum until their wavelength is extremely short, only one hundred-thousandth that of white light. Beams of these fast-moving electrons are focused on a cell sample and are absorbed or scattered in sample to form an image on an electron-sensitive photographic plate. If pushed to the

limit, electron microscopes can make it possible to view objects as small as the diameter of an atom. Most electron microscopes used to study materials down to a resolution of about 10 angstrom. In effect, it can magnify objects up to 1 million times.

There are 3 main modes of TEM operations, namely the bright field, dark field and image modes. TEM images allow the atomic structure to be captured and allow visual analysis. TEM employs the use of electrons transmitted through the sample to create the image, therefore the sample must be very thin, typically 50 - 100 nm in thickness. Fig. 3.5 shows the JEM-2010 TEM in the School of Materials Science and Engineering used in this analysis.

Fig. 3.5 JEM-2010 TEM in School of Materials Science and Engineering.

3.3.2.1 Analysis of TEM Images

Other than the real images, the diffraction also plays a major role in the TEM analysis [182]. The diffractions, which mathematically correspond to a Fourier transform of aperture function, result in spots (reflections) at well-defined positions [182]. Each set of parallel lattice planes is represented by spots which have a distance of $1/d$ (d : interplanar

spacing) from the origin and which are perpendicular to the reflecting set of lattice plane. Fig. 3.6 illustrates the mapping of a real image into its diffraction patterns. The basic lattice planes of the two-dimensional lattice shown below are transformed into sets of spots. The inter-spot distance is an inverse function of distance (d_1 , d_2 , etc). The complete set of all possible reflections of a crystal constitutes its reciprocal lattice [182].

Fig. 3.6 Mapping of a real image into its diffraction patterns.

3.4 Physical and Microstructural Characterizations

Figure 3.7a) XRD spectra of Si nc with milling hours from 2 to 100 hours and b) the average grain size for different milling hours derived from Scherrer's equation.

Fig. 3.7 shows a) the XRD spectra of Si nc with milling hours from 2 to 80 hours and b) the average grain size for different milling hours derived from Scherrer's equation. The spectra reveal broadening of XRD peaks from 0 to 20 hours. Beyond 20 hours, the broadening process is ceased. Additional peak at 26.8° appears when milling hours go beyond 20 hrs. This is attributed to the debris from the agate vials and balls. From Scherrer's equation, taking into account of the instrumental errors and x-ray induced broadening, the average grain size of the Si nc can be calculated. Fig. 3.7b) reveals that the smallest size achievable is ~ 10 nm which is observed at 20 hours of milling. The size starts to increase with further increasing milling hours beyond 20 hours and saturates at about 120 hours of milling. This is well ascribed to the process of cold-welding [6]. This phenomenon is also commonly observed in other ball milled materials [6]. Fig. 3.8 shows the TEM image of the Si nc generated by 20 hours of milling. The size showed by TEM image reveals similar size as featured in Fig 3.7b). This verified the calculation using the Scherrer's equation. To further confirm the size range, HRTEM images are used to find out the grain distribution for 20 hours of milling. Fig. 3.9 shows the grain diameter distribution of 35 grains taken from HRTEM images. It can be observed that this distribution is positively skewed and the grain diameter mean and mode occur in the range of 6 to 10 nm. Though the grain size is in nanometric range, it is observed that the Si grains are closely conglomerated together and can form huge particle sizes. This is largely due to the random attrition of the ball milling system.

Fig. 3.8 TEM image of the Si nc generated by 20 hours of milling

Fig. 3.9 Grain diameter distribution of 35 grains taken from HRTEM images

Fig. 3.10 DTA for the different milling hours.

Differential thermal analysis was performed to study the thermal stability of the SSR Si nc for possible endothermic and exothermic behavior. It is reported that amorphous Si crystallizes at 660 °C [7]. Fig. 3.10 shows the DTA for the different milling hours. It reveals no visible endothermic peak at 660 °C. At the same time, Raman scattering spectroscopy also reveals no prominent shifts in the 512 cm^{-1} Si peak. This confirms the absence of the amorphous Si phase in the milled Si nc.

3.5 Applied Stress, Residual Stress and TEM Analysis of Relaxed Lattice of Solid-State Reaction Si Nanocrystals

3.5.1 Introduction to Lattice Analysis of Solid-State Reaction Si nc

It has been updated that, structural defects and stress are induced during the SSR [16]. This is the result of fracturing and tearing of bulk materials into nanocrystalline and amorphous particles [16] during the milling process. As a result, these defects often

reside in the crystals as dislocations [16, 183]. However, when dislocations are subjected to external energies like heat treatment or lattice relaxation, they can be recovered [183]. The identification of the dislocations and its characteristics will provide possible explanations to their electrical and emission properties which are critical application development. As mentioned by Lu *et al.* [16] and Hull *et al.* [183], for further SSR, shear stress are capable of fracturing the crystals. Also, during the normal stress is capable of compressing the lattices resulting in residual stress and dislocations. Upon annealing, this normal stress is often released with lattice relaxation, and recrystallization will occur to bind the crystals. Many works [184, 185] have reported the spin lattice relaxation of SSR nanocrystals for different hours of milling and annealing temperatures. However, the correlation between the relaxation of the applied stress present in the Si nc and grain boundary formation has not been fully understood. The microstructural defects inside and around the interface of ion-implantation nucleated Si nc have been reported through high resolution transmission electron microscopy (HRTEM) [186]. On the other hand, SSR Si nc differs from ion-implanted Si nc as the earlier is synthesized by fracturing while the latter is by nucleation. It is inevitable that the microstructural defects inside and around the interface of these two forms of Si nc will be different. Numerous structural defects like dislocations, vacancies and faults are often reported in SSR Si nc. In addition, a group of high symmetrical structural defects, called twins, are also found in SSR crystals [183]. Past reports often discussed this form of defects in large crystal [9, 183] ($> 10 \mu\text{m}$), so far, little research has been done to investigate the nanograin of SSR materials in the nanoscale range due to the difficulties in capturing high resolution HRTEM images. In

this section, the structural evolution of the Si nc in terms of the hours left in room ambient (300 K) is studied by using HRTEM and XRD characterizations.

3.5.2 Sample Preparation and Experiments for the Study of TEM Images and Lattice Stress

For HRTEM characterization, 0.1 g of Si nc was allowed to dispersed and homogenized in 60 ml of ethanol. This suspension was centrifuged in Profuge 14D at 3000 rpm for 90 mins. The yellowish-orange supernatant was then extracted for HRTEM. This process would remove large agglomeration (> 40 nm diameter) that might be a result of compression during the SSR [187]. HRTEM images were captured using JEM 2010F operating at 200 kV acceleration equipped with Gatan imaging filter (GIF). In order to obtain reliable prevalence distribution of the grain boundaries, over 25 Si nanograins and over 40 grain boundary facets were recorded to carry out the statistical analysis and some of these HRTEM images are shown in the Appendix.

3.5.3 Lattice Relaxation Induced Coalescence of Solid-State Reaction Si nc

Fig. 3.11 shows the HRTEM image of a single Si crystal synthesized by SSR method with 20 hrs of milling and left at room temperature for 2 months. The size of this crystal is approximately 8 nm. This is the common observed size distribution as reported in Section 3.4. There is no defect observed in the lattice planes which is consistent with the findings of Wang *et al.* [186] despite of the different synthesis method used. Wang *et al.*

[186] has attributed this to possible reasons of high surface energy incompatibility with high energy defects and lower applied strain. It has been reported recently that twins are observed in nanocrystals [186, 188, 189]. For a cubic structure such as Si or diamond, it is well-known that the $\{111\}$ twinning angle between two adjacent twin variants is 70.53° [190, 191]. Fig. 3.12 shows the HRTEM of a typical multiple deformation twins formation in a (~ 30 nm) Si crystal after SSR with 20 hrs of milling and left at room temperature for 2 months. The inset reveals the FFT image of the Si nc. The HRTEM reveals similar characteristics in our SSR Si nc which indicates the formation of a $\Sigma=3$ twin (first order twins) at the continuous grain boundary of the $\{111\}$ planes as that reported in [186]. Many other HRTEM images ($\sim 70\%$ of the Si nc) in this investigation also reveals the $\Sigma=3$ twins and is consistent with Wang *et al.* [186] findings. Out of all these $\Sigma=3$ twins, it is recorded that 70% are deformation twins and the remaining 30% are annealing twins. Deformation twinning is a process in which a region of a crystal undergoes a homogeneous shear that produces the original crystal structure in a new orientation. In the simplest cases, this results in the atoms of the original crystal ("parent") and those of the product crystal ("twin") being mirror images of each other by reflection in a compositional plane as illustrated in sections 1 to 5 of Fig. 3.12. Fig. 3.13 illustrates the schematic arrangement of atoms in a twin related structure where x-y is the trace of the twin compositional plane. The open circles represent the positions of the atoms before twinning and the black circles are the position after the twinning. The atoms above the compositional plane x-y are mirror images of the atoms below the plane. The homogeneous shear of the lattice parallel to the compositional plane is denoted by the arrows. Deformation twinning can be induced by plastic deformation and is particularly

important in body-center cubic and close-packed hexagonal metals and many non-metallic crystals. Deformation twins have also been vastly reported for face-center cubic structure using high energy milling. It is prominent that the grain boundaries of the twins are at $\{111\}$ due to its dense atomic packing [192]. It is observed that there are numerous twins forming in the Si crystal. However, these twins do not resemble the coalescence of nanograins, but rather, the shearing of a single crystal.

From the illustration in Fig. 3.13, further analysis can be made on the multiple twins structure as featured in Fig. 3.12. It is observed from sections 1 to 5 that stacking faults occur as the twin boundary (TB) propagates from the edge in the $[113]$ direction into the core of the Si crystal. These twins with TB propagating from the edge of the crystal have more uniform atomic planes within 2 TBs. It is observed that section 2 has 5 defined atomic planes and section 3 has 4 defined atomic planes. This is unlike the twins observed from section 6 to 8 where many of the TB ends within the crystal with irregular amount of atomic planes within 2 TBs. For the uniform number of atomic planes from sections 1 to 5, this is probably attributed to the shear force during the SSR that causes dislocation $\{111\}$ sliding plane and allows ordered shearing in this plane. However, for sections 6 to 9, it can be seen that the twins occur in the core of the Si crystals. This is probably due to the random bombardment of high energy ball milling which results in non-homogenized shearing.

Beside this form of random deformation twins, the most interesting phenomena is the formation of highly ordered deformation twins without any heat treatment. Fig. 3.14

shows the (a) HRTEM of another typical $\Sigma=3$ twin and (b) enlargement of Fig. 3.14(a) along the [011] direction for samples at milling condition of 20 hours and left at room temperature for 2 months. Interestingly, this high energy grain-boundary twinning process takes place with no heat treatment (thermal energy). Fig. 3.14(b) reveals five self-arranged nanograins in an orderly way and coalescence by $\{111\}$ twinning. It can be observed that nanograin 2 acts as the seed nanocrystal that connects nanograin 1 to the other nanograins. It is further observed that nanograin 3 and 5 are connected in parallel by nanograin 4, with 5 atomic planes, forming poly-synthetic twins. In cases of high energy SSR, deformation twins of all orders as observed in Fig. 3.12 should be prominent due to the high shear stress, random shearing and compression during the synthesis process. However, it is interesting to note that all the nanograins are $\Sigma=3$ twins, and no other higher order twins are observed. Furthermore, the formation of these multiple twins are of ordered coalescence which resembles the highly ordered structure of annealing twins [186]. This suggests that these observed deformation twins probably undergo some transformational changes caused by input of external energy. Often, this form of highly ordered twins is created by subsequent annealing. However, in this case, no additional heat is being applied to this Si nc. It is interesting to find out that 30% of the $\Sigma=3$ twins in this study are of this form. The twins might be formed as a result of lattice relaxation and high surface energy which will be discussed later. Unlike the other 70% of the $\Sigma=3$ twins resume deformation twins in Fig. 3.12, ordered coalescence of nanograins with complete slip plane are observed. In Fig 3.14, it is also identified that the atomic planes are wavy lines in the center of the nanograins 1 to 4. These dislocations are probably multiple screw dislocations with twisted boundaries. As stacking faults are the only

structural defects observed in the case of nucleation of Si ions by ion-implantation [186], these screw dislocations are likely the products of the high energy milling process.

Fig. 3.11 HRTEM image of Si single crystal synthesized by SSR method with 20 hrs of milling and left at room temperature for 2 months.

Fig. 3.12 HRTEM of a typical multiple deformation twins formation in a (~30 nm) Si crystal after SSR with 20 hrs of milling and left at room temperature for 2 months. The inset reveals the FFT image of the Si nc.

Fig. 3.13 Arrangement of atoms in a twin related structure where x-y is the trace of the twin compositional plane.

Fig. 3.14 (a) HRTEM of a typical $\Sigma=3$ twin and (b) enlargement of Fig. 2(a) along the [011] direction for samples at milling condition of 20 hours and left at room temperature for 2 months.

Although twins are prominent in this investigation, they are not the only structures observed. Several observations in the SSR Si nc for larger Si nc (>8 nm), suggest a different prospective as compared with the results presented by Wang *et al.* [186]. Fig. 3.15 shows the HRTEM of two typical Si nc and their different grain boundaries with

milling condition of 20 hours and left at room temperature for 2 months. The inset reveals the selected area electron diffraction (SAED) of the Si nc on the right with a zone axis of $[011]$ while the Si nc on the left has a zone axis of $[111]$. Contrary to the $\{111\}$ grain boundary of a twin, another type of grain boundary is observed. The boundary consists of a $\{110\}$ plane and a $\{111\}$ plane. It had been reported by Eaglesham *et al.* [193] that $\{110\}$ plane has the highest surface energy as compared to $\{111\}$, $\{100\}$ and $\{311\}$ planes. Under this condition, it is not unusual for the $\{110\}$ facets to form boundary with another facet. However, this is unlike what Wang *et al.* [186] had reported where ordered twins coalescence occurred in the case of ion-implantation. Though this form of grain boundary is of infrequent occurrences ($<3\%$) in this study, this shows that grain boundary facets at $\{111\}$ are not absolute. In addition, the right grain exhibits edge dislocation which is another product of high energy SSR.

Fig. 3.15 HRTEM of two typical $\Sigma=3$ Si nc and their different grain boundaries with milling condition of 20 hours and left at room temperature for 2 months. The inset reveals the SAED of the Si nc on the right with a zone axis of $[011]$ while the Si nc on the left has a zone axis of $[111]$.

Fig. 3.16 Multiple $\{111\}$ facets coalescence without the formation of a twin. The inset reveals the FFT image of the Si nc.

Fig. 3.16 shows multiple $\{111\}$ facets coalescence without the formation of a twin. The inset reveals the FFT image of the Si nc. From the FFT image, it can be identified from the ring pattern that the zone axis is $[011]$. Further analysis of the HRTEM image reveals that the grain boundary occurs in a jigsaw manner with ordered boundaries of $\{111\}$ planes. This is unlike twins where a symmetrical inter-growth of crystals is observed. Though it is reported that $\{111\}$ planes have the lowest face energy [193] of 1.23 J/m^2 , it is interesting to note that most of the coalescence ($>90\%$ of all boundary facets) occurs at this $\{111\}$ plane for SSR Si nc as compared to other facets like $\{110\}$ and $\{311\}$. As Si has diamond structure with a preferred dislocation slip plane [192] at $\{111\}$, one might assume that a higher probability of grains bound with $\{111\}$ planes at the edge that cause the result of this investigation. However, it is interesting to note from

Fig. 3.14 to Fig. 3.16 that many of the grains do not have grains bound with $\{111\}$ planes at the edge. The other $\{100\}$ and $\{110\}$ planes of grain boundary and bounding planes are also identified despite the preferred slip plane. This is likely due to the high energy fracturing of the SSR process which results in random fracturing. At the same time, it is also unlikely a result of compression of grains during the SSR as it is a random process [16] that do not have a preferred plane of compression. One reason that might explain why most of the grain boundary formation is at the lowest surface energy plane of $\{111\}$ rather than the higher surface energy plane of $\{110\}$ is the relaxation of applied stress in the lattice planes after the SSR. This applied stress is likely to be induced in the lattice during the process of SSR. This relaxation energy might be the dominant source of the coalescence process.

Fig. 3.17 (a) The XRD spectra of unmilled Si particles and 20 hours milled Si nc after being left for 1.5 hrs, 5 hrs, 11 days (264 hrs), 48 days (1152 hrs) and 59 days (1416 hrs) and (b) the strain values with respect to the left hours for $\{111\}$ and $\{110\}$ planes respectively.

Fig. 3.17 shows (a) the XRD spectra of unmilled Si particles and 20 hours milled Si nc after being left for 1.5 hrs, 5 hrs, 11 days (264 hrs), 48 days (1152 hrs) and 59 days (1416 hrs) and (b) the strain values with respect to the left hours for {111} and {110} planes respectively. Using Scherrer's equation [179], the XRD spectra give an average grain size of 11 nm. It is consistent with HRTEM images, presented earlier, where the observed grain size of the Si nc ranges between 4 to 17 nm. Upon milling, there is a shift of peaks to the right. This represents a reduction in d-spacings of the grain. This is a common phenomenon observed for the synthesis of nanometric materials using the mechanical milling methods [16]. However, when this milled Si nc are allowed to rest over time, there is a left shift in the XRD peaks. From Bragg's law, this represents an expansion in d-spacings. To visualize these changes in d-spacings, it can be explained as an initial increase in applied stress during milling where the Si particles were subjected to high impact collisions. The lattice is being strained and compressed at this stage. However, upon resting, the applied stress is allowed to be released. This attributes to the lattice relaxation where expansion of the lattice is experienced. The strain in the grain can be calculated as $\Delta d/d$ in the Eqn 3.1. As the common shape of the Si nc is often assumed spherical [194] or near spherical [186], the stress, σ , induced in the Si nc can be assumed to be hydrostatic [191], where the three principal stresses are equal in the radial direction, as

$$\sigma = -\frac{E}{1-2\nu} \frac{\Delta d}{d} \quad (3.5)$$

where E is the Young's modulus, and ν is the Poisson ratio of respective planes. Table 3.1 shows the XRD peaks and strain values after 20 hours of milling left for 1.5, 5, 264 (11 days), 1152 (48 days) and 1416 (59 days) hours as compared to the unmilled Si nc. It

is commonly known that the $E\{111\} > E\{110\} > E\{001\}$ [192] and $\nu\{111\} < \nu\{100\}$ [195]. Judging from the strain values of Table 3.1 and Eqn 3.5, it can be identified that the stress of $\{111\}$ planes is the highest, followed by $\{110\}$. As observed from Fig. 3.18(b), the reduction of strain values from 1.5 hours to 1416 hours are 13.3 times and 8.7 times for $\{111\}$ and $\{110\}$ planes respectively. This may be attributed to the elastic energy relaxation of the high dislocation density in the $\{111\}$ planes, as observed in the earlier HRTEM images. The lower ν value, higher E and strain values of $\{111\}$ planes explain why majority (~90%) of the grain boundary facets occurs at $\{111\}$ planes as observed in the HRTEM images. Using the reported values by Wortman *et al.* [195] for Si of 185 GPa and 0.26 for $E\{111\}$ and $\nu\{111\}$ respectively and Eqn 3.5 for the Si nc left at 1.5 hours, it can be calculated that the value of $\sigma\{111\}$ is 35 KJ/mol, which is 60% of the reported sintering activation energy of SSR Si nc [196] at 58 KJ/mol. This energy may not be sufficient for sintering, but it is enough for grain boundary formation manifested as “necking” in the initial stage of sintering. It also accounts for the majority grain boundary at $\{111\}$ planes as the deduced $\sigma\{110\}$ is lower than $\sigma\{111\}$ owing to the 1.7 times difference in their strain values and the relatively lower $E\{110\}$. The strain values (which is proportional to stress) decay exponentially as observed in Fig 3.17(b). This might explain the absence of higher order ($\Sigma=3$ and above) twins [186] since there are insufficient time and energy, during the lattice relaxation, to enhance the formation. Moreover, it is also interesting to note that the d-spacings of the lattice planes do not reduce back to the original unmilled stage. This can be attributed to the presence of high energy defects like dislocations as described earlier.

Hrs (Days)	1.5	5	264 (11)	1152 (48)	1416 (59)	Unmilled
XRD Peak (2θ)						
{111}	28.451°	28.368°	28.313°	28.271°	28.242°	28.225°
{220}	47.357°	47.292°	47.195°	47.176°	47.158°	47.132°
Strain ($\Delta d/d$)						
{111}	-7.84×10^{-3}	-4.96×10^{-3}	-3.05×10^{-3}	-1.60×10^{-3}	-5.90×10^{-4}	0
{220}	-4.50×10^{-3}	-3.20×10^{-3}	-1.26×10^{-3}	-8.80×10^{-4}	-5.20×10^{-4}	0

Table 3.1 Different XRD peaks and strain values after 20 hours of milling left for 1.5, 5, 264 (11 days), 1152 (48 days) and 1416 (59 days) hours as compared to the unmilled one.

In conclusion, for 90% of the SSR Si nc, coalescence activities occur at {111} planes. This is in accordance with the release of applied stress induced in the Si nc during the milling process. 70% of these grain boundaries formed $\Sigma=3$ twins observed at {111} facets. Furthermore, 30% of these observed $\Sigma=3$ twins are of ordered coalescence that resumes annealing twins and the remaining 70% of these observed $\Sigma=3$ twins resume deformation twins. However, due to the exponential decay of strain values, no higher order twins are observed. Residual stress is still observed in the lattice. They can exist in the form of structural defects, such as dislocations, which are identified in larger (>8 nm) Si nc. However, in the case of Si nc with smaller diameters (<8 nm), no evident microstructural defects are observed. This can be attributed to the higher surface energy of smaller Si nc and its incompatibility with higher-energy state of defects.

3.5.4 Twins Formation Kinetics of Solid-State Reaction Si nc

Piecing up the information from the TEM images and data, the formation kinetics of the SSR can be deduced. It is proposed that there are 4 stages to the twins formation of SSR Si nc. They are namely, (1) Shear stressing, (2) Microcracks formation and fracturing, (3) Stress relaxation and (4) Twins formation. Fig. 3.18 shows the schematics of the 4 stages of twin formation kinematics of Si nc, namely stage 1) Application of shear stress to a parent crystals, 2) tearing of parent crystal into smaller crystals, 3) contact of two smaller crystal and stress relaxation and 4) twinning process.

During to the first stage, the high energy milling process induces large stress and strain to the parent Si powder. The normal and shear stress components are capable of creating dislocations to the lattice. In addition, the shear stress is capable of causing the lattice to go out of plane, as illustrated in Fig 3.13. The second stage involves the propagation of the shear stress which results in cracks forming at the edge into the parent crystal. Similar to edge dislocation, the dislocated part of the lattice is being moved out of the parent crystal. A smaller crystal is being sheared off from the parent crystal. Hull *et al.* [183] has reported on the fracturing through the twin boundary. This is similar to this case as it is observed that numerous deformation twins have been identified in the TEM images. Following the fracturing stage, these sheared crystals are being carried around in the milling vial by the spinning process. Further fracturing as mentioned continued to occur during the milling. At the end of milling, fracturing process ceased. This marked the entrance of the third stage where sheared crystals are in contact with other crystals. It

is also being observed from Table 3.1 that many of the lattices after the high energy milling are highly strained and many defects, such as edge and screw dislocations, are present in both the sheared and parent crystals. Energy is being stored in these defects. It is well established that there are two main deformations, namely elastic and plastic deformation. For elastic deformation, the strained regions can be relaxed and the original pre-stressed stage can be recovered known as applied stress relaxation. However, in the case of plastic deformation, the strain regions are often non-recoverable unless external energies like thermal energy are applied. This form of strain energy is commonly referred as residual stress. As it is noticed from the XRD results and the TEM images, many areas in the milled Si nc are being stressed. The applied stress relaxation is prominent observed as the XRD results indicate. As the stable state for two coalescence Si nc occur when they are perfectly aligned, the relaxation of the grain will try to reduce their high angle grain boundary. However, the perfect alignment requires external energy and is commonly known as recrystallization. In this case, the investigation is on the self-relaxation of the Si nc, so this high external energy is not being applied. Interestingly, the grains start to align themselves in a symmetrical arrangement upon the relaxation. This leads to the fourth stage of the twin formation process. Twinning occurs as result of the lower energy state of this structure. In the TEM images, numerous $\Sigma=3$ twins with twin angle of $\theta = 70.53^\circ$ are observed.

Fig. 3.18 Schematics of the 4 stages of twin formation kinetics of Si nc, namely stage 1) Application of shear stress to a parent crystals, 2) tearing of parent crystal into smaller crystals, 3) contact of two smaller crystal and stress relaxation and 4) twinning process.

3.6 Influences of Oxidizing Ambient to Solid-State Reaction Si Nanocrystals

3.6.1 Significance of Oxidation to Solid-State Reaction Si nc

As reported, for both optical and memory applications, the size of the Si nc is critical with typical dimension of less than 10 nm [2-6, 197]. However, as discussed earlier in section 3.4 [9], solid-state ball milling of Si powder with sizes greater than 10 nm had been synthesized and in order to experience quantum confinement effect, further size reduction of Si nc is necessary. It is reported that further post oxidation can reduce the size of a single Si nc or a single Si nanowire to dimension as small as 5 nm [60, 198-200]. However, in real situation, clusters of Si nc are often formed as a result of random formation [16, 76]. Upon high temperature oxidation, both sintering and oxidation occurred to the Si nc in the cluster. In this section, a realistic modeling of the change in Si nc grain size in a cluster is performed to observe the combinational effect of the competing factors of sintering and self-limiting oxidation on Si nc at 900 °C.

3.6.2 Sample Preparation and Experiments on Oxidized Solid-State Reaction Si nc

The dispersion of the SSR Si nc and the embedding of these milled Si nc in tetraethylorthosilicate (TEOS) thin film will be discussed later in Chapter 4. The thin film samples were oxidized at 900 °C for varying times from 0 hrs to 5 hrs. These thin films were oxidized in a Lindberg quartz tube furnace using a 500 sccm continuous O₂

gas flow. For the determination of sintering perimeters, an average grain size of 12.8 nm Si nc is used. A sample of 0.8 g of milled Si nc was used for varying temperature, ranging from 700 °C to 1050 °C, in N₂ ambient to estimate the sintering activation energy. All these samples, including those TEOS thin films with embedded milled Si nc, were characterized using x-ray diffraction (XRD), scanning from 20° to 60° at 2 °/min. Both XRD spectra for powder and thin film samples were collected by Shimadzu XRD-600. For the thin film samples, 2 θ scan with a fixed θ angle of 0.5° scan was used. High resolution transmission electron microscopic (HRTEM) images were captured using JEM-2101F. Dynamic light scattering (DLS) was used to detect the particle size distribution. This size distribution was taken using Zeta Plus from Brookhaven Instruments Corp.

3.6.3 Observation and Modeling of Oxidation Effects on Solid-State Reaction Si nc Grain Sizes

Oxidation Hours (hrs)	(111) Grain Size (nm)
0	12.8
0.2	15.7
0.5	14.6
0.8	16.0
1	15.3
2	14.8
3	9.8
4	8.3
5	9.3
8	7.7

Table 3.2 Grain size for (111) miller planes after 0 hr, 0.2 hr, 0.5 hr, 0.8 hr, 1 hr, 2 hr, 3 hr, 4 hr, 5 hr, 6 hr and 8 hr oxidation at 900°C.

Table 3.2 shows the grain size for (111) miller plane after 0 hr, 0.2 hr, 0.5 hr, 0.8 hr, 1 hr, 2 hr, 3 hr, 4 hr, 5 hr and 8 hr oxidation at 900 °C. Unlike those observed by Liu *et al.* [60] and Heidemeyer *et al.* [199], there is an initial growth followed by a peaking of the grain size before the self-limiting oxidation phenomenon steps in. This is probably due to the sintering or coalescence of individual Si nc [186, 198] in a cluster that causes the initial growth; and the competition between oxidation and sintering that results in the peaking in grain size growth. To illustrate the possibility of sintering that result in the initial growth, Fig. 3.19 shows the (a) TEM image of clusters of Si nc in TEOS thin film, (b) HRTEM of the grains necking in the cluster as shown in (a) after a soft bake of 150 °C and (c) DLS agglomerate size distribution. TEM reveals that agglomerate of ~103 nm that is near the lower limit of the DLS agglomerate size distribution as compared to an average Si nc grain size of 12.6 nm. The average grain size, as calculated from Bragg reflection linewidth using Scherrer formula [179], for the same sample, is found to be 12.8 nm. This is similar to the size observed by the TEM. Nonetheless, this form of clustering is not unique to SSR Si nc only, it has also been observed in ion implantation nucleated Si nc [201]. As shown in Fig. 3.20(b), for both clusters, there is a formation of neck between two individual Si nc which will probably lead to sintering. It has been reported that grain size will increase as a result of sintering following the classical Arrhenius relation [202, 203],

$$G^n = G_o^n + Dt \exp\left(\frac{-E_A}{k_B T}\right) \quad (3.6)$$

where G and G_o are the final and initial grain size respectively, t is the time of sintering, E_A is the activation energy, k_B is the boltzman constant, T is the sintering temperature and D and n (normally 3) [202] are constants. Fig. 3.21(a) and 3.21(b) shows the Arrhenius

plots of the sintering for estimation of activation energy E_A and constant D for Si nc respectively. It is found that the activation energy E_A is 59.7 kJ/mol and value of D is 283.7 nm³/s. The activation is relatively lower as compared to other materials [202, 203]. This is because as materials reduce to nanometric scale, the surface-to-volume (S/V) ratio will relatively increase, and hence, the surface free energy will increase [202]. In other words, sintering can take place at lower activation energy.

Fig. 3.19 (a) TEM image of clusters of Si nc in TEOS thin film, (b) HRTEM of the grains necking in the cluster as shown in (a) after a soft bake of 150 °C and (c) DLS agglomerate size distribution.

Fig. 3.20 Arrhenius plots of sintering for estimation of (a) activation energy E_A and (b) constant D for Si nc.

The Deal-Grove oxidation model [18] has stated that the oxidation growth rate to be

$$\frac{dx}{dt} = k \frac{C_i}{N} \quad (3.7)$$

where C_i is the concentration of oxidant at Si nc and N is the number of oxidant molecules incorporated into a unit volume of oxide. In addition, the diffusion coefficient is a constant as they are dealing with planar surfaces. However, in the case of Si nc where it is a curved surface, the diffusion coefficient may vary. Kao *et al.* [204] has reported that the oxidation of convex curvature has a retarding oxidation due to stress perpendicular to the Si nc, σ_{rr} , and the volume difference between Si and SiO₂, ΔV . This retardation in oxidation rate is not observed on planar surface. Kao *et al.* [204] later proposed a model that oxidation of convex curvature results in a change in diffusion coefficient due to difference in stress and expressed it as,

$$k = k_o e^{\frac{\sigma_{rr}(t)\Delta V}{k_B T}} \quad (3.8)$$

From these two equations, Eqn 3.7 and 3.8, the Heidemeyer *et al.* [199] used an assumption that $\sigma_{rr} \sim t$ to establish a relationship that gives oxidation of convex curvature Si nc an exponential decay function,

$$\frac{dx}{dt} = abe^{-bt} \quad (3.9)$$

where a and b are constants. Solving this first order differential equation gives,

$$x(t) = a(1 - e^{-bt}) + c \quad (3.10)$$

where c is a constant. Eqn 3.10 shows that as $t = 0$, the oxide thickness will be the native oxide thickness of c . But, as $t \rightarrow \infty$ the oxide thickness will be limited to $a+c$. Other than

just constants, this parameters (a, b and c) are also fitting parameters that can be later related us to the physical derivatives including stress, agglomeration size, etc. Using this retarding oxidation equation and taking the agglomerate as spherical with little or no pores, the author further developed the equation to find out the amount of Si nc remaining upon oxidation, Si_{remain} , is equivalent to as reported in [196],

$$Si_{remain} = A + Be^{-Ct} \quad (3.11)$$

where $A + B$ denotes initial agglomerate size (at $t = 0$), A is the self-limiting Si nc size (at $t = \infty$) and,

$$Ct = \frac{\sigma_r(t)\Delta V}{k_B T} \quad (3.12)$$

Fig. 3.22 shows the experimental data of the grain size with respect to oxidation time and the curve fitting of the sintering and oxidation regions. The curve fitting of the sintering and oxidation regions shows less than 8% deviation from the experimental data. The values of A , B , and C have been determined to be 8.3 nm, 291 nm and 2 hr^{-1} respectively. From this investigation, the agglomerate size and the self-limiting Si nc grain size are found to have a diameter of 300 nm and 8.3 nm respectively. DLS result reveals that the agglomerate size distribution peak at 270 nm and range from 102 nm to 648 nm. The diameter of the agglomerate, as modeled in Eqn. 3.11, is in good agreement with the DLS result. The critical stress, σ_{end} , as derived from Eqn. 3.12 has been given as [199]:

$$\sigma_{end} = \frac{k_B T}{\Delta V} \ln \frac{R}{BC} \quad (3.13)$$

The oxidation rate, R , that signifies the self-limiting oxidation is defined by both Si nanowire [60] and Si quantum dot [199] as 0.2 nm/hr. From Eqn. 3.13, the critical stress is found to be 2.9×10^9 Pa at 900 °C. This critical stress value is in agreement with the reported 1.67×10^9 Pa and 2.59×10^9 Pa at 700 °C and 850 °C respectively for Si quantum dot [199] and 2.45×10^9 Pa and 800 °C for Si nanowire [60].

3.6.4 Summary of Three Phases Oxidizing Kinetics of Solid-State Reaction Si nc

A detail analysis of the experimental data in Fig. 3.22 reveals 3 dominant mechanism regions, namely sintering, competing sintering-oxidation and self-limiting oxidation, classified as region I, II and III respectively. To visualize the transition between these regions, the inset of Fig. 3.22 illustrates the schematic of the regions I, II and III. Common to all the 3 regions, the oxidation process happens at all time. In region I, the surface area of the Si nc agglomerate which is closer to the oxidants will be oxidized first. The individual Si nc within the agglomerate, which are further away from the oxidants, will, hence be sintered first instead of being oxidised. As a result, the concentration of Si nc is reduced but the average grain size increased. Sintering of the Si nc is relatively fast as compared to other materials [202, 203] due to its low sintering activation energy as shown in Fig. 3.20(a). In region II, the oxidant reaches the sintered Si nc which still has necking with other Si nc. This enables continual crystal growth of Si nc through sintering. However, due to the increased oxide layer round the Si nc and the retarding oxide growth rate, there is a competition between the processes of sintering and oxidation. Owing to the relatively higher oxidation rate, the growth of the Si nc will reach

a maximum grain size and start to reduced in size. In Fig. 3.21, the maximum grain size of 18 nm occurs at 1.74 hrs of oxidation. In region III, the sintered Si nc is no more clustered to one another, and the sintering process [202] stops. As a result, oxidation dominates. However, due to the convex curvature of the agglomerate, the diffusion coefficient is retarded by the stress perpendicular to the Si nc surface caused by the volume difference between Si and SiO₂ [204]. The oxidation will eventually reach a critical stress which limits the progression of the oxidation process [60, 199, 200, 204]. Liu *et al.* [60] and Heidemeyer *et al.* [199] have demonstrated the self-limiting oxidation nature of Si nanowire at 700 °C and 850 °C. Scheer *et al.* [63] has further demonstrated this phenomenon to Si nc.

Fig. 3.21 Experimental data of the grain size with respect to oxidation time and the curve fitting of the sintering and oxidation regions. Inset: Transitional schematic of the regions I, II and III.

In conclusion, a realistic model for the oxidation of Si nc cluster has been presented. Three dominant mechanism regions have been identified, namely sintering,

competing sintering and oxidation, and self-limiting oxidation. The classical sintering model and Kao's two dimensional oxidation model considering the decrease of reaction rate with increasing stress perpendicular to Si surface, have shown to fit the experimental data well with less than 8% deviation. Low sintering activation energy of 59.7 kJ/mol has been found and attributed to the high surface free energy of small dimension Si nc grain. From Eqn 3.11, the agglomerate size and the self-limiting grain size have been found to be 300 nm and 8.3 nm respectively. The agglomerate size is in good agreement with DLS results. The limiting stress is also found to be 2.9×10^9 Pa. This study has enabled the understanding of oxidation effects on the Si nc clusters and permitted the formation of individual Si nc with smaller dimension of less than 10 nm.

3.7 Summary

In this chapter, SSR has been demonstrated as an inexpensive alternative to synthesize Si nc. Extensive structural characterizations have been carried out to study these SSRs Si nc. XRD results have revealed the crystallinity of the SSR Si nc and further evaluation using Scherrer's equation indicates a series of grain sizes ranging from 10 nm to 25 nm from different hours of milling. TEM images have further verified these calculations. In addition, the statistical studies using TEM images reveal that the grain size distribution of the 20 hours milled Si nc varying from 2 nm to 22 nm. This distribution is positively skewed with the majority grain sizes ranging from 2 nm to 10 nm. This is in agreement with the Scherrer's equation calculations. Most importantly, this falls in the range of typical grain size for electronic and optical applications.

Further investigations into the microstructure of these SSR Si nc have been carried out using HRTEM. It is revealed that more than 90% of the grain boundaries is in the $\{111\}$ orientations. This is expected due to its preferred orientation. However, it is intriguing to discover that 70% of the grain boundaries formed have the structure of ordered twin boundaries. Furthermore, 30% of these twins are of high symmetry forming poly-synthetic twins. Studies with XRD strain data reveal that these twins formation may be linked to the release of applied stress. The energy released during relaxation are employed for the formation of these highly symmetrical twins.

Further size reduction has been investigated through the oxidation of the SSR Si nc. Three phases of oxidation kinetics have been identified. They are (1) sintering, (2) compete sintering-oxidation and (3) self-limiting oxidation. For phase (1), this is due to the presence of Si clusters with neckings between the Si nc. This enhances the process of sintering. Entering phase (2), more and more Si is oxidized and oxidation rate is comparable with sintering rate. Eventually in phase (3), the Si nc have, no longer, any neckings between them. This results in pure oxidation. However, under increasing stress and strain in the core of the Si nc upon oxidation, the oxidation rate retards and self-limits. The final average grain size has reduced from an initial 12.8 nm to a final oxidized 8.3 nm in this investigation.

Chapter 4: Dispersion and Embedding of Solid-State Reaction

Si nanocrystal in Tetraethylorthosilicate Thin Film

4.1 Importance of Dispersion of Solid-State Reaction Si Nanocrystals in Ethanol

The incorporation of SSR Si nc in TEOS solution is a new avenue to create Si nc/SiO₂ matrix. It is also inexpensive as compared to other fabrication methods like ion implantation, chemical vapour deposition and co-sputtering. However, this method does have some certain difficulties in obtaining a uniform size distribution and dispersion as observed in the other mentioned processes. Mechanical milled Si nc have been found to have a smallest average grain diameter of about 10 nm [9, 205]. However, particle size may differ from grain size as a particle can be made up of many grains. Often, the resultant particle is in terms of one to tens of times the grain size. Furthermore, if these Si nc have not been well dispersed in the TEOS solution, these Si nc will further coagulated and form larger aggregates. This may cause further problems in the efficiency of light emitting application and charge storage.

Nevertheless, if the SSR Si nc can be segregated in different size ranges and dispersed in the TEOS solution, these difficulties can be overcome. Centrifugation of the Si nc in ethanol suspension have been shown to create a supernatant solution where large residual particles are removed and a range of Si nc ranging from 20 nm to 40 nm are

obtained [206]. To further reduce the size ranges and enhance the dispersion, the coating of these Si nc with organic vehicles has been adopted as a possible solution.

4.2 Process Flow to Disperse Solid-State Reaction Si nc in Ethanol and Subsequent Formation of Dispersed Si nc in TEOS Thin Film

Fig. 4.1 shows the process flow of the fabrication. In our approach, the SSR Si nc were dispersed and subsequently added to TEOS solution and spin coated to form Si nc in TEOS thin film.

Dispersion of these SSR Si nc are carried in 2 stages which comprises the macroscopic and microscopic studies, namely **I) Coating with texanol-based organic solvent**, where larger dispersed Si clusters (> 300 nm) can be produced and macroscopic studies can be performed, and **II) Subsequent Centrifugation and Filtration**, where much smaller dispersed Si clusters (< 100 nm) and single crystal can be obtained and microscopic studies can be carried out. In Stage I, the SSR Si nc are homogenized with organic vehicles using ball milling to coat them with these texanol-based organic vehicles at 20 wt% and 40 wt% respectively. The speed and duration of the ball mill is at 60 rpm and 5 hours respectively. Upon the coating of the organic vehicle, a physical layer is created between particles. A small portion of this organic vehicle coated Si nc is extracted to perform infrared absorption and TGA tests.

Fig. 4.1 Process flow of the fabrication

These characterizations allow the investigation of the bonding between the organic and the Si nc. When the coating process of particles by these organic vehicles is completed, this mixture is further mixed with ethanol to form a colloidal suspension with a total volume of 30 ml. This suspension is further homogenized using ball milling at 60 rpm for another 5 hours. At this point, a small portion of suspension is extracted for zeta potential test, settling test, dynamic light scattering (DLS) test, to characterize the stability of the suspension. Upon the coating of organic solvent and homogenization, the dispersion process is brought to the next stage. In Stage II, this suspension is centrifuged at 3000 rpm for 90 mins. Upon centrifugation [206], the supernatant is carefully extracted from

the centrifuge tube using a pipette and subsequent 0.1 μm filtration. As the supernatant consist of ultrafine particles (typically $< 20\text{ nm}$) , this supernatant is characterized using TEM imaging and atomic force microscopy (AFM) after drying. These suspensions are later mixed with TEOS solution and spin coated onto Si wafers to form the Si nc/SiO₂ matrix.

4.3 Characterization of Dispersion of Solid-State Reaction Si nanocrystals in Ethanol

4.3.1 Stage I: Colloidal Stability of Solid-State Reaction Si nc Coated with Texanol Based Organic Vehicle in Ethanol

In order to investigate the degree of conglomeration of the Si nc in the ethanol, settling test and zeta potential measurements are conducted. The test allows a well stirred solution of Si nc powder to rest and observe their conglomeration and flocculation with varying pH. As described in the Chapter 2 section 2.4, the surface charges on the particles will create a double layer with the solution. Therefore, by varying the pH level of the solution, the properties of the double layer will change and in turn affect the result in coagulation and flocculation. Fig. 4.2 shows the zeta potentials of Si nc with no organic vehicles, 20 wt% organic vehicles and 40 wt% organic vehicles respectively. It is observed that as the pH level increases, the zeta potentials become more negative. It is also observed that the zeta potential increases in absolute magnitude with increasing pH for both 20 wt% organic vehicles and no organic vehicles. The surface of Si nc is

normally oxidized as a result of the atmosphere, and this causes a O^- surface potential. However, when submerge into ethanol, a diffuse double layer will form as a result. As the organic vehicles has a functional group of OH, the zeta potential of the Si nc coated with 20 wt% organic vehicles will be lower than the Si nc without organic vehicles. The addition of the OH^- by the alkaline makes the negativity even more severe. This creates an even thicker double layer which repels particles apart. As shown in Fig. 4.2, it is clearly observed that the zeta potentials of Si nc coated 20 wt% organic vehicles are much negative than those without organic vehicles. In this way, electrostatic repulsion between Si nc is being optimized.

Fig. 4.2 Zeta potentials of Si nc with no organic vehicles, 20 wt% organic vehicles and 40 wt% organic vehicles respectively.

However, it is also noticeable that as the amount of organic vehicles increases to 40 wt%, the zeta potentials are not as stable as 20 wt%. This may be due to either large variation in size distribution or total screening effects of the Si nc surface charges by the organic vehicles. Therefore the optimal organic vehicle amount in this case will be at approximately 20 wt%.

Other than double layer interactions, the kinetic stability due to Brownian motion is also important in dispersion. Settling test as discussed in section 2.5, is employed for this characterization. Fig. 4.3 shows the sedimentation test for Si nc without and with 20 wt% organic vehicles for 4 rest hours and 20 rest hours in room temperature at varying pH level. For the suspension with no organic vehicles, it can be clearly seen that when the pH level is below 6, the suspension is extremely unstable and large amount of coagulation occurs. At 4 hrs of settling, the most stable pH level seen is about 7.5. However, at 20 hrs, there is a sudden instability even at pH 7.5. The total solid content at the bottom of the suspension is almost 9 times more than those at the top of the suspension. Although at around pH 9, the total solid content at the bottom over the top of suspension remains at 2.4 times, the amount of conglomeration is still considered significant. Furthermore, the instability over other pH levels also poses great inconsistency and gives rise to much uncertainty. Therefore, an organic vehicle to stabilize the suspension is essential.

Fig. 4.3 Total solid present in the bottom over the top of the solution with different pH level of the solution with and without organic vehicles.

With the addition of the organic vehicles, between pH 3 to 10, the total solid at the bottom of the suspension is less than 3 times than the top even at 20 hrs of settling. Furthermore, at a pH level of 7.8, the bottom is maintained at around 1.4 times of the top of the suspension. This shows great stability and indicates that the organic vehicles are capable of creating a stable suspension. However, it is also noticeable that at low pH (between pH 3 and pH 4), the amount of coagulation is significant but still insignificant as compared to those Si ncs without any organic vehicles. This is most likely due to the high concentration of H^+ ions which neutralized much of the surface charges on the Si ncs. At the same time, a higher possibility of hydrogen bonding occurs at the surfaces between the Si ncs. Both these effects are contributed to a higher occurrence frequency of coagulation and flocculation. $Si-O^- + H^+ \rightarrow Si-OH$ is the common reactions of $Si-O^-$ molecules with H^+ ions to form a stable Si-OH bond. This explains why there is a great amount of flocculation for Si ncs. The same problem occurs to those with organic vehicles, but with a lower degree. This indicates that the organic vehicles have not fully embodied the Si nc powder which results in exposure of $Si-O^-$ molecules to the H^+ ions.

By comparing the settling rate of Si nc with and without organic vehicle, it can be identified that the settling rate of Si nc without organic vehicles is at least 4 times faster than those coated with organic vehicles. Given the same particle density and solvent, Stokes equation [109] and other modified Stokes equation [207] show that the settling rate is proportional to the diameter square of aggregate. This signifies that Si nc without

organic vehicles are larger in aggregate size than those coated with organic vehicles by at least 2 times.

It can be observed that the settling test results tallies with the zeta potential test results for pH 8 and below. However, at pH 8 and above, it can be observed from Fig. 4.3 that the settling rate increases again. This represents that further increase in pH level leads to greater instability. However, Fig. 4.2 also reveals a greater (more negative) value in its zeta potential which signifies a greater electrostatic repulsive force. This contradicts the classical Derjaguin-Landau and Verwey-Overbeek (DLVO) theory [104, 208]. Other than the Van der Waals attraction and the inter-particle electrostatic repulsion, the author believes there is a steric force [104] that affects the stability of the suspension. However, no matter what the possible dominating stabilization force is, it can be determined from Fig 4.2 and 4.3 that the optimal pH level is between pH 7 – 8 in this case.

4.3.2 Stage II: Colloidal Stability of Solid-State Reaction Si nc Coated with Texanol Based Organic Vehicle in Ethanol after Filtration and Centrifugation

When the suspension of Si nc coated with organic vehicle and without organic vehicle undergo centrifugation and filtration, it can be observed visually that there is a difference of colour in the suspension. Fig. 4.4 shows the suspension containing (a) Si nc coated with organic vehicles and (b) Si nc without organic vehicle after centrifugation and filtration and c) solution of ethanol with organic vehicles only. It is observed that the suspension containing Si nc coated with organic vehicles presents a yellow suspension.

However, the suspension containing Si nc without organic vehicle presents a colourless suspension. This indicates that Si nc after coated with organic vehicles were segregated into smaller particle sizes upon the homogenization of the Si nc with organic vehicles. This colour difference can also be attributed to an increase of concentration upon the coating of the organic vehicle. To prevent the confusion of whether the colour is due to the colour of organic vehicle itself, Fig. 4.4(c) reveals that the addition of organic vehicle into ethanol alone will not have an effect in the colour. Therefore, it is shown that the yellow colouring of the suspension containing Si nc coated with organic vehicles is not a result of the organic vehicles itself.

Fig. 4.4 the suspension containing (a) Si nc coated with organic vehicles and (b) Si nc without organic vehicle after centrifugation and filtration and c) solution of ethanol with organic vehicles only.

Fig 4.5 Concentration curve based on UV-VIS absorption spectrum.

To verify the concentration of the Si nc in the ethanol, an UV-VIS absorption spectroscopy is performed and subsequent Beer Lambert's law is applied to investigate the concentration. Fig 4.5 shows the concentration curve based on UV-VIS absorption spectrum. The referencing experimental data are based on known concentration and plotted using Beer Lambert's law. As the UV-VIS absorption intensity of Si nc coated with and without organic vehicles is 1.889 and 0.778 respectively, the concentration of Si nc coated with and without organic vehicles after centrifugation and filtration can be identified, from Fig. 4.5, to be 458 ppm and 274 ppm respectively. Under the comparison of 3209 ppm (the usual 5 mol% that was used in Si nc in TEOS thin film), the yields for Si nc coated with and without organic vehicles after centrifugation and filtration are 14.27% and 8.54% respectively. There is a 1.7 times increase in Si nc concentration when organic vehicles are added to disperse the Si nc. This shows that there is a high probability that the addition of organic vehicles has resulted in significant dispersion of the Si nc into smaller size which results in a higher concentration remaining in the

supernatant. Although it can be observed that there is an increase in concentration, there is no physical data to indicate that the particle size of the Si nc cluster has reduced. Therefore, further experiments must be employed to investigate the effects of filtration and centrifugation on the segregation. In the next 2 sections, both experiment and visual evidences will be presented to demonstrate the significant reduction in particle size as a result of the coating of organic solvent and subsequent centrifugation and filtration.

4.3.2.1 Experimental Evidences: Dynamic Light Scattering Characterization

As particle size reduces to nanometric range, one of the best ways to characterize the size distribution is using dynamic light scattering (DLS) characterization as described in Chapter 2.

4.3.2.1.1 Effects of filtration and centrifugation in the segregation of Si nc clusters

As both filtration and centrifugation can reduce the amount of agglomerated Si nc, this section investigates the size distribution effect of these two methods. Fig. 4.6 shows the particle size distributions of the SSR Si nc in ethanol without and with 20 wt% organic vehicles. The range of sizes for Si nc without organic vehicle falls between 164 nm to 207 nm and has a maximum amount of Si nc falling in the size of 186 nm. However, after the addition of the organic vehicles to the Si nc, the range of sizes drops to between 134 nm to 164 nm and has a maximum amount of Si nc falling in the size of 146 nm. The organic vehicles are being adsorbed into the “microcracks” of the Si nc, which are being formed during the process of ball milling [16]. These microcracks are

self-annealing and disappear in high temperature or N_2 annealing ambient where the residual stress is relieved. The adsorption of the organic vehicles onto the surfaces of these microcracks may increase their depth and reduce the self-healing ability and thus reduce the energy required to rupture the Si nc mechanically.

Fig. 4.6 Particle size distribution of Si nc in ethanol without and with 20 wt% organic vehicles

Fig. 4.7 shows the lognormal particle size distribution of the suspension for the Si nc without organic vehicles, with coated organic vehicles and with coated organic vehicles followed by 0.1 μm filtration. It is observed that the size of Si nc reduces as a result of the addition of organic vehicles. Fig. 4.8 shows lognormal particle size distribution of the suspension without organic vehicle and with organic vehicles going through the 0.1 μm filtration. Upon filtration, the size of the Si nc with organic vehicle reduces even more to 124 nm. The filtered suspension of organic vehicles-coated Si nc in Fig. 4.8 shows that

the distribution contains particles with size ranges from 65 nm to 240 nm. Although this range is beyond the range of those from the organic vehicles-coated Si nc without filtration, it can be explained by the elimination of the majority large particles leaving only the smaller minority particles. Furthermore, due to the large amount of large sized Si nc going through the filter, the pores of the filter can easily be enlarged as a result. This can be observed by both the Si nc coated with and without organic vehicles as a wider size range of Si nc is observed. It is especially obvious with the Si nc without the organic vehicles going through the filter.

Fig. 4.7 Lognormal particle size distribution of the suspension without the Si nc without organic vehicles, with coated organic vehicles and with coated organic vehicles followed by $0.1\mu\text{m}$ filtration.

Fig. 4.8 Lognormal particle size distribution of the suspension without organic vehicle and with organic vehicles going through the $0.1\ \mu\text{m}$ filtration.

The particle size distribution can be obtained from dynamic light scattering. It is conclusive that the coating of Si nc with organic vehicles can reduce the size of the Si nc and maintain a well-dispersed suspension. However, TEM images are further required to verify the results. These will be presented in section 4.3.3.2.

To further reduce the cluster size, centrifugation [206] was employed to achieve this aim. Fig. 4.9 illustrates the particle size distribution of Si nc using filtration, centrifugation, filtration followed by centrifugation with and without organic vehicles. There is a significant reduction in size after the Si nc are coated with organic vehicles. Table 4.1 shows the peak concentration and FWHM of the particle size using filtration, centrifugation, filtration followed by centrifugation with and without organic vehicles. The comparison among the methods shows that the combination of filtration and

centrifugation is the best method. It is understood that as the pores of the filter tend to get enlarge as large particles are being forced against the pores. However, using prolonged centrifugation, the heavy particles (= larger particles) will settle down at the bottom of the centrifuge tube. Careful extraction from the top portion of the centrifuge tube can help to collect smaller particles and reduce the range of the particle sizes. The combination of filtration followed by centrifugation does not only reduce the peak particle size but it also reduces the range of particle size. It is believed that the filtration will first reduce the range of the particle sizes and the subsequent centrifugation will further narrow this range. In the application of memory and optoelectronic devices, a tight control of the size distribution is crucial for the performance. In this case, the combination of these two methods, giving a small particle size of 77.33 nm with a narrow FWHM of 60 nm, provides a potential avenue to attain Si nc with a well controlled size distribution.

Fig. 4.9 Particle size distribution of Si nc using filtration, centrifugation, filtration followed by centrifugation with and without organic vehicles.

Conditions and Methods	Peak Size	FWHM of Particle
	Concentration (nm)	Size Distribution (nm)
Without Organic vehicles with Filter only	278.08	269
With Organic vehicles with Filter only	125.5	118
Without Organic vehicles with Centrifugation only	119.28	125
With Organic vehicles with Centrifugation only	98.43	75
Without Organic vehicles with Centrifugation and Filter	188.27	126
With Organic vehicles with Centrifugation and Filter	77.33	60

Table 4.1 Peak size concentration of Si nc using filtration, centrifugation, filtration followed by centrifugation with and without organic vehicles.

4.3.2.1.2 Effects of weight percentage of organic vehicles and homogenizing/resting periods in the segregation of Si nc clusters

Fig. 4.10 shows the particle size distribution of Si nc using different weight percentage of organic vehicles and homogenizing/resting periods for a 5 hours homogenization time of of the Si powder and organic vehicles. Table 4.2 shows the peak particle size distribution of Si nc using different weight percentage of organic vehicles and homogenizing/resting periods for a 5 homogenization hours of of the Si powder and organic vehicles. It is further observed that an increased amount of organic vehicles does not significantly reduce the size of the Si nc. However, it is observed that the short homogenizing/resting period is capable of reducing the particle more than long milling hours. This is probably due to the higher periodicity of rest time that allows the organic vehicles to seep into the microcracks of the Si nc. Furthermore, prolonged hours of

milling or homogenizing time, within the homogenizing/resting period, generate high energy which can, in turn, create high temperature in the milling bowl [16]. This temperature is capable of evaporating part of the organic vehicles which results in the lesser concentration of organic vehicles.

Fig 4.10 Particle size distribution of Si nc using different weight percentage of organic vehicles and homogenizing/resting periods for a 5 hours homogenization time of of the Si powder and organic vehicles.

Milling Conditions	Periods	Weight% of Organic vehicles	Peak Size Concentration (nm)
5 min mill / 5 min rest	60	10	77.33
25 min mill / 5 min rest	12	10	83.83
25 min mill / 5 min rest	12	20	82.88

Table 4.2 peak particle size distribution of Si nc using different weight percentage of organic vehicles and homogenizing/resting periods for a 5 homogenization hours of of the Si powder and organic vehicles.

One interesting phenomenon observed after the segregation processes is the high stability of the particles. It is observed from Fig 4.3 that after the segregation processes, the suspension becomes a transparent suspension rather than the initial opaque suspension. This can be attributed to the reduction in concentration and the size of the Si

nc clusters. As discussed earlier in section 4.3.1, in most cases, the forces between particles, in a colloidal suspension, are governed by van der Waals attractions [104] and electrical double layers repulsion [104]. The resultant repulsive force, commonly known as Deryaguin and Landau and Verwey and Overbeek (DLVO) [209, 210] equation:

$$F_{\text{resultant}} = -\frac{aA_h}{12H^2} + \frac{2\pi\pi a_0 \epsilon \kappa \zeta e^{-\kappa H}}{1 + e^{-\kappa H}} \quad (4.1)$$

where

$$\kappa^{-1} = \left(\frac{2z^2 n_0 e^2}{\epsilon_0 \epsilon K T} \right)^{-\frac{1}{2}} \quad (4.2)$$

where a is the particle radius, A_h is the material property termed the Hamaker constant, H is the inter-particle separation, κ^{-1} is the Debye length and ζ is the zeta potential. From Eqn. 4.1, it can be seen that the particle size is of great importance; therefore a small range of size difference is essential. As centrifugation or filtration is employed to get the range of desired particle size groups, the effect of the size in Si nc cluster will definitely be a strong determinant in the stability of colloidal suspension.

Fig 4.11 Comparison of simulated resultant energy barriers over different sizes of Si nc in ethanol from Eqn 4.1.

Fig. 4.11 shows the comparison of simulated resultant energy barriers over different sizes of Si nc in ethanol from Eqn 4.1. It is observed that there is a longer range of repulsive force as size of particle gets smaller. This simulation is consistent with the experimental data. The filtered or centrifuged powder (with smaller sizes) results in longer dispersion. However as the size of the Si nc gets larger, large repulsive forces can only be experienced within a very short separation distance. As the separation distance gets further, overall energy drops near to zero at a faster rate. From this simulation, it is also shown that as the size gets larger the separation distance to maintain the repulsive force between the particles gets smaller. This can be understood by the reciprocal term of the V_r , increase in value which induces an increase in the gradient of V_r . When this phenomenon happens, the overall energy gets to zero and gravitational energy and buoyancy forces will be the prominent forces which will create an eventual aggregation of particles. It is also observed that the repulsive forces for larger particles are higher. This is due to the increase in surface area which results in higher zeta potential and lower Debye-Huckel ionic radius. From the DLVO equation, particle separation plays a critical role in the stability of the suspension. The Brownian motion is the key to aggregation when the separation distance may be brought to close proximity. When the separation is brought to a distance where strong Van der Waals attractive forces step in, aggregation will result. However, this phenomenon is less seen in larger particles with organic vehicles due to the increase of effective radius as a result of organic vehicle coating in a form of steric stabilization. This increase the distance between the particles and reduce the probability of Brownian motion induced collisions between the larger particles that result in aggregation of particles at close separation distances.

4.3.2.2 Verification of Particle Size using Microscopy

As illustrated in the previous section, there is a decrease in particle size upon the addition of organic solvent, and the centrifugation and filtration segregation process. However, the actual size of the particle is still unknown. In this section, different microscopy methods are employed to verify the particle size. These methods include optical microscopy, AFM and TEM. Fig. 4.12 shows the microscopic images using 100 times magnification for spin-coated TEOS thin film containing Si nc (a) with organic vehicles without any segregation, (b) without organic vehicles without any segregation, (c) with organic vehicles using filtration followed by centrifugation and (d) without organic vehicles using filtration followed by centrifugation. It is observed that the Si nc is much smaller after the addition of organic vehicles. Fig. 4.12(a) shows that there is a layer of organic component surrounding the Si nc. This layer of organic component has reduced the size of the particle as compared to Fig. 4.12(b). This is due to the presence of steric stabilization as this layer of organic component provides a “soft” barrier to segregate the particles. Coupled with the homogenization of the Si nc and the organic vehicles during ball milling, the organic vehicles is able to penetrate more deeply into the microcracks of the particles and boundaries between the particles. After filtration and centrifugation, the surface reveals no visible particles, the dots on the surface are primarily impurities inherited from the environment.

Fig. 4.13 shows the AFM images for (a) pure TEOS thin film and spin-coated TEOS thin film containing Si nc (b) with organic vehicles using filtration followed by

centrifugation and (c) without organic vehicles using filtration followed by centrifugation. It can be observed that Fig. 4.13(a) and Fig. 4.13(b) are similar. This is probably due to the small dimension of the Si nc which is undetectable at the surface or totally embedded inside the TEOS thin film. However, Fig. 4.13(c) shows pillars of protrusions with a dimension of 50 nm to 90 nm. This is probably contributed by the large size of Si nc (particle size) without organic vehicles. From these results, it is convincing that the particle of the Si nc has greatly shrunk from a few hundreds of nanometer (before segregation) to tens of nanometer (after segregation). Furthermore, the addition of organic vehicles to the Si nc can further reduce the size of the Si nc through steric stabilization.

Fig. 4.12 Microscopic images using 100 times magnification for spin-coated TEOS thin film containing Si nc (a) with organic vehicles without centrifugation and filtration, (b) without organic vehicles without centrifugation and filtration, (c) with organic vehicles after centrifugation and filtration and (d) without organic vehicles using filtration followed by centrifugation and filtration.

Fig. 4.13 AFM images for (a) pure TEOS thin film and spin-coated TEOS thin film containing Si nc (b) with organic vehicles using filtration followed by centrifugation and (c) without organic vehicles using filtration followed by centrifugation

Fig. 4.14 shows the TEM images of (a) Si nc without organic vehicles before segregation, (b) Si nc with organic vehicles before segregation, (c) Si nc with organic vehicles after filtration and centrifugation and (d) Si nc after filtration and centrifugation with the burnt out of organic vehicles. The Si nc are not spherical due to the random impact of

ball milling. The particle sizes for Si nc without organic vehicles before segregation, with organic vehicles before segregation, with organic vehicles after segregation and with organic vehicles after segregation and burnt out of organic vehicles from TEM results are about $253(\pm 119)$ nm, $194(\pm 8)$ nm, $90(\pm 68)$ nm and $12(\pm 4)$ nm respectively. It is observed that the TEM images size falls in the size distribution range of the DLS experiments. The two folds reduction in size after the addition of organic vehicles reveals the probable dispersion due to the steric effect of the organic vehicles. This result is also consistent with the settling test in the aggregate size estimation as mentioned above. Sedimentation of the heavier and larger particles through centrifugation has allowed the extraction of smaller agglomerates as shown in Fig. 4.14(c). The agglomeration as seen in Fig. 4.14(c) reduces from ~ 194 nm to ~ 90 nm after centrifugation. Although it seems that the agglomerates in Fig. 4.14(c) are an aggregate of Si nc, a higher magnification into these agglomerates reveal a different perspective. Fig. 4.14(d) shows the TEM images of Si nc after filtration and centrifugation with the burnt out of organic vehicles. It reveals a highly dispersed Si nc with a combination of small agglomerates (~ 20 nm) and single crystals (~ 8 nm). The organic vehicles have in fact provided a physical barrier and steric stabilization between the particles. The steric (repulsive) forces are well-described as a combination of “entropic” and “mixing” effect [104]. Upon contact [211] or overlapped [212] of the absorbed organic vehicles layer, the particles will experience a repulsive force that keeps them apart. It has been demonstrated by Ottewill *et. al.* [213] that the repulsive steric force due to organic surfactants is a function of the length of the adsorbed surfactants which falls in the range of a few nm. This explains why these particles are packed in agglomerate (Fig. 4.14(c)) without adhering to one another.

Fig. 4.14 TEM images of (a) Si nc without organic vehicles before segregation, (b) Si nc with organic vehicles before segregation, (c) Si nc with organic vehicles after filtration and centrifugation and (d) Si nc after filtration and centrifugation with the burnt out of organic vehicles.

Fig. 4.15 Selected area electron diffraction patterns of (a) Si nc without organic vehicles and (b) Si nc with organic vehicles before segregation.

Fig. 4.15 shows the selected area electron diffraction patterns of (a) Si nc without organic vehicles and (b) Si nc with organic vehicles before segregation. The intensity of the diffractions observable greatly reduced as a result of the addition of organic vehicles. This represents a reduction in the grain size. This can be explained in the reduction of surface energy by the organic vehicles as seen in the case of SSR with the addition of organic vehicles [16]. The organic vehicles are able to fill into the microcracks of the Si nc and reduce the size of the Si nc by shear stress and strain [16].

4.4 Surface Chemistry and Bonding

Fig. 4.16 (a) Thermogravimetric analysis of Si nc with organic vehicles from 27 °C to 600 °C and (b) Infrared absorption (FTIR) spectra of the organic vehicles, SSR Si nc without and with organic vehicles at varying annealing temperatures in N₂ ambient.

Texanol-based organic vehicles coated on Si nc have been demonstrated to have a large range of stability from pH 3 to 11 as seen in Fig. 4.2 and Fig. 4.3. This is largely due to the OH functional bonds with the Si nc consisting of esters group protruding and dissolving into the ethanol that provides for sufficient steric stabilization. Fig. 4.16 shows

(a) the thermogravimetric analysis of Si nc with organic vehicles from 27 °C to 600 °C and (b) the infrared absorption (FTIR) spectra of the organic vehicles, SSR Si nc without and with organic vehicles at varying annealing temperatures in N₂ ambient. Fig 4.16a) reveals that there are 2 major weight losses at around 100 °C and 280 °C respectively. The first weight loss at 100 °C can be attributed to the evaporation of water. The second weight loss is at 31 °C higher than the boiling point at ~249 °C for the texanol-based organic vehicle. This reveals that there might be some chemical bonding occurring at the Si nc surface and the organic vehicle. Lu *et al.* [16] has reported that there is an increase in temperature in the vials during the milling rotation process and this can induce bonding between the Si nc and organic solvent. The probable formation is the removal of a water molecule and the formation of Si-O-C-... during the homogenization of Si nc and organic solvent in the milling vials. This explains the presence of the weight loss that ends at 280 °C, which is higher than texanol-based organic vehicle boiling point temperature. The FTIR in Fig 4.16b) shows that the coating of the organic vehicles gives rise to the carbon and hydrogen bonds. The presence of Si-OH bonds is attributed to the polar attraction of the oxidised Si nc surface and the functional groups of the texanol-based organic vehicles. At 300 °C, it is identified that the C=O and CH bonds are calcinated. This is common as the organic solvent, which contains esters and organic components, burnt out at ~249 °C. With increasing temperature, it is further observed that the Si-OH bonds decrease and at 900 °C, most of the organic and water components, like C-H, C=C, C=O and O-H bonds, are removed. Fig 4.17 summaries the reaction of the organic vehicles on the Si nc surface. Other than the organic bonds, the FTIR spectrum reveals no trace of anions or cations. In other words, the organic vehicles contain no ions that alter the

double layer of the suspension since ionic organic vehicles may result in the attraction of Si nc to form agglomerates. As the hard bake temperature for TEOS thin film commonly falls between 800°C to 950°C, the incorporation of texanol-based organic vehicle to Si nc represents an avenue to create dispersed Si nc in TEOS thin film [9].

Fig 4.17 Reaction of the organic vehicles on the Si nc surface.

4.5 Sol-Gel Process of Solid-State Reaction Si nanocrystals in TEOS thin film Layer

4.5.1 Introduction

The sol-gel process is a well accepted technology used for the formation of thin film. This process is simple and can be applied to a substrate by spin, dip or drain coating. In this project, spin coating is used as it is capable of producing a thinner and more uniform layer as compared to the other two methods.

The sol-gel process is the process where a solution or sol undergoes a sol-gel transition [214]. A solution is a pure single-phase liquid whereas a sol is a stable suspension of colloidal particles. At the transition, this solution or sol becomes a rigid and porous mass through the processes of destabilization, precipitation, or supersaturation [214]. There is a complicated list of intermediates and products arising from sol-gel process. However, the most important reagent is a hydrolysable organometallic that is commonly known as a metal alkoxide, $M(OR)_x$, where (OR) is an alkoxy group [215]. Hydrolysis will result when this metal alkoxide and water are mixed in common solvent.

In this project, the metal alkoxide [215] used is TEOS. It is commonly used to form SiO_2 thin film. When in contact with water, it reacts slowly to form silanol. The solvent used in this project is a common alcohol, ethanol. The TEOS and water are immiscible and only when TEOS is dissolved in a solvent, then can these two ingredients be able to react. Often, an acid, such as HCl, is used as a catalyst for the reaction. The chemical reactions to form the TEOS thin film are basically hydrolysis and polymerization [216].

As the water and excess organic elements are removed under annealing, pores will be formed. These pores will act as potential sites for the SSR Si nc to reside in.

4.5.2 Fabrication and Thickness Characterization of Solid-State Reaction Si nc in TEOS Thin Film Layer

SSR Si nc in TEOS (SNT) thin film will be used as the MOS capacitor dielectric layer and LED emission layer, therefore the thickness control is of utmost importance. Fig 4.18 illustrates the SNT layer thickness variation using different mole ratio of ethanol containing dispersed Si nc to TEOS and spin speed. The sol is made up of TEOS, ethanol containing dispersed Si nc and water at the mole ratio of 1: x : 4, where x is variable. After the mixing of these 3 components, 0.1 mole ratio of HCl is added as catalyst for hydrolysis. The sol is allowed to hydrolyze for 48 hours before being spin coated onto Si wafer. All the mixing and spin coating of the sol is performed in a N₂ box with a controlled humidity of ~14%. This is to prevent uncontrolled hydrolysis due to ambient moisture.

Fig 4.18 SNT layer thickness variation using different mole ratio of ethanol to TEOS and spin speed.

Spin Speed (rpm)	1000	2000	4000	6000
Ethanol (mol ratio)				
8	540	462	228	200
10	320	180	85	34.5
12	110	53	30	25

Table 4.3 thickness (nm) for the selected spin speed and mole ratio of ethanol

Table 4.3 illustrates the thickness (nm) for the selected spin speed and mole ratio of ethanol. It can be seen that the thickness of the SNT layers decreases as the spin speed increases. In addition, the rate of decrease in thickness is decreasing as the speed increases. This is in good agreement with those report in [18] which states that the thickness increases proportionally to the reciprocal of square root of spin speed. Increaseing the ethanol content can also reduce the thickness of the SNT layers. This reduction is even more pronounced at slower spin speed of 1000 rpm. This indicates that the control of the SNT layer thickness can be achieved by fined tuning the spin speed and mole ratio of ethanol. This is critical as it determines the dielectric thickness which will have a direct influence on the electric field strength across the dielectric. At the same time, the amount of Si nc is also proportional to the volume of the SNT layer formed on the Si wafer. This indicates that a larger volume of the SNT layer (associates directly with thickness) will have a greater amount of Si nc. Hence, control of luminescence intensity and charge trapping sites can also be controlled in this sense too.

4.6 Summary

In this chapter, dispersion of Si nc has been demonstrated using texanol-based organic vehicles. Macroscopic studies on larger Si clusters (> 200 nm) with this organic vehicle reveals well-dispersed colloidal suspension for a minimum of 20 hours from the pH range of 3 to 9. At the same time, the zeta potential indicates the thickening of electrical double layers, for pH 5.5 and above, with the addition of the organic vehicle. However, from TEM images, many of the Si clusters can still be observed.

Further refinements of the Si clusters are achieved through filtration and centrifugation. As a result, smaller Si nc clusters (< 12 nm) can be segregated from the larger Si clusters (> 200 nm) and more detail microscopic study on the dispersion of Si cluster is realized. In the comparison of Si clusters with and without organic vehicle, superior results were achieved in the case of Si nc with organic vehicle. Upon subsequent removal of the organic solvent, well dispersed small Si cluster (< 12 nm) and single Si nc are observed. A successful steric stabilization method using texanol-based organic vehicle has been proven viable for the segregation of SSR Si nc. With this segregation, the problems associated with Si nc clustering can be greatly reduced and further progress can be made in the later part of the project for the development of single-electron devices and minimization of the problems of lateral spreading of charges in memory application.

It is also demonstrated that these dispersed Si nc in ethanol can be homogenized in TEOS reagent which can be further developed into thin film. This has resulted in the

possible realization of dispersed Si nc in SiO₂ matrix which is a major challenge to current Si nc technology.

Chapter 5: Photoluminescence Study of Solid-State Reaction Si Nanocrystal and Solid-State Reaction Si Nanocrystal Embedded in TEOS Films

5.1 Introduction

It is believed that the SSR Si nc alone is not sufficient to make light emitting devices like LED or LASERs. A SiO₂ matrix is therefore employed to contain this SSR Si nc. For this SiO₂ matrix, it has also been established that the matrix itself is not capable of effective emitting of visible light due to its high bandgap (~9 eV) [18]. As native oxide is commonly passivated on the SSR Si nc during milling, the surface terminated group is most likely to be oxygen-based. However, hydrides and siloxanes can also be formed when expose to surrounding moisture during handlings or milling. Therefore the possible mechanism of luminescence due to these two groups cannot be eliminated. Furthermore, in the case of oxygen deficiencies introduced during synthesis or by external irradiation [217], both amorphous and crystalline SiO₂ is capable of emission in the UV and visible regions. Emissions at about 1.9 eV, 2.2 eV, 2.7 eV and 4.8 eV have been reported [217-220]. This chapter presents a study of photoluminescence (PL) from SSR Si nc and SSR Si nc embedded in tetraethylorthosilicate (TEOS) thin film. The aims are to investigate (a) the mechanisms for the luminescence for nanocrystalline Si synthesized by SSR and SSR Si nc embedded in TEOS thin film and (b) the performance of SSR Si nc embedded

in TEOS thin film as an alternative avenue to form nanocrystalline Si in amorphous SiO₂ matrix.

5.2 Fabrication of Solid-State Reaction Si Nanocrystals in TEOS Film

The synthesis of SSR Si nc used has already been described in Chapter 3. The tetraethylorthosilicate (TEOS) thin film was made from 99.999% pure TEOS solution purchased from Sigma-Aldrich Co. One mole of TEOS was mixed with twelve moles of ethanol, four moles of deionized water. After thorough stirring, 0.1 mole of hydrochloric acid (37 wt% in water) was added into the solution to catalyse the hydrolysis. 5 mole% SSR Si powder was then added to this solution and homogenized. The mixing of TEOS solution was done in N₂ environment so as to prevent gelation. P-type <100> Si wafers were used as the substrates. Each layer of sol-gel film was spun onto the substrate at 3000 rev/min for 35 s after 24 hours of hydrolysis. The preparation and spin coating process were all carried out in class 100 clean room environment. The spin coated films were further separated in two batches annealed in O₂ ambient at 900 °C. One batch was annealed for 15 mins and the other batch was annealed for 15 min, followed by 1 hour with PL measurement after each anneal step (once for 15 min and once for 1 hour). The FTIR spectra were collected with the Perkin-Elmer 2000 FTIR spectrometer in the range of 4000-400 cm⁻¹. For powder sample, 1 mg of powder was compressed with 100 mg of KBr to form pellets for the FTIR measurement. The powder sample (~300 mg) was compressed into pellets for both Raman spectroscopy measurements and PL characterization. These pellets, together with the TEOS thin films, were photo-excited by a continuous argon laser at a wavelength of 488 nm at room temperature with a step of 1

nm for 250 ms. The photoluminescence excitation (PLE) spectra were collected with the Spex Fluorolog-3 spectrofluorometer at room temperature. The source of excitation was a xenon lamp.

5.3 Investigation of Luminescence Mechanism of Solid-State Reaction Si Nanocrystals in TEOS Thin Film

Fig. 5.1 TEM image of SSR Si nc in TEOS thin film.

Fig. 5.1 shows the TEM image of 20 hrs SSR Si nc embedded in TEOS thin film. Si ncs, between 8 nm to 10 nm, are observed. The grain size, as calculated from Bragg reflection linewidth using Scherrer formula [179], for 20 hrs SSR Si is found to be 10 nm. This is similar to the size observed by the TEM. SSR Si ncs at other sizes, between 10 nm to 25 nm, are also synthesized at different hours of milling. The Raman spectra of SSR Si

nc at sizes of 10 nm, 14 nm, 19 nm and 25 nm show that there is only one sharp peak at 520 cm^{-1} indicating the presence of crystalline Si [47]. There is no boardening of the peak which signifies the absence of amorphous Si. Therefore, it rules out the possibility of amorphous Si as the mechanism of PL in this case.

Fig. 5.2 Infrared absorption spectrum of the Si nc at different milling hours.

Past literature has attributed photoluminescence to the presence of hydrides [39, 43, 151] and siloxene [42] groups. To prevent complications of these mechanisms, these components should be eliminated or minimized. Fig. 5.2 shows the infrared absorption spectrum of the Si nc at different milling hours. There are traces of peaks between 2000–2190 cm^{-1} in the as-received Si powder which indicates the presence of Si-H_n ($n = 1, 2, 3, \dots$) modes [9]. However, upon milling, these peaks are eliminated. Similarly, the huge 3400 cm^{-1} peak presented in the as-received Si powder is minimized and eliminated upon prevailing milling. This shows that much of the hydride and siloxene groups are eliminated after the ball milling process. The FTIR further reveals the increased quantity of the Si-O groups. As featured in Fig. 5.2, three modes of Si-O vibrations are identified. They are the

stretching, bending and rocking modes [9] which are represented by 1120 cm^{-1} , 700 cm^{-1} and 500 cm^{-1} respectively.

Fig. 5.3 (a) PL spectra and (b) PL peak wavelength of SSR Si nc with average diameters of 10, 14, 19 and 25 nm respectively.

Fig 5.3(a) shows the PL spectra and Fig 5.3(b) shows the PL peak wavelength for SSR Si nc at the sizes of 10 nm, 14 nm, 20 nm and 25 nm respectively. It is observed that the PL peaks of SSR Si nc, at sizes of 10 to 25 nm, are between the wavelengths of 868 to 889 nm (± 0.5 nm). For the SSR Si nc size from 10 to 14 nm, the wavelength increases from 868 to 889 nm. However, for the SSR Si nc size from 14 to 25 nm, the wavelength actually decreases from 889 to 872 nm, indicating a blue-shift in emission wavelength. There is no direct relationship observed between the size of SSR Si nc and wavelength as described in quantum confinement model [1, 7]. To further illustrate the SSR Si nc relationship with quantum confinement, equations relating size and PL emission energy has been employed to explore. C. Delerue *et al.* [221] has illustrated quantum confinement theory through PL emission energy as a function of Si nc size:

$$E_{PL}(d) = E_0 + (3.73/d^{1.39}) \quad (5.1)$$

And G. Ledoux *et al.* [222]has further modified eqn. (5.1)

$$E_{PL}(d) = E_o + (3.73/d^{1.39}) + (0.881/d) - 0.245 \tag{5.2}$$

Fig. 5.4 PL emission energy with respect to Si nc size utilizing C. Delerue’s equation, G. Ledoux and experimenetal data using SSR Si nc.

Under the comparison of Fig 5.4, it can be observed that the PL emission energies will go into deep infrared regions with a decreasing PL emission energy. However, from the author’s experimental results, at 14nm and beyond, there is an increase in PL emission energy which is opposed to the quantum confinement theory. This provides strong evidences that quantum confinement may not be the mechanism for PL of the SSR Si nc.

Fig. 5.5 FTIR of SSR Si nc in TEOS thin film, TEOS thin film and 10 nm SSR Si nc.

Fig. 5.5 shows the infrared absorption spectra of SSR Si nc at 10 nm, TEOS thin film and SSR Si nc embedded in TEOS thin film. It is observed that there is no presence of Si-OH and Si-H vibration modes. However, stretching, bending and rocking modes of SiO₂ are observed at 1120 cm⁻¹, 700 cm⁻¹ and 500 cm⁻¹ respectively. It is also noticeable that SSR Si nc embedded in TEOS thin film possess large amount of these three modes as compared to SSR Si nc alone. This indicates that SSR Si ncs has the least SiO₂ component.

Fig. 5.6 PLE spectra of SSR Si nc at the size of 10 nm and SSR Si nc in TEOS dried at room temperature and annealed at 900 °C in O₂ ambient for i) 15 mins and ii) 1 hr using an excitation energy of 2.54 eV.

Fig. 5.6 shows the PLE spectra of SSR Si nc at the size of 10 nm and SSR Si nc in TEOS dried at room temperature and annealed at 900 °C in O₂ ambient for i) 15 mins and ii) 1 hr. The excitation energy employed for the PLE measurement is 2.54 eV ($\approx$ 488 nm) and the emission energies detected are at approximately 1.38 eV, 1.55 eV, 1.70 eV and

1.88 eV respectively. The bandgap energies of bulk Si and SiO₂ is about 1.16 eV and 9 eV respectively. With these excitation and emission energies, the most probable recombination sites fall within the bandgap of Si or SiO₂. Coupled with the absence of quantum confinement effects and the hydride groups, the results greatly suggest that it is the defects in amorphous SiO₂, rather than the Si nc, causing the PL. It has been reported that the nonbridging oxygen hole centers (NBOHCs) is the origin of oxygen passivated nanocrystalline Si emission. Other groups [223, 224] have subsequently verified the existence of NBOHCs in these oxygen passivated nanocrystalline Si in amorphous SiO₂ matrix using electron spin resonance. These centers have been reported in silica optical fibers and their PL ranges between 600 - 670 nm at room temperature, with a FWHM at around 0.35 eV [153]. The red-shift as seen in SSR Si as compared to the silica optical fibers is attributed to the minor displacement of O ion from its lattice site and strong interaction with the surrounding ions as theoretically predicted [225]. Three different NBOHCs have been identified [153]. The first type of NBOHC is stabilized with a hydrogen bond upon irradiation. This type of defect is seen in silica containing high concentrations of hydroxyls and hydrides that exists only in temperature below 350 °C [59, 226]. The second type of NBOHC is the Si-O- due to the breakage of the peroxy linkages [225], which gives a lower energy with lower quantum efficiency. However, this type of NBOHC does not change appreciably with heat treatment [154]. The third type of NBOHC is likely caused by the strain of bonding between two materials of different bond length, density or structure. This type of NHOBC has been reported after drawing of oxide clad fibers and after high temperature annealing [154], and it is the least understood.

Samples	PL Intensity (Arb. Unit)
SSR Si nc in TEOS annealed at rm temp	34671.58
SSR Si nc in TEOS annealed in O ₂ at 900 °C	
15 minutes	30683.88
1 hour	7573.79

Table 5.1 PLE intensity at about 1.88 eV of SSR Si nc at the size of 10 nm and SSR Si nc in TEOS dried at room temperature and annealed at 900 °C in O₂ ambient for i) 15 mins and ii) 1 hr.

It can be observed that the SSR Si nc and TEOS thin film possess the second type of NBOHCs. This is largely due to the absence of Si-OH and Si-H bonds as reflected in the FTIR spectra. However, when the SSR Si nc was embedded into the TEOS thin film, the third type of NBOHCs starts to appear. Multiple emission peaks at 1.38 eV, 1.55 eV, 1.70 eV and 1.88 eV have been observed in Fig. 5.5. The existence of the second type of NBOHC had been used to explain the 1.38 eV, 1.55 eV and 1.70 eV emission by Shen *et al.* [47] and Prokes *et al.* [59]. However, the luminescence at about 1.88 eV provides greater insight to the existence of the third type of NBOHC. Table 5.1 shows the PLE intensity at about 1.88 eV of SSR Si nc in TEOS dried at room temperature and annealed at 900 °C in O₂ ambient for i) 15 mins and ii) 1 hr respectively. It is observed that at about 1.88 eV, the emission intensity experiences an approximately five fold drop from 34671 to 7573 for the samples with 1 hr O₂ annealed. The presence of TEOS alone does not influence the drop in intensity. It is observed that when Si nc in TEOS thin film was dried at room temperature, the 1.88 eV intensity remains the same as the Si nc at 10 nm. However, with increasing annealing time at 900 °C, the quenching of PL intensity steps

in. Nagasawa *et al.* [154] has reported the interfacial strain between fiber and glass cladding can induce a third type of NBOHC at approximately 2 eV. The absorption loss of the fiber using glass cladding is six times more than fiber using silicone cladding. In this case, it is similar to Si nc in a glass matrix (amorphous SiO₂). It has been shown that as oxidation prevails with longer hours, strain between the Si nc and the surrounding amorphous SiO₂ increases [227, 228]. This is also been observed in the oxidation of Si nc alone in Section 3.6 where this strain induces self limiting oxidation. This strain incurred, with high annealing temperature, is capable of altering the Si crystal structure and bond length at the SSR Si nc/SiO₂ interface. Interfacial oxide defects, induced by this interfacial strain, can form a new emitting center [154]. This observation indicates that there is presence of the third type of NBOHCs in the structure of SSR Si nc/SiO₂ systems.

5.4 Summary

In conclusion, SSR Si nc, with grain size from 10 nm to 25 nm, has been synthesized to investigate its emission mechanism. These samples consist of SSR Si nc and SSR Si embedded in TEOS thin film via spin coating. PL results reveal that infrared emission has been observed in this form of SSR Si nc/SiO₂ system. The mechanisms for PL related to quantum confinement effect, amorphous Si component, Si-H, or Si-OH bond are excluded based on the experimental data of PL, Raman and infrared spectra for the SSR Si nc and SSR Si nc embedded in TEOS thin film. The experimental data also suggest that it is the oxide defects, such as NBOHCs that are responsible for PL. The NBOHCs

due to Si-O with lower quantum efficiency are observed for the SSR Si nc and TEOS thin film. On the other hand, the NBOHCs associated with strain between interfaces can be observed in the oxidized SSR Si nc/SiO₂ system.

Chapter 6: Electrical Studies of Solid-State Reaction Si Nanocrystals Embedded in TEOS Films

6.1 Introduction to Electrical and Electronic Applications of Si Nanocrystals

Silicon nanocrystals have interest many researchers in the area of memory applications [4, 5, 163, 201, 205, 229-233]. It serves as a potential substitute for bulky floating gate electrical erasable programmable read-only memory (EEPROM). This form of memory is commonly known as non-volatile memory (NVM). The driving force of this memory is derived from the short comings of EEPROM where dissipation of heat, charge loss and slow switching are becoming more critical with the evolution of high speed electronics [197]. It is visualized that if the floating gate of this EEPROM is small enough for the storage of one electron at a time, the mentioned problems will be solved. This leads to the evolution of quantum dot floating gate [197] called single electron tunneling devices. Many works [157, 158, 197, 234] have been done to investigate the mechanisms of these single electron tunneling devices. To observe and study single electron tunneling, early works reveal a few generally accepted properties [157, 158, 197]. They are:

- 1) this form of tunneling requires very small “islands” (< 10 nm) to store single electron where lateral spreading is minimized.
- 2) to observe single electron tunneling, the thermal fluctuations must be minimized. This is due to the fact that the tunneling electron contains two forms of energies – coulomb

energy and thermal energy. The coulomb energy is the interaction energy of electrons which is the area of interest. The thermal energy is proportional to temperature and tends to suppress the coulomb component at high temperature. Therefore, most of the coulomb blockage experiments must be done at ultra low temperature (<77 K).

Though it may seem that the characterization of single electron tunneling is somewhat difficult, it is fortunate that current NVM devices do not require such stringent conditioned environments. Single electron tunneling is only a mere basis for theoretical study. For real devices, small islands that do not allow charges to spread sideways or communicate are good enough for NVM. To realize quantum dot memory devices, many methods in creating silicon nanocrystal (Si nc)-based memory devices have been demonstrated. They include ion-implantation, chemical vapour deposition and co-sputtering, etc.. Alternatively, Si nc can also be produced by SSR [17, 187, 205, 235]. This is a simple and inexpensive method to create Si nc in bulk quantity. Such Si nc has been reported of its photoluminescence in the infrared range [9, 47] and is an inexpensive emission source that is compatible with today Si technology. In parallel to the light emission research, the electrical properties of Si nc embedded in SiO₂ layer has also been actively researched [205]. Ever since the first Si nc memory device has been reported by Tiwari *et al.* [4], memory effects of Si nc have been widely studied [4, 5, 163, 201, 205, 229-233]. However, there has not been any reported Si nc memory devices fabricated using the method of SSR and spin-coating. In this study, capacitor using this method has been fabricated. Extensive study on the charging ability has been carried out.

At the same time, the conduction phenomena of the charges within the Si nc is also critical. Various mechanisms of tunneling through the Si nc have been reported [236-239]. These mechanisms include space-charge limited current (SCLC) [236-238, 240, 241], Poole-Frenkel (PF) tunneling [236, 242] and percolation theory [239]. In depth investigation of the conduction mechanisms through these Si nc allows for better understanding of the behavior of charges inside or around the Si nc and the kinetics for the trapping phenomena.

In this chapter, the electrical properties of SSR Si nc are investigated. The author also reports on the fabrication of first metal-insulator-semiconductor (MIS) structure fabricated using the spin-coating Si nc, synthesized by SSR, embedded in tetraethylorthosilicate (TEOS) thin film (represented by SNT) followed by short duration of dry oxidation. Different considerations of the oxide integrity issues will also be addressed in this chapter. This MIS structure will be used to study the charging/discharging phenomena of the SSR Si nc. Other than the MIS structure, capacitor structure that utilizes high concentration of SSR Si nc as the insulator layer has also been fabricated. The conduction mechanisms of these SSR Si nc will also be studied in detail.

6.2 Fabrication of Solid-State Reaction Si nc Capacitors

In this section, two structures of capacitors are fabricated. Fig 6.1 shows the fabrication schematic flow of these two structures. The first structure resembles a MIS structure where Si nc are embedded as a layer inside the insulator. It involves the method of spin-coating SSR Si nc embedded in tetraethylorthosilicate (TEOS) thin film (represented by SNT). This is similar to the conventional capacitor structure for Si nc NVM [1-3]. However, there is a slight deviation from the conventional structure. In this study, the control SiO₂ layer will not be fabricated. The reason is due to the complication of the growth of subsequent SiO₂ control oxide. However, this structure, alone, is already capable of displaying good performance of charging/discharging ability which will be revealed in the subsequent sections. As for the second structure, the bulk insulator is the Si nc and the insulator is used to fill up the gaps in between the Si nc. In other words, this structure can be visualized as a minority species of TEOS embedded among the Si nc (represented by TSN). As the majority species are SSR Si nc, this structure allows in-depth study of the conduction mechanism through the Si nc rather than the conventional MIS structure where the majority species are SiO₂ [156, 230].

Fig. 6.1 Fabrication schematics of these SNT and TSN structures

6.2.1 Fabrication of SNT Capacitors

The fabrication of SNT capacitor requires little or no agglomeration of Si nc as this will be the first step to NVM devices. To achieve this, the author employed the method as described in Chapter 4. The 20 hrs SSR Si nc were further treated with 20 wt% texanol-based solvent to segregate the Si nc agglomeration and later dispersed in ethanol. This suspension was centrifuged and the supernatant was extracted. The embedding of Si nc in TEOS thin involved the mixing of the TEOS solution, 99.999% pure TEOS solution

purchased from Sigma-Aldrich Co, with ethanol, deionized water and the supernatant. TEOS was first mixed with either the supernatant or residue and deionized water in the mole ratio of 1:4:4, resulting in 4.19 g of solution. After thorough stirring, hydrochloric acid (37 wt% in water) was added into the solution to catalyze the hydrolysis. The steps to synthesized SiO_2 from TEOS are similar to the method as described in Chapter 5. However, this TEOS thin film will be too thick for dielectric layer. Further dilution of the TEOS solution is necessary for this structure. Therefore, after hydrolysis for 48 hours, 50.72 g of the supernatant was added to the solution. This mixture was stirred for another 24 hours. The mixing of the solution was done in N_2 environment so as to prevent gelation. N-type <100> Si wafers with a resistivity of 5~10 Ωcm were used as the substrates. Each layer of film of ~ 28 nm thickness containing Si nc, was spun onto the substrate at 3000 rev/min for 30 s. The thickness of each film layer is characterized using Filmetric F20 from Filmetric Inc. The film containing Si nc was annealed in O_2 for 15 min, followed by N_2 for 15 min, at 900 $^\circ\text{C}$ to reduce Si wafer/ SiO_2 interfacial traps and defect density in the device [24]. Aluminum (Al) was evaporated as the top electrodes (100 μm in diameter). The native SiO_2 on the backside of the Si wafer was etched away before Al bottom electrode was being deposited. The preparation and spin coating process were all carried out in class 100 clean room environment.

6.2.2 Fabrication of TSN Capacitors

After milling for 20 hrs the Si nc were dispersed in ethanol. This suspension was centrifuged and the residue was extracted. The embedding of Si nc in TEOS thin film

involved the mixing of the TEOS solution, 99.999% pure TEOS solution purchased from Sigma-Aldrich Co, with ethanol, deionized water and the residue. TEOS was mixed with ethanol and deionized water in a mole ratio of 1:4:4. After thorough stirring, hydrochloric acid (37 wt% in water), at a mole ratio of 1:10 with TEOS, was added into the solution to catalyze the hydrolysis. After hydrolysis for 48 hours, the residue, at a mole ratio of 8:1 with TEOS, was added to the solution. This mixture was stirred for another 24 hours. The mixing of the solution was done in N_2 environment so as to prevent gelation. P-type $\langle 100 \rangle$ Si wafers with a resistivity of 10~20 Ω cm were used as the substrates. Each layer of film, containing SSR Si nc, was spun onto the substrate at 3000 rev/min for 30 s (~300 nm thick). The thickness of each film layer was characterized using Filmetric F20 from Filmetric Inc. The film containing SSR Si nc was annealed in air for 6 min at 800 °C to densify the film. Aluminum (Al) was evaporated to form the top electrodes (150 μ m in diameter). The native SiO_2 on the backside of the Si wafer was etched away before the Al bottom electrode was deposited. The preparation and spin coating processes were all carried out in a class 100 clean room environment.

6.3 Capacitance-Voltage (CV) and Memory Characterization of Si Nanocrystal MOS Capacitor

As demonstrated by Tiwari et al., the basic function of Si nc-based MOSFET is a memory device. Fig 2.10 in Chapter 2 shows the basic unit of a transistor operating with nanocrystals embedded in the gate oxide and operations such as Write, Store and Erase are carried out in the nanocrystals [4]. The only difference between the Si-based MOS

capacitor and MOSFET is the absence of the source and drain. To achieve the memory effect, the Si nc must have the ability to be charged and discharged. MOS capacitor is a simplified structure to study the charging/discharging effects of the Si nc. It is well-known that stored charges in dielectric layer will results in a shift in band flat voltage (V_{FB}) [18]. The shift in V_{FB} is given as [18]:

$$\Delta V_{FB} = -\frac{Q_{ox}}{C_{ox}} \quad (6.1)$$

where ΔV_{FB} is the flat-band voltage shift, Q_{ox} and C_{ox} are the stored charges and capacitance of oxide respectively. Therefore, a change of V_{FB} in the CV measurement can be used to monitor the charging and discharging behaviour of the Si nc in the Si nc-based MOS capacitor [205, 243-247].

6.3.1 Engineering a High Integrity Oxide

As featured in Eqn. 6.1, though the stored charges can be due to the Si nc, it can also be due to defects of the host SiO_2 itself. It is widely accepted [18] that there are four main types of charge trapping elements in the oxide. They are the mobile ionic charges, fixed oxide charges, oxide trapped charges and interface trapped charges [18]. These charges are present in the oxide as a result of impurities and process imperfections. They can also contribute to the shift in V_{FB} [18]. These charges are undesirable and result in a low integrity oxide. Therefore, further treatment to the TEOS thin film must be carried out to increase the integrity of the oxide.

It is well known that wet oxide has a higher defect density than dry oxide [18], therefore, two additional annealing steps have been implemented in the fabrication process. This includes 1) an O₂ anneal to densify the TEOS thin film and reduce the interfacial defects at the Si wafer and SNT/TSN layer and 2) a N₂ anneal to reduce the defects in the TEOS thin film. Fig 6.2 illustrates the CV characteristics of SNT structure annealed a) in air at 500°C for 5 min, b) in N₂ ambient only at 900 °C for 15 min, c) in O₂ ambient only at 900 °C for 15 min and b) in O₂ ambient followed by N₂ ambient at 900°C for 15 min respectively.

Fig 6.2 CV characteristics of SNT structure annealed (a) in air at 500°C for 5 min, (b) in N₂ ambient only at 900 °C for 15 min, (c) in O₂ ambient only at 900 °C for 15 min and (d) in O₂ ambient followed by N₂ ambient at 900°C for 15 min respectively.

Fig 6.2(a) reveals that, without any annealing, no visible switching in CV trend is observed. This is probably due to the massive amount of defects and interface traps between the Si wafer and the SNT layer. Therefore, it is inevitable that there is large amount of interface traps which results in such a CV trend. Upon N_2 annealing at $900\text{ }^{\circ}\text{C}$, as featured in Fig 6.3(b), visible trend of CV switching is observed. Nonetheless, the CV behaviour is still unstable with inconsistent double CV sweep characteristics. This is probably due to the degradation of the structure upon the charging/discharging of the SNT structure at the interface. To reduce the interfacial traps problem, O_2 annealing is necessary to create creates more SiO_x ($x = 1, 2$) bonds between the Si wafer and the SNT layer. It will help to bridge the poor adhesion of the Si wafer and the SNT layer. As observed in Fig 6.3(c) when SNT structure is oxidized at $900\text{ }^{\circ}\text{C}$ for 15 min, the CV behaviour is consistent upon oxidation even in the CV double sweep characterization. However, one problem remains, that is the existence of oxide defects. This can be observed from Fig 6.3(c) where there is a V_{FB} shift of $\sim 0.3\text{ V}$. But, at the same time, oxide defects can also trap charges. At a low voltage of -4 V , the Si nc should not be able to store charges as the E-field is not strong enough to sweep the electrons to the Si nc. The most probable reason is the presence of massive amount of oxide defects. To verify and correct this problem, a subsequent N_2 anneal step is employed. This is well known [18] that N_2 anneal is capable of annealing defects in oxide. Fig 6.3(d) reveals the effect of the subsequent N_2 anneal at $900\text{ }^{\circ}\text{C}$ for 15 min. The V_{FB} shift has been eliminated with this anneal step. This also proves that the V_{FB} shift in Fig 6.3(c) is an effect of oxide defects, which is consistent with other reports of wet oxide [18]. At the same time, the N_2 anneal also results in the relaxation of stress which indirectly reduces the amount of stress

induced defects. With the problem of oxide defects and interfacial traps being eliminated, the SNT structure will be a reasonable oxide structure to study compared with those derived from other synthesis methods such as ion-implantation, CVD and sputtering [163, 229-233].

6.3.2 V_{FB} Shift Si nc in TEOS Thin Film

Fig. 6.3 shows the schematic cross section of metal-Si nc/SiO₂-Si substrate capacitor using the spin coating method. A single layer of Si nc in TEOS solution is spin coated onto the Si wafer. Upon oxidation, part of the Si substrate will be oxidized, forming the SiO₂ layer. Another thinner layer of SiO₂ is also grown between the electrode and Si nc as a result of continuous grown of oxide layer. This is different from other Si nc capacitors [1-3] where injection of electrons occurs from the electrode via direct tunneling to the Si nc when a bias voltage is applied. The resultant stored charges screen the gate charges and effectively shift the V_{FB} more positive. The magnitude for a single electron per nanocrystal is approximately (as modified from S. Tiwari [4]):

$$\Delta V_{FB} = \frac{qn_{nc}}{\epsilon_o\epsilon_{ox}} \left(t_{cnd} + \frac{\epsilon_{ox}}{\epsilon_{Si}} t_{nc} \right) \quad (6.2)$$

where n_{nc} is the concentration of nanocrystals, t_{cnd} is the thickness of control oxide, t_{nc} is the diameter of the nanocrystal sphere and ϵ_{Si} and ϵ_{ox} are the permittivity of the silicon and oxide respectively.

Fig. 6.3 Schematic cross section of metal-Si nc/SiO₂-Si substrate capacitor using spin coating

Fig. 6.4 shows the C-V characteristics of (a) the pure TEOS thin film and (b) Si nc without organic vehicle in TEOS thin films annealed in O₂ ambient at 900 °C for 1 hr with a CV double sweep from -8 V to 8 V then back to 8 V. Hysteresis effects are observed in the SNT films. This signifies the charging effect of Si nc. A V_{FB} shift of 0.39 V is observed. For Si nc of 10 nm in size and a control oxide thickness of 10 nm, the concentration is found to be $6.3 \times 10^{11}/\text{cm}^2$ using Eqn 6.2. This is much lesser (1 order) than many other Si nc fabrication methods [4, 6, 201]. Furthermore, by assuming a 5 nm spacing between each Si nc as observed in Fig.6.6b, the density of Si nc is only $4.44 \times 10^{11}/\text{cm}^2$, which is lower than the calculated amount of $6.3 \times 10^{11}/\text{cm}^2$. This signifies that there might be more than 1 electrons trapped in one SSR Si nc which will be further illustrate in section 6.4.1. Nonetheless, it is a much inexpensive method of fabrication of Si nc/ SiO₂ MOS capacitor as a form of memory device using SSR and spin coating. From the AFM of the surface profile of this Si nc/ SiO₂ system, the smooth surface has good compatible form for subsequent metal deposition and will greatly reduce the noise in C-V signals. This advantage can be observed in Fig. 6.5(a) where very little noise is detected.

Fig. 6.4 C-V characteristics of (a) the pure TEOS thin film and (b) Si nc without organic vehicle in TEOS thin films annealed in O_2 ambient at $900^\circ C$ for 1 hr with a CV double sweep from -8 V to 8 V then back to -8 V

Fig. 6.5 shows the C-V characteristics of Si nc coated with organic vehicles in TEOS thin film annealed in O_2 ambient for (a) 1 hr and (b) 2 hr respectively. Though the saturation capacitance is unstable (due to the uneven interfacial contact between the film and Al contact), the V_{FB} does not shift considerably as compared to Si nc without organic vehicle. The presence of the V_{FB} shift indicates that the Si nc are not fully oxidized after 2 hr of oxidation at $900^\circ C$, indicating the possible self-limiting oxidation [60, 199, 200] of Si nc. The V_{FB} shift for Si nc coated with organic vehicles in TEOS thin film annealed in O_2 for 1 hr is 0.31V and for 2 hr is 0.3V. As compared to the Si nc without organic vehicle in TEOS thin film, there is no significant difference in the V_{FB} shift. However, the density of Si nc with organic vehicles is higher than Si nc without organic vehicle as demonstrated in Chapter 4. If the author assumes that the TEOS thin films containing the

Si nc are identical, the charging effect of the Si nc will depend on either the bulk mass of the Si nc or the interface between the Si nc and SiO₂ or both. It has been observed by many other researchers [37] that Si nc exists in a spherical form. So, the change in surface area ($\Delta S/S$) and volume ($\Delta V/V$) can be derived as:

$$\frac{\Delta S}{S} = \left(\frac{d_2}{d_1} \right)^2 - 1 \quad (6.3)$$

$$\frac{\Delta V}{V} = \left(\frac{d_2}{d_1} \right)^3 - 1 \quad (6.4)$$

where d is the diameter of the spherical Si nc. Therefore, as the size of the Si nc reduces, the V_{FB} shift should reduce drastically if the charges are trapped in the bulk of the Si nc and should only reduce a little if the charges are trapped at the interface of Si nc and SiO₂. The percentage difference between the change in V_{FB} shift of Si nc with organic vehicles and without organic vehicle is approximately $\frac{3.9-3.1}{3.9} \times 100\% = 2.05\%$.

However, using the peak particle size concentration of Si nc with and without organic vehicle in Table 4.2, percentage of $\Delta S/S$ and $\Delta V/V$ are approximately 137.9% and 266.6% respectively. From this difference between the change in V_{FB} shift, surface area and volume, it is difficult to conclude whether the charges are trapped in the surface area or bulk Si nc or both as the decrease due to $\% \Delta S$ and $\% \Delta V$ are much greater than decrease in $\% \Delta V_{FB}$. Nevertheless, by using Eqn. 6.2, it can be understood that the amount of V_{FB} shift is dominantly controlled by the number of nanocrystals, rather than the size of the nanocrystals.

Fig. 6.5 C-V characteristics of Si nc with organic vehicles in TEOS thin film annealed in O₂ ambient at 900°C for (a) 1 hr and (b) 2 hr.

6.3.3 CV Characterization of SNT Structure Without Control Oxide

Fig. 6.6 shows (a) the SNT capacitor structure, (b) the TEM image of Si nc in the SNT layer and (c) the cross-sectional TEM of the SNT structure.

Fig. 6.6 shows (a) the SNT capacitor structure, (b) the TEM image of Si nc in the SNT layer and (c) the cross-sectional TEM of the SNT structure. This is the first report on the use of Si nc synthesized by SSR metal-insulator-silicon capacitor for electronic devices. Compared to other conventional Si nc in SiO₂ matrix system [4, 201, 243-245], the SNT capacitor structure has no control oxide. From the TEM observation, the average size of the Si nc is between 4 to 10 nm. This size is consistent with the results obtained from X-ray diffraction and Scherrer's equation. At the same time, this is also the common size range used for the study of electrical properties of Si nc [4, 5, 201]. An approximately 6 nm of thermal oxide is formed between the SNT layer and Si substrate during the O₂ annealing. This layer will also enhance the interface integrity between the SNT layer and Si substrate. Fig. 6.7 shows the C-V characteristics when the SNT capacitor is biased for 1 sec with (a) positive 13 V and (b) negative 25 V respectively. The V_{FB} shift reveals that there are stored charges in the SNT layer. According to Eqn 6.1, the SNT will experience hole trapping when it is biased at +13 V and electron trapping when it is biased at -25 V. This phenomenon contradicts the conventional Si nc/SiO₂ capacitor case where positive bias voltage leads to electron trapping and vice versa [4]. This is primarily due to the absence of the control oxide which results in electrode injection of carriers instead of substrate injection. This charge trapping phenomenon is unlikely due to electric field induced defects in the oxide. Interfacial defects, which can be observed from substantial reduction of CV gradient [18], is an indication to defects formation during voltage biasing. However, this is not being observed in Fig 6.7. Many groups have attributed the charging and discharging phenomenon of Si nc to charge-quantization within the Si nc core [157, 234, 248, 249].

However, it has also been reported [250, 251] that traps present at the interfaces of Si nc or defects of Si nc are capable of inducing charge trapping as well. Lu *et al.* [16] has reported that high energy ball milling is often capable of creating structural defects like surface defects and dislocations, etc. These defects can act as efficient charge trapping centers [250, 251]. These two mechanisms may be working concurrently to enable charge trapping in these Si nc.

Fig. 6.7 C-V characteristics when the SNT capacitor is biased for 1 sec with (a) positive 13 V and (b) negative 25 V respectively.

Fig. 6.8 V_{FB} shift, due to varying bias voltages for 1 sec, of (a) TEOS thin film only and (b) SNT layer.

Nonetheless, it is important to differentiate between charging effects contributed by the Si nc, the bias voltage-induced traps in the TEOS oxide and the possible remains of

texanol-based solvent. Texanol-based solvent has a low boiling point of 260 °C and most of the organic bonds are eliminated at 900 °C. It is reported [18] that the presence of a high electric field can create defects in the oxide that lead to its breakdown. These complications from oxide defects can also cause confusions to whether it is the Si nc or oxide traps that create the charging and discharging of the SNT layer. Fig 6.8 shows the V_{FB} shift, due to varying bias voltages for 1 sec, of (a) TEOS thin film only and (b) SNT layer. Considerable amount of V_{FB} shift in TEOS thin film can only be observed with bias voltages less than -30 V or greater than +17 V. This implies that at bias voltage less than -30 V or greater +17 V, significant amount of traps and defects are induced. However, the V_{FB} shift in the SNT layer as shown in Fig. 6.9(b), can be observed in lower bias absolute values at approximately -23 V and +8 V. Charging effects are already being observed in SNT layer before the critical bias voltage when traps and defects are being significantly developed in the oxide media. This indicates that the Si nc indeed has charge trapping ability. The V_{FB} shifts, experienced by the SNT capacitor, induced between -23 V to -30 V and +8 V to +17 V can be attributed to the presence Si nc.

Fig 6.9 Retention time characteristics of the SNT capacitor biased at 16 V for 1 sec.

Fig 6.9 shows the retention time characteristics of the SNT capacitor biased at 16 V for 1 sec. It had been reported that single-electron trap can have a retention time of at least 12 hours (4.32×10^4 sec) at temperature around 50 mK [248, 252]. It is further reported that the Si quantum dots in SiO₂ matrix with a top control oxide has long retention time (up to 5×10^4 sec) with about 10% change in threshold voltage [244]. An exponential decay curve has been used to fit the SNT capacitor retention time behavior in Fig 6.9. This decay in V_{FB} in this SNT structure is probably due to the absence of top control oxide. The early drastic decay at the initial 300 sec is probably due to the discharge from shallow traps of both the oxide and Si nc. However, decay rate starts to reduce and stabilize as time prevails. Upon linear interpolation, the time required to discharge the SNT capacitor by 10% is 4480 sec. As the bias voltage employed in the retention time characterization is below the critical bias voltage for TEOS thin film to induce traps and defects that can cause V_{FB} shift, this provides further evidences to the charge trapping ability of the Si nc. The significantly lower retention time, as compared to other reported Si nc/SiO₂ capacitor [244], is largely due to the absence of the top control oxide which can act as an energy barrier for the tunneling of electrons to and from the electrodes. Nonetheless, it is shown that even though there is no control oxide in this SNT capacitor and the SNT layer is near the electrode, the decay in charges is not instantaneous or drastic throughout. Hence it should be possible to build an SNT capacitor with excellent charge retention if a control oxide is fabricated on top of the SNT layer.

6.3.4 SNT structure with control oxide

6.3.4.1 Structure of SNT with TEOS control oxide capacitors

Fig 6.10 Structure of SNT with TEOS control oxide capacitor

Fig 6.10 shows the structure of SNT with TEOS control oxide capacitor. This structure is fabricated to investigate the integrity and the effectiveness of the TEOS control oxide. The fabrication steps are similar to those in Fig 6.1. However, an additional spin coating of TEOS solution is inserted before the annealing. The eventual specifications of this SNT with TEOS control oxide structure has a tunnel oxide ~ 8 nm, Si nc ~ 20 nm and control oxide ~ 25 nm. These thickness measurements are taken using the Filmetric F20 from Filmetric Inc.

6.3.4.1.1 CV characterization of SNT with TEOS control oxide capacitor

Fig 6.11 Flat-band voltage shift due to (a) positive and (b) negative gate bias.

Fig 6.11 shows the flat-band voltage due to (a) positive and (b) negative gate bias. As observed from Fig 6.11(a), using a positive bias, a net V_{FB} shift of -1.2 V is experienced. On the other hand, when a negative bias is being used, a net V_{FB} shift of 0.53 V is observed. This shift represents charge trapping in Si nc. This charge trapping phenomena is not observed in the pure SiO_2 layer (which is derived from TEOS spin coating). This presents the feasibility of creating memory devices using such derived structure. However, from the direction of the shift in V_{FB} , it can be observed that upon a positive bias, net hole trapping occurs while net electrons trapping occurs for negative bias. This is similar to the SNT without TEOS control oxide. It has been shown [4, 5, 201] that the control oxide of Si nc capacitors are high integrity oxide with little leakage. This is often achieved with dry oxidation. However, in this case, the control oxide is fabricated using a layer of TEOS. This form of oxide is similar to wet oxide. When compared with dry oxidation, the oxide integrity is poorer and leakage is relatively higher and hence ineffective as a control oxide.

Fig 6.12 Hysteresis due to (a) positive and (b) negative gate bias.

Fig 6.12 shows the hysteresis due to (a) positive and (b) negative gate bias. Onset of hysteresis can be observed at a positive bias voltage of 4 V to cause a V_{FB} shift of -0.35 V and negative bias voltage of -8 V to cause a V_{FB} shift of 0.34 V. This implies a small programming voltage is required for storage charges in the Si nc. Increment of biasing voltage creates increased charges trapped in the Si nc. This is shown by the increased hysteresis in Fig 6.13. However, as bias voltage increases, the capacitance starts to deviate to form similar C-V characteristics as observed in cases of heterostructure. Fig 6.14 shows the C-V characteristics of the SNT with TEOS control oxide capacitor stressed at a voltage of 15 V. Two V_{FB} , at approximately -4.45 V and -0.8 V respectively, can be identified. This similar hole-trapping phenomenon is also observed by Chandrasekaran *et. al.* [253]. In his paper, a strained Si MOSFET C-V characteristics is been modeled. This suggests that the Si nc in this case might be strained too. This is possible as ball milling can cause lattice strain to the Si nc which is widely published [16].

Fig. 6.13 C-V characteristics of the SNT with TEOS control oxide capacitor at stressed at a voltage of 15 V

6.3.4.1.2 Retention time characterization of SNT with TEOS control oxide capacitor

Fig. 6.14 Retention time characteristics of pure TEOS thin film, Si nc in TEOS layer only and Si nc thin film with TEOS control oxide.

To further verify the leakage due to the presence of carbons and low integrity oxide, a retention time test is carried out for the three samples stressed at +15 V. Fig 6.14 shows the retention time characteristics of pure TEOS thin film, Si nc in TEOS layer only and Si nc thin film with TEOS control oxide. There is virtually no V_{FB} shift experienced by the pure TEOS thin film. The Si nc in TEOS layer only presents a fast saturation as compared to Si nc layer with TEOS control oxide. The reduced V_{FB} can be attributed to the “loosely-attracted” charges on the Si nc interfaces. This also shows that the TEOS control oxide might be of lower integrity. However, the presence of this oxide still causes a barrier between Si nc and the gate as compared to that with no control oxide. Furthermore, it is observed that for Si nc layer with TEOS control oxide, as the time

approaches 1500 sec, the V_{FB} shift saturates at a value of $1.26 (\pm 0.01)V$. However, for Si nc layer in TEOS layer only, the V_{FB} shift continues to reduce as it approaches 2000 sec. It can be deduced that although charges are trapped in the Si nc, during the capacitance measurements, discharging from the Si nc is occurring simultaneously without the control oxide. Hence, the presence of the TEOS control oxide is capable of retaining the charges in the Si nc.

6.3.4.1.3 Effect of stress time of V_{FB} shift of SNT with TEOS control oxide capacitor

Fig. 6.15 Variation of V_{FB} shift at different stress time.

Fig 6.15 shows the variation of V_{FB} shift at different stress time. Shift in V_{FB} is not of consistent direction with respect to different stressing time. There is an initial negative V_{FB} shift but as stressing time proceed beyond 0.25 sec, positive V_{FB} shift is experienced. This indicates a shift from holes trapping to electrons trapping. The shift in holes trapping into electrons trapping can be attributed to the competition between the tunneling from

the substrate to Si nc and from Si nc to the top Al electrodes [254]. This phenomenon is also observed for AlN nanocrystals [254]. Fig 6.16 shows the schematics of tunneling kinetics in the case of Si nc in TEOS thin film with control oxide. With a short period of positive voltage bias, due to the thin tunnel oxide, the electrons tunneling from substrate dominates over the electrons tunneling from Si nc to gate electrode. Nevertheless, due to the TEOS control oxide being of a lower integrity oxide with higher amount of traps, the tunneling of electrons from Si nc to the gate electrode is also relatively high at high electric field (E-field). However, at longer period of positive voltage bias, holes trapping dominate as the tunneling of electrons from the Si nc becomes traps assisted tunneling. Furthermore, due to the higher integrity oxide as seen in the tunnel oxide, the electron tunneling from oxide remains lower relative to the tunneling in the TEOS control oxide. This explains why even at short period of positive voltage bias, the V_{FB} shift into the positive region is low as compared that reported by Liu *et. al.* [254].

Fig 6.16 Schematics of tunneling kinetics in the case of Si nc in TEOS thin film with control oxide.

Fig 6.17 (a) Current - voltage characteristics of Si nc in TEOS thin film with control oxide and TEOS thin film only, (b) Current density - E-field characteristics of Si nc in TEOS thin film with control oxide and TEOS thin film only.

Fig 6.17(a) shows the current – voltage (IV) characteristics of Si nc in TEOS thin film with control oxide and TEOS thin film only and 6.17 (b) shows the current density - E-field (J-E-field) characteristics of Si nc in TEOS thin film with control oxide and TEOS thin film only. There are two major humps for the Si nc in TEOS thin film with control oxide at 5.5 V and 10.5 V respectively. FN tunneling is ruled out since on increased ramp due to FN tunneling is not experienced. It is known that the energy barrier for thermal oxide and Si wafer is approximately 3.1 eV. If the 5.5 V hump corresponds to the energy barrier of the Si wafer and thermal oxide, this will results in a large movement of electrons from the Si wafer to the Si nc when the energy required to overcome the energy barrier is reached. However, the second hump is only 5 V higher. By proportionality, this corresponds to an energy barrier of 2.81 eV. This represents an energy bandgap of approximately 1.41 eV and is in agreement with the quantum confinement theory. This

energy bandgap also corresponds to the photoluminescence results which occur at 1.42 eV [9, 47]. This verified the effect of bandgap expansion as a result of nanometric sizes.

6.3.4.1.4 Summary of SNT with TEOS control oxide capacitor

Charge trapping can be observed by SSR Si nc in TEOS thin film. Furthermore, good retention of these charges is being observed. Other phenomena, such as heterostructure behaviours, hole trapping during positive bias and completing substrate and Si nc injection of electrons during positive bias, have also been observed in this structure. These phenomena are very different from conventional Si nc in SiO₂ matrix capacitors [4, 201] are explained. For a better comparison and facilitation of substrate injection carriers (which is the common operation of FLASH memory [4, 201]), a higher integrity control oxide must be fabricated to prevent electrode injection.

6.3.4.2 Structure of SNT with PECVD control oxide capacitors

Fig 6.18 Structure of SNT capacitor with PECVD control oxide.

SNT capacitor with PECVD control oxide used as a replacement for the TEOS control oxide is then fabricated to investigate the integrity and the effectiveness of the PECVD control oxide. However, an additional PECVD step of silane and oxygen is

inserted before the annealing. The eventual specifications of this SNT with TEOS control oxide structure has a tunnel Oxide ~ 10 nm, Si nc ~ 30 nm and Control Oxide ~ 20 nm. These thickness measurements are taken by Filmetric F20 from Filmetric Inc. Fig 6.18 shows the structure of SNT with PECVD control oxide capacitor. In this study, PECVD oxide used is believed to be of a higher integrity and less conducive oxide.

6.3.4.2.1 V_{FB} shift of SNT with PECVD control oxide capacitor

Fig. 6.19 V_{FB} shift with respect to stress voltage for SNT with PECVD control oxide capacitor

Fig. 6.19 shows the V_{FB} shift with respect to stress voltage for SNT with PECVD control oxide capacitor. Hole trapping can be observed at negative voltage of <-10 V, whereas electron trapping can be observed at positive voltage of >15 V. This is consistent with conventional Si nc memory. Two turning points in V_{FB} shift is observed at 30 V and -50 V respectively. This is due to the PECVD oxide giving way to the tunneling charges. It is important to note that this is a 62 nm thick SNT capacitor, and at 30 V, the electric field (E-field) is approximately 4.84 MV/cm. For conventional SiO₂ thermal oxide, the

onset of FN tunneling occurs generally at 5 MV/cm which is close to this E-field. It is further verified by a positive stressing of 5.9 MV/cm on pure PECVD oxide where holes trapping start to show up in its CV graph. As discussed earlier, for the tunneling in the negative stress region, carriers tunneling probability is generally lower due to the minority carriers in the N-type substrate forming the inversion layer as compared to accumulation. Therefore the onset of negative stress FN tunneling occurs at a much higher E-field. It is also verified by a negative stressing of 7.6 MV/cm on pure PECVD oxide where electrons trapping is observed in its CV graph.

6.3.4.2.2 Retention time of SNT with PECVD control oxide capacitor

Fig. 6.20 shows the comparison of retention times for both SNT without control oxide capacitor stressed at 20 V and SNT with PECVD control oxide capacitor stressed at -16 V. Discharging rate is high for both structures at shorter times (<1500 sec). This is largely due to discharging at shallow traps. The SNT without control oxide capacitor, the discharging continues at a decreasing rate. However, for SNT PECVD control oxide capacitor, there is virtually no discharging after 1500 sec. This is largely attributed to the PECVD control oxide which greatly reduces the probability of tunneling. Interestingly, it is noticeable that in the case of SNT without control oxide, the charge trapping capability is still high. This is contrary to normal perception that discharge is drastic due to the proximity of the electrode and Si nc. This is probably due to the charges trapping at the surfaces and defects in SSR Si nc.

Fig. 6.20 Comparison of retention times of SNT without control oxide capacitor stressed at 20 V and SNT with PECVD control oxide capacitor stressed at -16 V.

6.3.5 Summary on SNT capacitors

It has been demonstrated that SNT structures are able to store charges which are possible candidates for NVM devices. Long retention times and low stress voltage is achieved even without control oxide. However, this leads to electrode injection as compared to conventional devices with substrate injection. Longer retention time can be achieved for devices with control oxide. For such device, the challenge is the development of a high integrity control oxide. Thermal oxidation as the control oxide is impossible as this will lead to the oxidation of the Si nc which will consume most of the Si nc in the process. Therefore, in this study, TEOS and PECVD control oxides have been used as alternatives for the control oxide of SNT. From the investigations, it is revealed that TEOS control oxide possesses longer retention than SNT without control oxide. However, the charges are injected from electrode. This represents a high

conductivity of the oxide which is of low oxide integrity. The SNT with PECVD control oxide possesses excellent retention and charges injected from substrate. However, breakdown of the PECVD oxide occurs at a relatively low E-field of 5 MV/cm.

6.4 Carrier Transport and Conduction Mechanism of Solid-State Reaction Si Nanocrystals

Very few investigations of the macroscopic electronic conduction mechanism across Si nc films have so far been reported [236, 237]. There are also numerous reports indicating that electronic transport through a single nanocrystal shows strong single-electron charging effects at low temperature [157, 158, 197]. However, this effect is not fully understood in the practical cases where there are large amounts of nanocrystals. At high bias, it is possible to observe electron emission from thin films of nanocrystals [255]. Currently, there are a few models, such as the percolation model [239] and space-charge limited current model [236, 237, 240, 241], being reported to describe the macroscopic electronic conduction mechanisms in nanocrystal films. Although SSR Si nc provides an easy method to fabricate high density Si nc film, none of these models has been used to investigate the macroscopic electronic conduction mechanism of this form of Si nc film. In this project, investigation on the dominating conduction mechanism of SCLC in this SSR Si nc film has been carried out. At the same time, the characteristic temperature and trap density of this form of SSR Si nc film are derived using the SCLC model. Furthermore, the possible candidates of the traps are also identified using HRTEM images.

6.4.1 SCLC Modeling

Fig. 6.21 TEM image of the SSR Si nc in the film.

Fig. 6.21 shows the TEM image of the SSR Si nc in the film. From the TEM observation, it is observed that the average size of the Si nc is between 4 to 10 nm. Using Lambert-Beer's law, the UV-visible spectroscopy results reveal that the weight ratio of Si nc to ethanol (of the residue) is 1:0.12. Using the volume of the thin film, weight ratio of Si nc with ethanol and zinc-blende structure of Si, it is derived that the eventual Si nc number density is $\sim 1.36 \times 10^{16} \text{ cm}^{-3}$. Fig. 6.22(a) shows the IV characteristics of a 150 μm diameter diode from 305 K to 400 K on a log-log plot. The inset of Fig 6.22(a) shows IV characteristics of the device from -10 to 1.5 V (linear scale) at 305 K. A positive voltage is applied to the substrate contact which corresponds to a forward biased substrate. The IV curve reveals a rectifying behavior. The rectifying ratio at 300 K, $I_F/I_R = 165$ at $|V| = 2.5 \text{ V}$, and the turn-on voltages for forward and reverse bias are $V_F \sim 1.25 \text{ V}$ and $V_R \sim -9.1 \text{ V}$ respectively. This rectifying nature is due to the p-Si/Si nc/top Al

electrode [237]. The IV characteristics of this device can be represented by a serial combination of a diode and a resistor [236, 238]:

$$I = I_o \exp\left[\frac{q(V - IR)}{nkT}\right] \tag{6.5}$$

where I_o is the saturation current in reverse bias, n is the ideality factor, and R is a resistance usually assumed to be independent of applied voltage. Fig 6.22(b) illustrates the curve fitting of IV characteristic at 300 K based on Eqn. 6.5. The general behavior of the IV curve is reproduced with an ideality factor n of ~ 13.1 and a series resistance R of $\sim 1487 \, \Omega$. This high ideality factor suggests that the IV characteristic of this device is not limited by the metal/semiconductor Schottky barrier, but rather the carrier transport through the SSR Si nc itself [236, 238].

Fig. 6.22(a) IV characteristics of a 150 μm diameter diode from 305 K to 400 K on a log-log plot. Inset: IV characteristics of the device from -10 to 1.5 V (linear scale) at 305 K. 6.23(b) Curve fitting of IV characteristic at 305 K based on Eqn (6.5).

When the voltage applied is above its turn-on voltage, the current increases along a straight line in the log-log plot as shown in Fig 6.22(a). This relationship corresponds to the power law where $I \propto V^m$. In the range from 305 K to 400 K, it is found that m varies from 2.68 to 1.03 with a corresponding threshold voltage from 1.25 V to 0.42 V. The reduction in m leads a convergence of the IV behavior from 305 K to 400 K where the curves can be extrapolated to meet at a single point as shown in Fig 6.23(a). It has been demonstrated [237] that Si nc, fabricated by plasma decomposition of SiH₄, exhibits a similar trend from 200 K to 300 K. Rose [241] and Mark *et al.* [240] explained this behavior by using SCLC model with an exponential density of traps. In our devices, free carriers are injected from the substrate into the transport states in the Si nc film. An exponential distribution of traps will reduce the amount of free carriers during the transport [241]. With an increasing voltage where Fermi level is of higher magnitude than the trap levels, free carriers will fill the traps and there will be an increase amount of free carriers [237]. Assuming a constant mobility with an exponential distribution of traps and majority hole carriers, the current density can be modelled as [236, 237, 240, 241]

$$J = q^{1-l} \mu_p N_v \left(\frac{2l+1}{l+1} \right)^{l+1} \left(\frac{l}{l+1} \frac{\epsilon_s \epsilon_o}{N_t} \right)^l \frac{V^{l+1}}{d^{2l+1}} \quad (6.6)$$

where N_t is the trap density, ϵ_o is the permittivity of free space, ϵ_s is the dielectric constant, μ_p is the hole mobility, N_v is the density of transport states, d is sample thickness, and $l = T_t/T$ where T_t is the characteristic temperature and T is the measurement temperature. T_t is, in turn, related to the characteristic energy of the trap distribution as $E_t = k_B T_t$, where k_B is the Boltzmann constant. Eqn 6.6 can be simplified into a power law dependence where $J \sim V^m$ with the exponent factor $m = l + 1$. In this way, the gradient in

the log-log plot of the J-V relationship will directly gives the characteristic temperature and thus the characteristic energy.

Fig. 6.23(a) SCLC power law fits to the data in Fig 6.23(a) from 305 K to 400 K and (b) variation of exponent factor m with respect to inverse temperature.

Fig 6.23 shows (a) the SCLC power law fits to the data in Fig 6.23(a) from 305 K to 400 K and (b) the variation of exponent factor m with respect to inverse temperature. It reveals that m decreases as temperature increases (or inverse temperature decreases). This is as predicted by the SCLC theory. The calculated values of T_i and E_i are 2056 K and 0.17 eV respectively. Kumar *et al.* [256] has further approximated Eqn 6.6 to an Arrhenius form

$$J = \frac{1}{2} \left(\frac{qV\mu_p N_v}{d} \right) \exp \left[-\frac{E_t}{kT} \ln \left(\frac{qN_t d^2}{2\epsilon_s \epsilon_o V} \right) \right] \quad (6.7)$$

where the activation energy is

$$E_a = \frac{E_t}{k} \ln \left(\frac{qN_t d^2}{2\epsilon_s \epsilon_o V} \right) \quad (6.8)$$

Using Eqn 6.7, a plot of $\ln J$ vs $1/T$ at a constant voltage will give a gradient of E_a as shown in Eqn 6.8. From Eqn 6.5, the total trap density can then be determined. Using this

method, a graph of $\ln I$ vs $1/T$ is plotted and N_t is found to be $1.46 \times 10^{18} \text{ cm}^{-3}$ at a bias of 1 V. By a further examination of Eqn 6.7, it is revealed that the current is almost independent of temperature, where $E_a = 0$, at a crossover voltage [236, 237]:

$$V_c = \frac{qN_t d^2}{2\epsilon_s \epsilon_0} \quad (6.9)$$

Extrapolation of the curves from Fig 6.22(a) results in the convergence of the curves at a point. The corresponding voltage at this point is the crossover voltage $V_c \sim 100 \text{ V}$ as shown in Fig 6.23(a). From Eqn 6.9, it is derived that N_t is $1.44 \times 10^{18} \text{ cm}^{-3}$, which is close to the N_t determined from Eqn 6.8.

Fig 6.24 High resolution TEM images revealing evidences of (a) dislocations and (b) grain boundaries present in the SSR Si nc.

The value of N_t obtained is about 100 times larger than the Si nc density. This is quite different from the results reported by Rafiq *et al.* [237] who observed that the values of N_t and the nanocrystals density (N_{nc}) were similar. For SSR Si nc, other than the potential well existing in the Si nc [237, 257], defect states also play a major role in the contribution to the trap density. It has been reported [250] that traps present at the interfaces of Si nc or defects in Si nc are capable of inducing charge trapping as well. Lu *et al.* [16] has reported that high energy ball milling is often capable of creating structural defects, dislocations and grain boundaries, etc. Fig 6.24 shows high resolution TEM images revealing evidences of (a) dislocations and (b) grain boundaries present in the SSR Si nc. These dislocations and grain boundaries may act as deep traps that contribute to the approximate 100 traps per Si nc. It has been reported that in CdSe nanocrystals, a N_t/N_{nc} ratio of 100 was also observed for deep traps [258]. They are similar to the SSR where dislocations are prominent. This explains why a higher E_t at 0.17 eV, as a result of higher T_i at 2056 K for the SSR Si nc is required to “free” the trapped holes as compared to the E_t of 0.14 eV for Si nc by plasma decomposition [237] and 0.08 eV for amorphous Si nc [236]. These defects in Si nc are reported to be efficient charge trapping centers [250].

In conclusion, the SCLC theory can be used to model the macroscopic electronic conduction mechanism of SSR Si nc thin film. N_t and E_t values are found to be $1.46 \times 10^{18} \text{ cm}^{-3}$ and 0.17 eV respectively. The N_t/N_{nc} ratio is ~ 100 owing to the existence of structural defects on these Si ncs. This is attributed to the dislocations which act as deep traps. The high E_t value, as compared to Si nc synthesized by plasma deposition and

amorphous Si, shows that higher energy is required for the release of holes in these deep traps. The high N_t/N_{nc} ratio and E_t values provide evidences of larger charge trapping ability and longer retention times of the SSR Si nc which are of high importance to Si nc memory devices.

6.5 Summary

The charge trapping capability has been demonstrated in SSR Si nc in TEOS thin film (SNT). It has been demonstrated that even without a control oxide, less only 10% charge loss is experienced by the SNT structure after 4480 sec of stage time. The addition of a PECVD control oxide, indeed, increases the retention time drastically with virtually no loss of charges ($< 1\%$) for 6000 sec. This excellent time retention performance is comparable to other Si nc in dielectric materials, and moreover it has higher economical value in terms of cost and throughput.

The transport mechanism of the Si nc in TEOS dielectric is being investigated and the TSN results indicate that it is most probably due to the traps and grain boundaries in the Si nc playing a major role in the conduction mechanism. It is well evident in the TEM images that numerous dislocation sites and grain boundaries are formed in the process of ball milling and spin coating of the TSN layer. Using the SCLC model, a N_t/N_{nc} ratio of ~ 100 is obtained. This amount is nearly 100 times more than those reported. This result is promising in terms of the charge trapping capability. It further illustrates why the SNT structure can retain charges for such a long duration of time even without a control oxide.

It can be concluded that solid state reaction Si nc in TEOS thin film do have the potentials to meet the criteria as an inexpensive alternative for Si ncmemory devices.

Chapter 7: Conclusion and Recommendations

7.1 Conclusion

The need for higher-integration, lower-power consumption and high-speed ICs has always been a challenge to researchers. The leap in photolithography technology has surged in the down scaling of dimensions in MOSFET. However, this is not able to quench the thirst of researchers and entrepreneurs for even smaller dimensions. At the same time, higher and higher speed devices are in need for greater capacity machines. As a result, this leads to the realization of Si-based nano-memory devices and single electron devices. Not only can Si-based nano-memory devices answer the call for dimension minimization, optical data transmission via Si-based optical ICs is also a most promising role to overcome the bottleneck of interchip and intrachip communication.

In this thesis, synthesis Si nc using inexpensive and high production SSR has been demonstrated. Current techniques, such as ion-implantation, CVD and co-sputtering, etc, to synthesize Si nc involves an embedding matrix which is difficult to be removed. This makes Si nc difficult to be studied in its own form. However, SSR allows Si nc to be synthesize in powder form and this allows the Si nc to be studied in its own form.

To further develop these Si nc into devices, the dispersion of SSR Si nc in TEOS has been successfully demonstrated and subsequently spin coated onto Si wafer as thin film. Such films are considered as potential candidates for Si-based light emitting devices and

single electron devices. In this study, the author has explored the physical properties of these films, and the investigations enhance our understanding of the optical and structural properties of Si nanocrystals embedded in TEOS thin film.

In addition, SSR Si nc in TEOS capacitor has been first demonstrated in this thesis. Extensive investigations into the charge storage and charge transport properties of these SSR Si nc in TEOS thin film have been performed. Many characterizations and studies have been carried out in this project.

Structural Characterization

Various structural characterization techniques including XRD, TEM, FTIR, zeta potential, Raman scattering, PL, and PLE have been used to study these Si nc and its subsequent embedded thin films. By XRD and TEM analysis, the relaxation of applied stress in Si nc has been identified when left for hours of rest. The formation of highly symmetrical twins has been correlated to the release of this applied stress. TEM images also reveal formation of dislocations and grain boundaries that remains as residual effects of SSR. This may be the reason for the low emission intensity. On the other hand, these defects can act as charge trapping centers in memory application. Other than the after SSR Si nc characterization, the oxidation effects on these Si nc have also been investigated. The oxidation of these Si nc has shown substantial reduction of grain size from 12.8 nm to 7.7 nm. A three phase sintering and oxidation model has been developed to explain the evolution of initial size growth to reduction and eventual saturation.

Dispersion Study

TEM images reveal initial inhomogeneous dispersion of the nanocrystals in the TEOS thin film. The conglomeration of these Si nc is also not desirable as this leads to clustering instead of the nanocrystal. The coating of these nanocrystals with a organic vehicle has proven to be a viable option. Settling test has provides evidence that these Si nanocrystals coated with organic can provide a homogeneously dispersed suspension for up to 20 hours. Stable zeta results (<-30 mV) are observed at pH 7 and above. Upon centrifugation and filtration, it is further shown by TEM images that uniform Si clusters as small as 12 nm can be synthesized. It is found that the steric stabilization is the dominating stabilizing mechanism in these Si nc coated with the organic vehicles.

Light Emission Studies

Infra-red radiation has been emitted by both the nanocrystalline Si powders and TEOS thin film embedding the powders. However, the intensity is weak as compared to direct bandgap materials like GaAs and ZnO. For the emission by the nanocrystalline Si powder, there is no fixed shift in emission energy with reducing sizes. This strongly suggests that quantum confinement of the nanocrystals is not the reason for the emission. The absence of amorphous Si component, Si-H or Si-OH bonds denies the proposed mechanism of luminescence by the hydrides group. Upon the comparison of the different mechanisms, such as quantum confinement model, presence of hydrides and presence of oxide-related defects, etc. It is discovered that other defects, such as NBOHCs, in the amorphous SiO₂ are the probable components that cause photoluminescence of the SSR Si.

Electrical Studies

Charge trapping characteristics have been demonstrated in SNT capacitors. Long retention time (less than 1% loss of charge for 5000 sec) has been demonstrated in this device with a PECVD control oxide. The IV characteristics have been investigated and discovered that the results are in good agreement with the SCLC model. It is simulated that the number of trap sites per nc is ~ 100 . This proposed that the dislocations and grain boundaries as observed in earlier TEM characterization are the source of addition trap sites in the SSR Si nc. This is attributed as the reason for long retention time and high trapping ability observed in SSR Si nc.

7.2 Recommendations for Future Research

The following recommendations are made to extend the research on SSR Si nc embedded in TEOS film:

- The dispersion of SSR Si nc can be carried out using other organic vehicles, such as non-ionic and zwitterionic surfactants, as alternative dispersants. The study and comparison using surfactants' stabilization and steric stabilization can be carried out. Other than the dispersion, it is also interesting to find out the effects of ionic contents in the zwitterionic surfactants over the charge trapping and conduction mechanisms in the subsequently developed MOS capacitors and MOSFETs.

- Electroluminescence (EL) devices such as light emission diodes (LEDs) can also be synthesized using the Si nc/SiO₂ as the active layer. At present, the emission characterizations are carried out only in the form of photoluminescence tests. Electrically pump stimulated emission, like EL, can provide a different perspective to the emission mechanism, such as whether light emission is due to the electron-hole recombination within the nc-Si or via defects? At the same time, rare earth doped Si nc in SiO₂ matrix can also be fabricated and characterized as it has been demonstrated as a method to increase the EL efficiency drastically.
- For the realization of single electron devices, a better understanding of single electron tunneling and Coulomb blockade effect is critical. In order to observe these effects, low temperature I-V and C-V measurements are crucial for the elimination of thermal fluctuations. SCLC model, as presented in Chapter 6, is very much influenced by temperature. These measurements can add on to more in-depth studies into the influences of traps to the conduction mechanism.
- Si nc has been demonstrated to be dispersed in TEOS solution and developed into functional MOS capacitor for memory application. This inspires further development in MOSFET. It is interesting to find out the electrical influences of the source, gate and drain on the memory characteristics of such devices.
- Other than technical fabrications and characterizations, theoretical simulations and calculations can be useful methods to predict and forecast the behaviours of such Si nc and related devices. First-principle calculations, such as *ab initio*, can be employed to simulate and calculate the band gap energy deviations and dielectric function changes due to the influence of structural defects. Comparison

between these simulated and experimental results can be carried to complement both practical and theoretical aspects.

Author's Publications

Journals

- 1) **H. W. Lau, O. K. Tan, Y. Liu, C. Y. Ng, T. P. Chen, K. Pita and D. Lu**, "Defect-Induced Photoluminescence From Tetraethylorthosilicate Thin Film Containing Mechanically Milled Silicon Nanocrystals", *J. Appl. Phys.*, Vol. 97, pp.104307 (2005).
- 2) **H. W. Lau, O. K. Tan, B. C. Ooi, Y. Liu, T. P. Chen and D. Lu**, "Characteristics of Mechanically Milled Silicon Nanocrystals Embedded in TEOS Thin Films", *J. Cyst. Growth*, Vol. 288, p. 92-95 (2006).
- 3) **H. W. Lau and O. K. Tan**, "Influence of Oxidizing Ambient to Tetraethylorthosilicate Thin Films Containing Solid-State Reaction Silicon Nanocrystals", *Appl. Phys. Lett.*, Vol. 88, p. 103101 (2006).
- 4) **H. W. Lau, O. K. Tan, Y. Liu, D. A. Trigg and T. P. Chen**, "Charge Trapping Phenomena of Solid-State Reaction Si Nanocrystals in Tetraethylorthosilicate Thin Film", *Nanotechnology*, Vol. 17, p. 4078-4081 (2006).
- 5) **H. W. Lau, O. K. Tan and D. A. Trigg**, "Charge injection and tunneling mechanism of solid-state reaction silicon nanocrystals film", *Appl. Phys. Lett.*, Vol 89, p. 113119 (2006)

- 6) **H. W. Lau**, O.K. Tan, Y. Liu, T.P. Chen and D. A. Trigg, "Synthesis and Charge Trapping Effects of Solid-State Reaction Silicon Nanocrystals ", IEEE Trans. Nanotechnology (Submitted).

Conferences

- 1) **H. W. Lau**, O. K. Tan, B. C. Ooi, Y. Liu, T. P. Chen and D. Lu, "Characteristics of Mechanically Milled Silicon Nanocrystals Embedded in TEOS Thin Films", 3rd International Conference on Materials for Advanced Technologies, 3-8 July 2005, Singapore.
- 2) Y. Liu, T. P. Chen, **H. W. Lau**, L. Ding and O. K. Tan, "A Study of Photoluminescence from SiO₂ Films Containing Nanocrystals", 3rd International Conference on Materials for Advanced Technologies, 3-8 July 2005, Singapore.
- 3) **H. W. Lau** and O. K. Tan, "Segregation of Mechanically Milled Agglomerate of Silicon Nanocrystals" 2nd MRS-S Conference on Advanced Materials, 18-20 January 2006, Singapore.

- 4) **H. W. Lau, O. K. Tan, Y. Liu, T.P. Chen and D. A. Trigg, "Synthesis, Characterization and Oxidation Effects of Solid-State Reaction Silicon Nanocrystals", 6th IEEE conference on Nanotechnology, 17-20 July 2006, USA, Cincinnati.**

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Appendix

In this part, as correspond to Chapter 3 Section 3.5.2, the HRTEM details taken to compute the twins and grain statistics are presented. Each grain is label with “S” at the front.

Fig. A.1 Five ($\Sigma=3$) twins formation at $\{111\}$ planes

Fig. A.2 Coalescence of $\{001\}$ and $\{111\}$ planes

Fig. A.3 Two ($\Sigma=3$) twins formation at $\{111\}$ planes

Fig. A.4 Extension of Fig A.3: Five ($\Sigma=3$) twins formation at $\{111\}$ planes

Fig. A.5 Six ($\Sigma=3$) twins formation at $\{111\}$ planes

Fig. A.6 Three ($\Sigma=3$) twins formation at $\{111\}$ planes

Fig. A.7 Two interlocking grains at {111} planes

Fig. A.8 Presence of single Si nc